

HIGH-LEVEL AB INITIO QUANTUM CHEMICAL STUDIES OF THE COMPETITION
BETWEEN CUMULENES, CARBENES, AND CARBONES

by

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(Under the Direction of WESLEY D. ALLEN)

ABSTRACT

High-accuracy computations involving coupled-cluster methods in concert with series of correlation-consistent basis sets are utilized to explore the geometric structures, relative energetics, and vibrational spectra of some molecular systems with unusual properties, namely $\text{C}(\text{BH})_2$, $\text{C}(\text{AlH})_2$ and HCNO . Reliable focal point analyses (FPA) targeting the CCSDT(Q)/CBS limit for the ground electronic state of $\text{C}(\text{BH})_2$ reveals a relative energy difference of only $0.02 \text{ kcal mol}^{-1}$ between a linear and a bent ($\angle\text{BCB} \approx 90^\circ$) structure, thus identifying an unusual case of an “angle-deformation” isomer. Highly accurate CCSD(T)/cc-pVTZ and composite c~CCSDT(Q)/cc-pCVQZ anharmonic vibrational frequency computations precisely reproduced the experimental IR spectra for linear $\text{C}(\text{BH})_2$, and made excellent predictions for the hitherto unobserved bent isomer. With the aid of elaborate bonding analyses, linear $\text{C}(\text{BH})_2$ is described as a cumulene, while bent $\text{C}(\text{BH})_2$ can be best characterized as a carbene with a little carbene character. A similar FPA treatment yields bent $\text{C}(\text{AlH})_2$ ($\angle\text{AlCAI} \approx 98^\circ$) as the ground electronic structure, comfortably placing it $9.60 \text{ kcal mol}^{-1}$ below its linear counterpart, thus confirming the dominance of a carbene/carbone model for the Al analogue of $\text{C}(\text{BH})_2$. Confident predictions for the heretofore undetected bent $\text{C}(\text{AlH})_2$ are made through anharmonic frequency computations

at the CCSD(T)/cc-pV(T+d)Z level. Next, a highly accurate and computationally demanding AE-CCSDT(Q)/CBS treatment predicts a bent ground electronic structure for the classic quasilinear HCNO molecule ($\angle\text{HCN} \approx 174^\circ$), lying a miniscule 0.22 cm^{-1} below the corresponding linear geometry, thus indicating an intermediate between a cumulene and a carbene model. Exhaustive investigation is carried out on the geometric structures and for the harmonic vibrational frequencies for both linear and bent HCNO, and a similarly elaborate benchmarking is pursued for the HCN molecule. Finally, a rigorous theoretical analysis of the topology of polytwistane is performed to reveal a non-repeating, helical, carbon nanotube. Utilizing homodesmotic equations and including explicit computations as high as CCSD(T)/cc-pVQZ, the FPA treatment of the enthalpy of formation ultimately yields $\Delta_f H_0^\circ(\text{polytwistane}) = +1.28\text{ kcal (mol CH)}^{-1}$, thus demonstrating the thermodynamic and synthetic viability of this polymer when compared to acetylene.

INDEX WORDS: Cumulene; Carbene; Carbone; Coupled-cluster theory; Correlation-consistent basis sets; Basis-set extrapolation; Focal point analysis; Angle-deformation isomer; Vibrational perturbation theory; Isotopic shifts; Intrinsic reaction path; Quantum tunneling; Quasilinear; Homodesmotic equations; Carbon nanotube; Saturated polymer; Double helix; Irrational periodicity.

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B.A., Berea College, Berea, KY, 2008

A Dissertation Submitted to the Graduate Faculty of The University of Georgia in Partial
Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

ATHENS, GEORGIA

2014

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DEDICATION

To my Dad, *Mr. Mukul Ratan Barua*, whose constant encouragement and support have brought me this far.

ACKNOWLEDGEMENTS

A lot of people have influenced me in positive ways, but the one person who stood a mile ahead of everyone else was my Dad. His constant encouragement, his support, and his compassion for the growth and success of his two children were unparalleled in my opinion. He was not only my father, but a great friend as well. Despite his limited income as a government official, he provided the best education available out there in Bangladesh for his two children, and I am ever so grateful to him for that. From thousands of miles away during our phone conversations, however brief they might be, he always mentioned how happy he would be to see me get my Doctorate. I could not fulfill his wish during his lifetime, nor could I be there when he breathed his last on May 3rd 2013. As I inch closer to my degree, I realize that he would be the happiest person in the world right now; happier than me would probably not be an exaggeration. I would like to take this opportunity to show my utmost gratefulness to the best Dad in the world for always being there for me and believing in me. Thank You. Thank You from the depth of my heart.

My family members have always played a huge supporting role in my life. My elder brother Parag and my mom have backed me up and urged me forward. It's sad how the three of us are so far apart from each other right now; my mom in Bangladesh, my brother in Sydney, and me being here in the States. Hopefully some day we could all live close together as a family once again. Special thanks to all my cousins (Muna, Nina, Turna, Upama, Pallab, Kallol, Hillol), who still remain the closest people in my life no matter how much time passes between our phone conversations. I have a lot of friends here in the States and back in Bangladesh that I need to

mention right now, but would soon run out of pages if I do so. However, I would especially like to thank my friend Kelsey Turner for providing me the support that I needed during my father's death, and for always being there for me when I needed somebody to rely on.

I often jokingly call my group-mate Jowa as my "semi-mentor", and rightly so. He has helped me enormously throughout my research work. Being completely unaware of how computational quantum chemistry actually works, I had to learn everything from scratch. Jowa was patient with me and taught me well. I was very lucky to have someone like him to guide me through. He is an excellent co-worker and a very good friend, and I am still trying to find a way to beat him in badminton. I would also like to thank my friend Kedan for keeping me entertained with her lively smile in the office; I'll definitely miss our fun and random conversations.

Last, but not least, I would like to show my sincere gratefulness to the faculty members at the CCQC, Dr. Schaefer and Dr. Allen. Dr. Schaefer has provided us with a wonderful facility conducive for state-of-the-art research work. I admire his friendly personality and great stories during his lectures. My mentor, Dr. Allen, has been very supportive, caring, and accommodating towards all his students. Our group has a good number of international students, and he has never said no to any of our requests for visiting our respective homelands. The only thing he would ask for is whether we have internet access back home so that we could continue our research work away from the office. His Advanced Quantum course gifted me many sleepless nights and hundreds of pages of homework assignments. In hindsight, the struggle was totally worth it since I learned an outrageous amount in that class. It has surely been a pleasure working under Dr. Allen for the last six years or so.

Now, off to some quantum chemistry...

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CHAPTER 1

HIGH-LEVEL AB INITIO QUANTUM CHEMICAL THEORY AND ITS APPLICATION IN CARBON CHEMISTRY

1.1 INTRODUCTION

For hundreds of years, the world of carbon chemistry has been mostly concerned with tetravalent carbon(IV) compounds since most organic molecules that are stable in a condensed phase contain carbon atoms with all the four valence electrons involved in chemical bonds. Cumulene, a general term used for a molecule containing “cumulated double-bonds” around the central carbon atom, is a classic example of such carbon(IV) compounds. It was not until 1991 that divalent carbon(II) compounds or carbenes were brought into the limelight when Arguendo et al.¹ introduced imidazolin-2-ylidenes (N-heterocyclic carbenes, NHCs) as synthetically useful and stable molecules. Later in 2004, the successful isolation of the first stable carbenes was carried out,² and since then the scope of carbene chemistry has been significantly extended. Carbenes usually have only one σ -type lone-pair orbital, while the other two valence electrons of carbon are used in forming covalent bonds with the adjacent atoms. On the other hand, some recent quantum chemical studies³⁻⁶ showed that there exists a class of divalent carbon(0) compounds called carbones, with the general molecular formula CL_2 (L stands for any ligand), in which the carbon atom formally retains its four valence electrons as two lone pairs. The CL bond in carbones arises from the $L \rightarrow C$ donor-acceptor interactions where L is a strong σ -donor.

According to Frenking and Tonner,³ carbones are conceptually different from carbenes and cumulenes, but the bonding situation in a real molecule may be intermediate between the three models. Thus, in addition to a detailed bonding analysis, the application of a high-level *ab initio* quantum chemical method in determining the geometric structures and relative energetics could elucidate the bonding situation of the comparatively elusive carbenes and carbones.

Coupled cluster (CC) theory, a highly efficient *ab initio* quantum chemical method, was first introduced by Čížek and Paldus⁷⁻⁹ in the late 1960s in an effort to provide a reliable and accurate solution to the electronic Schrödinger equation. For the last two decades or so, the CC technique¹⁰ has successfully proved to be the most effective tool for the quantum chemical treatment of the electron correlation problem. Techniques such as CC singles and doubles (CCSD),¹¹⁻¹⁴ and CC singles and doubles with perturbative corrections for the triples [CCSD(T)]¹⁵⁻¹⁷ have been routinely used as computationally affordable methods in high-accuracy calculations. Nonetheless, higher-order methods such as full triples (CCSDT),¹⁸⁻²¹ quadruples (CCSDTQ),²²⁻²³ and pentuples (CCSDTQP)²⁴ could be used in computations that demand very high precision. However, the computational cost for the full CC method scales roughly as $N^{(2n+2)}$, where N is the number of basis functions used in a computation involving n as the highest excitation in the cluster operator,²⁴ and this significantly increases the computational expense.

With the current extension in available computational resources, one might find it possible to perform a full triples (N^8) computation for modestly sized molecules, but such calculations reveal that it is often necessary to include correlation effects beyond CCSDT to obtain more accurate results.¹⁹ On the other hand, employing a full quadruples (N^{10}) method has shown to reach an accuracy better than 0.25 kcal mol⁻¹ in thermochemical applications,²⁵⁻²⁸ but

the method turned out to be extremely expensive computationally. A good balance in accuracy and computational cost can be achieved by introducing the perturbative quadruples method [CCSDT(Q)].²⁹⁻³¹ Apart from being far less expensive than CCSDTQ, the CCSDT(Q) technique (N^9) was on average within 0.06 kcal mol⁻¹ of its full quadruples counterpart in determining the total energies of a variety of diatomic, triatomic, and tetra-atomic molecules with one or two heavy atoms.²⁹⁻³¹ Thus, CCSDT(Q) is a monumental advancement in carrying out very high-accuracy electron correlation energy calculations at a reasonable computational cost. In Chapters 2 and 3 of this dissertation, we further demonstrate the effectiveness of the state-of-the-art CCSDT(Q) method in accurately pinpointing the relative energetics of modestly sized molecules, and subsequently providing some unprecedented insight into the competition between cumulenes, carbenes, and carbones. Finally, Chapter 4 elaborates a rigorous theoretical analysis of the topology of a helical hydrocarbon nanotube, polytwistane, accompanied by the application of *ab initio* quantum chemical theory to probe the thermochemistry and synthetic viability of this saturated polymer.

1.2 THEORETICAL METHODS

1.2.1 Schrödinger Equation

The foundation of modern quantum chemistry is based upon an apparently simple but elegant formula known as the Schrödinger equation,³² the non-relativistic time-independent version of which is given by:

$$\hat{H}\Psi = E\Psi, \tag{1.1}$$

where the Hamiltonian operator, $\hat{H}$, is the sum of the kinetic and the potential energy of any system, Ψ is the wavefunction representing the quantum state of the system, and E is the corresponding energy. Under the Born–Oppenheimer approximation,³³ the nuclear kinetic energy is considered insignificant due to the large difference in nuclear and electronic masses, and the total wavefunction, Ψ , can be represented as the product of the individual nuclear and electronic components, $\Psi = \Psi_{Nuclear} \times \Psi_e$. Consequently, this gives rise to the non-relativistic time-independent electronic Schrödinger equation, $\hat{H}_e \Psi_e = E_e \Psi_e$, where $\hat{H}_e$ for a system of N electrons and M nuclei can be written in atomic units as³⁴

$$\hat{H}_e = \left(- \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}. \quad (1.2)$$

In the above equation, ∇_i^2 represents the Laplacian operator involving differentiation with respect to the i th electron coordinates, Z_A and Z_B represent the atomic numbers of nuclei A and B respectively, r_{iA} represents the distance between electron i and nucleus A , r_{ij} represents the distance between electrons i and j , and R_{AB} represents the distance between nuclei A and B . The first term in Eq. (1.2) describes the total kinetic energy of the electrons, the second term represents the total nuclear-electronic Coulomb interaction, the third term equals the Coulombic repulsion between the electrons, and finally, the non-electronic fourth term is added to account for the constant nuclear-nuclear repulsion. Both $\hat{H}_e$ and Ψ_e explicitly depend on the electronic coordinate vector, $\mathbf{r}$, but only have a *parametric* dependence on the nuclear coordinate vector, $\mathbf{R}$.

1.2.2 Hartree–Fock Theory

The Hartree–Fock (HF) theory is a variational method that utilizes a one-electron Hamiltonian known as the *Fock* operator, $\hat{F}$, which is very similar to Eq. (1.2) above. However,

the term, $1/r_{ij}$, representing the electron-electron repulsion in Eq. (1.2) is replaced in $\hat{F}$ by the potential, $v^{HF}(i)$, which is the average field experienced by the i^{th} electron due to the presence of the remaining $(N-1)$ electrons.³⁴ The HF ground-state wavefunction, Ψ_0 , for a system of N electrons is constructed from an *antisymmetrized* product of a set, $\{\psi_N\}=(\psi_1,\psi_2,\dots,\psi_N)$, of occupied molecular orbitals (MOs), and is known as the *Slater determinant*:

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \dots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \dots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \dots & \psi_N(\mathbf{x}_N) \end{vmatrix}. \quad (1.3)$$

The MOs in Eq. (1.3) are one-electron functions obtained from a linear combination of atomic orbitals that are described by the set of electronic *spin coordinates*, $\{\mathbf{x}_N\}=(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$. Each spin coordinate includes three spatial variables and one formal spin variable. Depending on the initial guess for $\{\psi_N\}$, an approximation for $v^{HF}(i)$ is made. Subsequently, a series of HF eigenvalue equations is solved iteratively by updating both $\{\psi_N\}$ and $v^{HF}(i)$ at each step until “self-consistency” in the eigenvalue equation is reached, which is why this method is often referred to as Self-Consistent-Field (SCF) theory.³⁴

One major inadequacy of the HF method is that it does not account for any explicit electron correlation, even though the theory includes *exchange correlation* between parallel spins. In order to approximate a total energy eigenvalue close to the full configuration interaction (FCI)³⁴ limit, a high-quality post-Hartree–Fock electron correlation energy needs to be computed and added to the HF result. In the next sub-section, a non-variational, iterative, size-consistent (consistency in energy at infinite separation), and size extensive (consistency in linear scaling with the number of electrons)³⁵ electron correlation method called Coupled-Cluster Theory is discussed in detail.

1.2.3 Coupled-Cluster Theory

In Coupled-Cluster (CC) theory, the electronic wave function is given by applying a wave operator, $e^{\hat{T}}$, on the HF ground-state reference wavefunction, $|\Psi_0\rangle$.^{29,34}

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Psi_0\rangle, \quad (1.4)$$

where the cluster operator, $\hat{T}$, is defined as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_m, \quad (1.5)$$

in which $m \leq N$ is the chosen cut-off for the excitation level in a system of N electrons. The general form of $\hat{T}_m$ can be represented as¹⁰

$$\hat{T}_m = \left(\frac{1}{m!}\right)^2 \sum_{ijk\dots abc} t_{ijk\dots abc}^{abc\dots} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \dots \hat{a}_k \hat{a}_j \hat{a}_i. \quad (1.6)$$

with indices $i, j, k\dots$ referring to occupied orbitals and $a, b, c\dots$ referring to the virtual ones, $\hat{a}$ and $\hat{a}^\dagger$ describing the annihilation and creation operators respectively, while $t_{ijk\dots abc\dots}^{abc\dots}$ denotes the cluster amplitudes. Inserting Eq. (1.4) into the electronic Schrödinger equation yields $\bar{H}|\Psi_0\rangle = E_{CC}|\Psi_0\rangle$, where

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}} \quad (1.7)$$

is the similarity-transformed Hamiltonian. Here, $\hat{H}$ represents the electronic Hamiltonian from Eq. (1.2), and is chosen over the notation $\hat{H}_e$ for simplicity. Since $\bar{H}$ is a non-Hermitian operator, it has different left and right eigenfunctions. One of the right eigenfunctions is simply the HF reference determinant, $|\Psi_0\rangle$, while the corresponding left eigenfunction is $\langle\Psi_0|\hat{\Lambda}$, in which $\hat{\Lambda} = e^{\hat{T}^\dagger} e^{\hat{T}}$. The *de-excitation* operator, $\hat{T}^\dagger$, is the adjoint of the excitation operator, $\hat{T}$ [cf. Eq. (1.5)], and $\hat{T}_m^\dagger$ is defined similarly to $\hat{T}_m$ [cf. Eq. (1.6)].^{29,36} The CC energy equation can now be expressed as

$$\langle\Psi_0|\hat{\Lambda}\bar{H}|\Psi_0\rangle = E_{CC}, \quad (1.8)$$

in which the orthonormality property, $\langle \Psi_0 | \hat{A} | \Psi_0 \rangle = 1$, is assumed. The usual form of the CC energy equation is $\langle \Psi_0 | \bar{H} | \Psi_0 \rangle = E_{CC}$, which basically serves the same purpose. Now, distributing the electrons in the occupied and virtual orbitals in all possible ways, a complete basis of Slater determinants is obtained, and the corresponding matrix representation of $\bar{H}$ is given by²⁹

$$\begin{pmatrix} E_{CC} & \bar{H}_{0p} & \bar{H}_{0q} \\ 0 & \bar{H}_{pp} & \bar{H}_{pq} \\ \bar{H}_{q0} & \bar{H}_{qp} & \bar{H}_{qq} \end{pmatrix}. \quad (1.9)$$

In Eq. (1.9), the subscript 0 represents the reference HF determinant, $|\Psi_0\rangle$. p is the set of determinants obtained by exciting one, two, three, etc. electrons from the reference determinant, (i.e. $|S\rangle$, $|D\rangle$, $|T\rangle$, etc.), while q represents all the higher-order determinants that lie outside the projection space used in the CC amplitude equations, $\langle \Psi_{ijk\dots}^{abc\dots} | \bar{H} | \Psi_0 \rangle = 0$.

The Hamiltonian in perturbation theory (PT) is given by the sum of the zeroth-order Hamiltonian, $\hat{H}_0$, and the perturbation operator, $\hat{V}$.^{10,34}

$$\hat{H} = \hat{H}_0 + \hat{V}. \quad (1.10)$$

If canonical HF orbitals are used in the reference determinant, then

$$\hat{H}_0 = \hat{F}^{ii} + \hat{F}^{aa}, \quad (1.11)$$

$$\text{and} \quad \hat{V} = \hat{V}_2, \quad (1.12)$$

where $\hat{F}^{ii}$ and $\hat{F}^{aa}$ are the diagonal elements of the occupied-occupied and virtual-virtual blocks of the Fock operator respectively, and $\hat{V}_2$ is the two-electron part of the normal-ordered Hamiltonian. In PT, the energy, E , along with the $\hat{T}$ and $\hat{A}$ operators can be expanded with respect to the order of the perturbation, $[n]$, as³¹

$$E = E^{[0]} + E^{[1]} + E^{[2]} + \dots, \quad (1.13)$$

$$\hat{T} = \hat{T}^{[0]} + \hat{T}^{[1]} + \hat{T}^{[2]} + \dots, \quad (1.14)$$

$$\hat{A} = \hat{A}^{[0]} + \hat{A}^{[1]} + \hat{A}^{[2]} + \dots, \quad (1.15)$$

Inserting Eqs. (1.10) and (1.14) into Eq. (1.7), $\bar{H}$ can be expanded in a similar fashion, and a detailed analysis³⁰⁻³¹ subsequently yields

$$\bar{H}^{[0]} = \hat{H}_0, \quad (1.16)$$

$$\bar{H}^{[1]} = [\hat{H}_0, \hat{T}^{[1]}] + \hat{V}, \quad (1.17)$$

and
$$\bar{H}^{[2]} = [\hat{H}_0, \hat{T}^{[2]}] + [\hat{V}, \hat{T}^{[1]}]. \quad (1.18)$$

In general, the n th-order contribution of $\bar{H}$ is represented as

$$\bar{H}^{[n]} = [\hat{H}_0, \hat{T}^{[n]}] + [\hat{V}, \hat{T}^{[n-1]}] + [[\hat{V}, \hat{T}^{[1]}], \hat{T}^{[n-1]}] + \dots. \quad (1.19)$$

The n th-order cluster amplitude equations in this perturbation analysis are derived by equating the elements of the n th-order non-Hermitian, similarity transformed Hamiltonian to zero,

$$\langle \Psi_{ijk\dots}^{abc\dots} | \bar{H}^{[n]} | \Psi_0 \rangle = 0. \quad (1.20)$$

Since the zeroth-order Hamiltonian, $\bar{H}^{[0]}$, is diagonal, the equations for the n th-order cluster amplitudes in Eq. (1.20) can be solved using^{31,37}

$$\hat{T}_m^{[n]} = \hat{R}_m(\bar{H}^{[n]} - [\hat{H}_0, \hat{T}^{[n]}]), \quad (1.21)$$

and
$$\hat{R}_m(\hat{X}) = \sum_{ijk\dots abc\dots}^N \frac{\langle \Psi_{ijk\dots}^{abc\dots} | \hat{X} | \Psi_0 \rangle}{D_{ijk\dots}^{abc\dots}} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \dots \hat{a}_k \hat{a}_j \hat{a}_i, \quad (1.22)$$

where $\hat{R}_m$ is the *resolvent* operator, and the energy denominator, $D_{ijk\dots}^{abc\dots}$, expresses the difference between the diagonal Fock matrix elements of the occupied-occupied and the virtual-virtual block,¹⁰ $D_{ijk\dots}^{abc\dots} = f_{ii} + f_{jj} + f_{kk} + \dots - f_{aa} - f_{bb} - f_{cc}$. Using Eqs. (1.17), (1.18) and (1.22), the first-order and the second-order cluster amplitudes can be expressed as $\hat{T}_2^{[1]} = \hat{R}_2(\hat{V})$,

$\hat{T}_1^{[2]} = \hat{R}_1 (V\hat{T}_2^{[1]})$, and $\hat{T}_3^{[2]} = \hat{R}_3 (V\hat{T}_2^{[1]})$.³¹ On the other hand, the λ amplitudes are determined by solving the Λ equations introduced in CC gradient theory:³⁶

$$\langle \Psi_0 | (1 + \hat{\Lambda}) (\bar{H} - E) | \Psi_{ijk\dots}^{abc\dots} \rangle = 0. \quad (1.23)$$

In order to determine the λ amplitudes of various order, the perturbation expansions for E , $\hat{T}$, and $\hat{\Lambda}$ [cf. Eqs. (1.13), (1.14), and (1.15)] are inserted into Eq. (1.23) to obtain³¹

$$\langle \Psi_0 | \bar{H}^{[n]} + \hat{\Lambda}^{[n]} (\bar{H}^{[0]} - E^{[0]}) + \hat{\Lambda}^{[n-1]} (\bar{H}^{[1]} - E^{[1]}) + \dots \dots | \Psi_{ijk\dots}^{abc\dots} \rangle = 0. \quad (1.24)$$

Similar to $\hat{T}_m^{[n]}$ in Eq. (1.21), the perturbative $\hat{\Lambda}$ operator can be solved using³¹

$$\hat{\Lambda}_m^{[n]} = \hat{R}_m (\bar{H}^{[n]} + \hat{\Lambda}^{[n-1]} (\bar{H}^{[1]} - E^{[1]}) + \dots \dots). \quad (1.25)$$

The corresponding first-order and second-order $\hat{\Lambda}$ operators turn out to be the adjoints of their excitation operator counterparts, and are given by $\hat{\Lambda}_2^{[1]} = \hat{R}_2^\dagger (\hat{V}) = \hat{T}_2^{[1]\dagger}$, $\hat{\Lambda}_1^{[2]} = \hat{R}_1^\dagger (\hat{\Lambda}_2^{[1]} \hat{V}) = \hat{T}_1^{[2]\dagger}$, and $\hat{\Lambda}_3^{[2]} = \hat{R}_3^\dagger (\hat{\Lambda}_2^{[1]} \hat{V}) = \hat{T}_3^{[2]\dagger}$. Hence, it is justified to replace $\hat{\Lambda}_m$ by $\hat{T}_m^\dagger$ for $m = 1, 2, 3$.

Finally, the energy corrections for CCSD(T) and CCSDT(Q) methods are represented as:³¹

$$\Delta E_{\text{CCSD(T)}} = E_{\text{CCSD(T)}} - E_{\text{CCSD}} = \langle \Psi_0 | (\hat{T}_1^\dagger + \hat{T}_2^\dagger) \hat{V} \hat{T}_3^{[2]} | \Psi_0 \rangle, \quad (1.26)$$

$$\Delta E_{\text{CCSDT(Q)}} = E_{\text{CCSDT(Q)}} - E_{\text{CCSDT}} = \langle \Psi_0 | (\hat{T}_2^\dagger + \hat{T}_3^\dagger) \hat{V} \hat{T}_4^{[3]} | \Psi_0 \rangle. \quad (1.27)$$

In Eqs. (1.26) and (1.27), curly brackets are used instead of square brackets to indicate that the lower-rank perturbative cluster amplitudes were replaced by the converged ones while constructing the $\hat{T}_m^{[n-1]}$ clusters. Using Löwdin's partitioning technique,³⁸ the full configuration interaction (FCI) energy can be expressed as¹⁶

$$E_{\text{FCI}}(\mathcal{L}|\mathcal{R}) = \langle \mathcal{L} | \bar{H} | \mathcal{R} \rangle + \langle 0 | \mathcal{L} \bar{H} | q \rangle [\langle q | E_{\text{exact}} - \bar{H} | q \rangle]^{-1} \langle q | \bar{H} | \mathcal{R} | 0 \rangle, \quad (1.28)$$

where $\mathcal{L}$ and $\mathcal{R}$ are the p space [cf. Eq. (1.9)] projections of the exact left and right eigenvectors of $\bar{H}$. The error associated with the CCSDT energy is then given by^{16,29-30}

$$\Delta E_{\text{CCSDT}} = E_{\text{FCI}} - E_{\text{CCSDT}} = \Delta E^{[4]} + \Delta E^{[5]} + \dots . \quad (1.29)$$

The fourth-order contribution from the above Eq. (1.29) is the non-iterative, perturbative quadruples correction to be added to E_{CCSDT} to obtain $E_{\text{CCSDT(Q)}}$:

$$\Delta E_{\text{CCSDT(Q)}} = E_{\text{CCSDT(Q)}} - E_{\text{CCSDT}} = \Delta E^{[4]}. \quad (1.30)$$

1.3 BASIS-SET EXTRAPOLATION

As mentioned earlier in Section 1.2, the HF wavefunction is constructed from a set of one-electron functions that is commonly referred to as the “basis set”. The one-electron nature of the wavefunction, accompanied by the one-electron Fock operator, leads to the relative insensitivity of the HF method to the choice of its basis set. Feller³⁹ demonstrated that the HF energy exhibits an exponential decay relative to the largest angular momentum contained in the basis set, and thus, shows rapid convergence to the complete basis set (CBS) limit. Since computations become increasingly expensive with the basis-set size, extrapolation techniques turn out to be crucial in minimizing basis-set truncation error. A family of basis sets that is widely used, and is ideal for extrapolation due to its systematic convergence to the CBS limit, is Dunning’s correlation-consistent series of basis sets.⁴⁰ The family is denoted by cc-pVXZ, which is the acronym for “correlation-consistent polarized valence X zeta”, where X refers to the “cardinal number” that is equal to the maximum angular momentum of the basis functions. Enlarging the basis set is tantamount to incrementing the maximum angular momentum value, and the term “correlation-consistent” indicates that each added function during the enlargement contributes similar amounts of electron correlation energy, a property that is imperative for extrapolation.

For the HF method, the “three-point” energy extrapolation formula for a given cardinal number X can be expressed as:³⁹

$$E_{\text{HF}}(X)=E_{\text{HF}}^{\text{CBS}}+ae^{-bX}, \quad (1.31)$$

for which three different energy values need to be explicitly computed to solve for the three unknown parameters in the equation. The “two-point” version of the extrapolation formula is given by:⁴¹

$$E_{\text{HF}}(X)=E_{\text{HF}}^{\text{CBS}}+a(X+1)e^{-9\sqrt{X}}. \quad (1.32)$$

In the above two equations, $E_{\text{HF}}^{\text{CBS}}$ represents the HF complete basis set limit as $X \rightarrow \infty$. Contrary to the mean-field HF method, electron correlation methods involve wavefunctions that can describe instantaneous electronic interactions. As two electrons approach each other, a decay in the electronic wavefunction results, and a cusp appears at the coalescence point due to the singularity in the Coulomb operator, $1/r_{ij}$ (cf. Eq. 1.2, term 3). This cusp is extremely difficult to model with one-electron basis functions. Consequently, electron correlation methods have more basis-set dependence and exhibit slower asymptotic convergence when compared to the HF method. The relevant formula for extrapolating the correlation energy is:

$$E_{\text{corr}}(X)=E_{\text{corr}}^{\text{CBS}}+aX^{-3}, \quad (1.33)$$

in which $E_{\text{corr}}^{\text{CBS}}$ represents the correlation limit as $X \rightarrow \infty$. The total energy at the CBS limit is therefore given by:

$$E_{\text{Total}}^{\text{CBS}}=E_{\text{HF}}^{\text{CBS}}+E_{\text{corr}}^{\text{CBS}}. \quad (1.34)$$

1.4 FOCAL POINT ANALYSIS

Focal point analysis is a method developed by Allen and co-workers⁴²⁻⁴⁶ that can accurately pinpoint relative energies by eliminating errors arising from both inexact electron

correlation treatment and basis-set truncation. The method depends on some key assumptions that are necessary in making the approach tractable and successful. First, geometry optimization is performed at the highest possible level of theory for the individual species for which relative energies are to be determined. The energy is known to vary quadratically with respect to small displacements around the equilibrium structure on an “exact” potential energy surface. With the assumption that the optimized geometries at high level differ only slightly from their equilibrium counterparts, small deviations from the equilibrium structure introduce very small errors in the absolute energies. Moreover, the minute errors get largely canceled when the relative energies between the species are considered. Hence, no re-optimization of the geometry is necessary in the focal point analysis. In fact, the aforementioned error-cancellation means that geometry optimization even at a modest level of theory can make very reliable predictions for relative energies within the focal point approach.

A hierarchical series of single-point energies are computed at the optimized reference geometries by increasing the basis-set size and the correlation treatment level as far as possible. Coupled-cluster theory, which is size-consistent as well as size-extensive, is usually chosen as the electron correlation hierarchy in the focal point regime since N -fold coupled-cluster excitations for an N -electron system yields the exact energy within a one-electron basis. Energy extrapolation to the CBS limit is carried out for the excitation levels for which at least cc-pVTZ and cc-pVQZ energies can be explicitly computed; cc-pVDZ energies are not used for extrapolation due to their inconsistency. For excitation levels such as CCSDT [cf. Eq. (1.5), $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$] or higher, cc-pVTZ and cc-pVQZ explicit computations can be extremely expensive and unfeasible, and hence an additivity approximation needs to be introduced.

The additivity approximation assumes that the energy difference between the unfeasible level of theory (e.g. CCSDT) and the highest level of theory for which energy extrapolation can be performed [e.g. CCSD(T)] is independent of the basis set, and there is a good physical justification for the assumption. The strong basis-set dependence that arises around a Coulomb hole or the coalescence point of two electrons is fundamentally a two-body problem. The wavefunction at the coalescence point of two electrons with opposite spins is non-zero and does not violate the Pauli Exclusion Principle. Consequently, there is non-zero energy contribution at and around the coalescence point, and it is vital to accurately model the two-body wavefunction by improving the basis set. Moreover, the energy contribution from the repulsion between two electrons around the Coulomb hole region becomes significantly large as the denominator, r_{ij} , in the electron-electron repulsion term [cf. Eq. (1.2), term 3] approaches zero. As a result, wavefunctions corresponding to CCSD(T) level have strong dependence on the basis set size.

On the other hand, wavefunctions corresponding to full triples and higher excitations at the CCSDT level and beyond can avoid such problems. The CCSD(T) and CCSDT levels both contain two body-terms that essentially get cancelled when the relative energy is calculated, and the remaining three-body terms in CCSDT cause very little concern. Firstly, the energy contribution from these three-body terms is small to begin with. Secondly, Pauli Exclusion Principle is violated at the coalescence point of three or more electrons, and the corresponding wavefunction as well as the energy contribution at the Coulomb hole must be zero. Since the probability of finding all three electrons around the Coulomb hole region significantly diminishes, there remains no cusp to model, and consequently, the three-body and higher terms can be easily modeled using a small basis set (e.g. cc-pVDZ). Under the additivity approximation, the energy difference between two successive levels of theory is explicitly

computed in a small basis, and then the difference is appended to the CBS extrapolated energy at the lower level. For example, consider the case where the CBS limit for the CCSD(T) level can be extrapolated using the explicitly computed cc-pVTZ and cc-pVQZ energies, but only cc-pVDZ energies are possible for the CCSDT level. The CCSDT/CBS limit is then approximated in the focal point regime using the formula:

$$E_{\text{CCSDT}}^{\text{CBS}} \approx E_{\text{CCSD(T)}}^{\text{CBS}} + E_{\text{CCSDT}}^{\text{cc-pVDZ}} - E_{\text{CCSD(T)}}^{\text{cc-pVDZ}}. \quad (1.35)$$

A focal point table includes all the energies from a systematic increase in the correlation treatment and basis set size even though those energies might not affect the final focal point result. For example, CCSD/cc-pVQZ energy will be reported but will not have any influence on the final target energy. The inclusion of these extra energies is crucial in monitoring convergence with respect to the level of theory, and thus assists in estimating the error bar for the final relative energy. An effective focal point table displays rapid, systematic convergence in energies with respect to correlation treatment. Most of the included results are obtained automatically from the higher-level computations. For example, a CCSD(T) energy computation requires Hartree-Fock (HF) theory to construct the molecular orbitals, perturbation theory to make an initial guess for the iterative CCSD procedure, which in turn is necessary for the CCSD(T) result. Hence, a single CCSD(T) calculation yields complementary HF, second-order Møller-Plesset perturbation theory (MP2),⁴⁷ and CCSD energies. In conclusion, although the absolute energies obtained from explicit computations and extrapolations within the focal point approach may not be highly accurate, the relative energies do make excellent predictions largely due to systematic error cancellation.

1.5 AUXILIARY CORRECTIONS

The quality of the final focal point energy is often improved by adding a few auxiliary terms for core electron correlation, the diagonal Born–Oppenheimer correction (DBOC),⁴⁸⁻⁴⁹ relativistic effects,⁵⁰⁻⁵¹ and zero-point vibrational energy (ZPVE). The focal point analysis is often carried out under the frozen core-orbital approximation due to the large energy separation between the core and the valence electrons. Nevertheless, correlating the core-electrons slightly improves the final focal point result, but is often too expensive to be employed for all the explicit computations in the table. Consequently, a single core-correlation correction, later added to the final focal point energy, is obtained by differencing all-electron (AE) and frozen-core (FC) energies computed at some suitably high level, in association with the “core-valence” form (cc-pCVXZ) of the corresponding cc-pVXZ basis set.

The Born–Oppenheimer (BO) approximation greatly simplifies electronic structure theories, and provides an adiabatic approximation that yields potential energy surfaces. The BO approximation ignores the derivatives of Ψ_e with respect to the nuclear coordinates by taking into account the large difference in electronic and nuclear masses, but that approximation becomes less valid when hydrogen atoms are present in the molecular system. Consequently, a first-order adiabatic energy correction obtained from the “diagonal” elements (same electronic state) of the exact Hamiltonian matrix is introduced to the potential energy surface. The off-diagonal matrix elements involve the non-adiabatic interactions between potential energy surfaces of different electronic states, and give rise to the “vibronic coupling” effect. The DBOC is mass dependent, which means isotopically substituted molecules will evoke distinct corrections.

The non-relativistic time-independent Schrödinger equation [cf. Eq. (1.1)] assumes that the classical speeds of the electrons surrounding the nuclei are much smaller than the speed of light. This assumption requires only a small relativistic correction for a system consisting of small nuclei. However, larger nuclei can significantly speed up the motion of the core electrons, and may require a somewhat larger correction. Nevertheless, the systems considered in our research work are comprised of hydrogen and the first-row elements only (except aluminum), and hence it is sufficient to use a first-order relativistic correction for one-electron mass-velocity and Darwin terms. Finally, in order to match experimental results, the zero-point vibrational energy (ZPVE) is added to the final focal point energy to approximate the relative energy at the $v=0$ vibrational level for the ground electronic state.

1.6 ANHARMONIC VIBRATIONAL FREQUENCIES

Anharmonic vibrational frequencies can be computed using the second-order vibrational perturbation theory (VPT2)⁵²⁻⁵⁵ in which the exact Hamiltonian operator is partitioned into two terms; a zeroth-order term for which the exact solution is known and is very close to the full Hamiltonian, and a small perturbative term that is added to the zeroth-order Hamiltonian to approximate the exact solution. The harmonic oscillator Hamiltonian is chosen to be the zeroth-order term in VPT2.

First, the potential energy, $V(\mathbf{Q})$, can be expanded in terms of normal coordinates, $\mathbf{Q}$, with indices $i, j, k, l, \dots$, using a power series expansion:

$$V(\mathbf{Q}) = V_0 + \frac{1}{2} \sum_{ij} H_{ij} Q_i Q_j + \frac{1}{6} \sum_{ijk} H_{ijk} Q_i Q_j Q_k + \frac{1}{24} \sum_{ijkl} H_{ijkl} Q_i Q_j Q_k Q_l + \dots, \quad (1.36)$$

in which the gradient term is absent because the expansion is assumed to be centered at a stationary point on the potential energy surface. The tensor elements, $H_{ijkl\dots}$, represent the force

constants, and $Q_i, Q_j, Q_k, Q_l, \dots$ describe the displacements from equilibrium (stationary point). Under the harmonic oscillator approximation, the potential energy surface is quadratic around equilibrium, and thus, only the first two terms in Eq. 1.36 are considered. Consequently, only the second derivatives of the energy with respect to nuclear displacements need to be evaluated, and the analytic solutions for them already exist.

The inadequacy of the harmonic approximation stems from the fact that its associated potential energy surface overestimates the curvature, thus resulting in frequencies that are usually higher than the fundamental frequencies. The VPT2 theory adds perturbative corrections to the harmonic frequencies by introducing the anharmonic (cubic and quartic) potential terms (cf. Eq. 1.36, terms 3 and 4), as well as anharmonic kinetic energy terms, including Coriolis effects and centrifugal distortion. An important point to note is the implicit assumption that the harmonic approximation estimates bulk of the target result, and the perturbation terms contribute only a small amount to the final value. If this is not true, as in the case of weakly-bound systems and molecules with floppy bending modes, perturbation theory fails to produce the desired result.

Another problem with VPT2 is the occurrence of Fermi resonance due to the proximity of an overtone or a combination band to the frequency of a fundamental, subject to symmetry restrictions. In order to understand this resonance phenomenon, it is necessary to have a closer look at some of the equations representing the anharmonicity constants. The diagonal anharmonicity constants are represented by:

$$\chi_{rr} = \frac{1}{16} \phi_{rrrr} - \sum_s \frac{\phi_{rrs}^2 (8\omega_r^2 - 3\omega_s^2)}{16\omega_s (4\omega_r^2 - \omega_s^2)}, \quad (1.37)$$

in which the tensors, ϕ , are the force constants in dimensionless normal coordinates. If $2\omega_r \approx \omega_s$, the diagonal anharmonicity constant approaches $-\infty$, provided the cubic force constant, ϕ_{rrs} , in

the numerator is non-zero. This leads to the breakdown of the VPT2 analysis, and an alternative formula needs to be introduced. Consequently, the second term in Eq. 1.37 is factored using:

$$\frac{\phi_{rrs}^2(8\omega_r^2 - 3\omega_s^2)}{16\omega_s(4\omega_r^2 - \omega_s^2)} = \frac{\phi_{rrs}^2}{32} \left[\frac{1}{2\omega_r + \omega_s} - \frac{1}{2\omega_r - \omega_s} + \frac{4}{\omega_s} \right], \quad (1.38)$$

and the overtone-type Fermi resonance issue can be fixed by making the subsequent replacement:

$$\frac{\phi_{rrs}^2}{32} \left[\frac{1}{2\omega_r + \omega_s} - \frac{1}{2\omega_r - \omega_s} + \frac{4}{\omega_s} \right] \rightarrow \frac{\phi_{rrs}^2}{32} \left[\frac{1}{2\omega_r + \omega_s} + \frac{4}{\omega_s} \right]. \quad (1.39)$$

An analogous treatment is carried out for the off-diagonal anharmonicity constants, χ_{rs} , involving the combination-type Fermi resonance, $\omega_r \approx \omega_s + \omega_t$, and is described in detail in the literature.⁵⁵

Once the anharmonicity constants are evaluated, the vibrational energy levels of an asymmetric top are given by:

$$G(\mathbf{v}) = \sum_r \omega_r \left(v_r + \frac{1}{2} \right) + \sum_{r \geq s} \chi_{rs} \left(v_r + \frac{1}{2} \right) \left(v_s + \frac{1}{2} \right) + \dots, \quad (1.40)$$

in which the higher-order terms are neglected due to their small contributions. The zero-point vibrational energy is then given by:

$$G(0) = \sum_r \frac{\omega_r}{2} + \sum_{r \geq s} \frac{\chi_{rs}}{4}, \quad (1.41)$$

with some additional kinetic energy contributions. Furthermore, the fundamental vibrational frequency, ν_r , is defined as:

$$\nu_r = \omega_r + 2\chi_{rr} + \sum_{r \neq s} \frac{\chi_{rs}}{2}, \quad (1.42)$$

in which the total anharmonic correction to the harmonic frequency, ω_r , is given by the sum of the third and the fourth terms.

One last point to note is that the normal coordinate system employed in the VPT2 analysis has a mass-dependence, and so do the force constants necessary for computing isotopic shifts. In order to compute the fundamental vibrational frequencies, at most the semi-diagonal quartic force constants, ϕ_{iijj} , are needed. However, in our computational analysis, we compute the full set of quartic force constants, ϕ_{ijkl} , which allows transformation to any quartic representation of the potential energy.

1.7 RESEARCH OVERVIEW

The ground electronic state of $\text{C}(\text{BH})_2$ is thoroughly investigated in Chapter 2 using coupled-cluster theory and correlation-consistent basis sets in an effort to pinpoint the equilibrium geometric structures, relative energetics, and vibrational spectra. Focal point analysis (FPA) method is employed to obtain the most accurate relative energies. Similar treatment is carried out for the aluminum analogue, $\text{C}(\text{AlH})_2$. The computed anharmonic vibrational frequencies for the linear $\text{C}(\text{BH})_2$ species are compared with the available infrared (IR) data. The *ab initio* quantum chemical computations are followed by exhaustive bonding analyses utilizing the atoms-in-molecules (AIM) approach, molecular orbital plots, various population analyses, local mode vibrations and force constants, unified reaction valley analysis (URVA), and other methods. In Chapter 3, high-accuracy coupled-cluster method, as far as the CCSDT(Q)/CBS level, is used to investigate the ground electronic structure of the classic quasilinear fulminic acid (HCNO) molecule. Harmonic and anharmonic vibrational frequencies are also obtained at very high levels, and compared with the available IR data. Extensive benchmarking is carried out on the structurally similar HCN molecule. Finally, a rigorous topological analysis of polytwistane is carried out in Chapter 4 to reveal a non-repeating, helical, hydrocarbon nanotube structure.

Homodesmotic equations, accompanied by the FPA treatment, are utilized to determine the enthalpy of formation of polytwistane. The thermodynamic and synthetic viability of this polymer with respect to acetylene are discussed.

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CHAPTER 2

NEARLY DEGENERATE ISOMERS OF $\text{C}(\text{BH})_2$: CUMULENE, CARBENE, OR CARBONE?[†]

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2.1 ABSTRACT

The ground electronic state of $\text{C}(\text{BH})_2$ exhibits both a linear minimum and a peculiar angle-deformation isomer with a central B–C–B angle near 90° . Definitive computations on these species and the intervening transition state have been executed by means of coupled cluster theory including single and double excitations (CCSD), perturbative triples [CCSD(T)], and full triples with perturbative quadruples [CCSDT(Q)], in concert with series of correlation-consistent basis sets (cc-pVXZ, $X = \text{D}, \text{T}, \text{Q}, 5, 6$; cc-pCVXZ, $X = \text{T}, \text{Q}$). Final energies were pinpointed by focal point analyses (FPA) targeting the complete basis set limit of CCSDT(Q) theory with auxiliary core correlation, relativistic, and non-Born Oppenheimer corrections. Isomerization of the linear species to the bent form has a minuscule FPA reaction energy of $0.02 \text{ kcal mol}^{-1}$ and a corresponding barrier of only $1.89 \text{ kcal mol}^{-1}$. Quantum tunneling computations reveal interconversion of the two isomers on a time scale much less than 1 s even at 0 K. Highly accurate CCSD(T)/cc-pVTZ and composite c~CCSDT(Q)/cc-pCVQZ anharmonic vibrational frequencies confirm matrix-isolation infrared bands previously assigned to linear $\text{C}(\text{BH})_2$ and provide excellent predictions for the heretofore unobserved bent isomer. Chemical bonding in the $\text{C}(\text{BH})_2$ species was exhaustively investigated by the Atoms-In-Molecules (AIM) approach, molecular orbital plots, various population analyses, local mode vibrations and force constants, Unified Reaction Valley Analysis (URVA), and other methods. Linear $\text{C}(\text{BH})_2$ is a cumulene, whereas bent $\text{C}(\text{BH})_2$ is best characterized as a carbene with little carbene character. Weak B–B attraction is clearly present in the unusual bent isomer, but its strength is insufficient to form a CB_2 ring with a genuine boron-boron bond and attendant AIM bond path.

2.2 INTRODUCTION

Recent theoretical¹ and experimental² studies have revealed a class of divalent carbon(0) compounds CL_2 that exhibit peculiar bonding and chemical reactivity clearly distinguishable from carbenes CR_2 . These compounds have been designated as carbones and may be viewed as donor-acceptor complexes $L \rightarrow C \leftarrow L$ between a bare carbon atom in the excited ^1D state and two σ -donor ligands L . In contrast, carbenes involve two electron-sharing bonds between the substituents R and a ground-state ^3P carbon atom.¹ Stable carbones, which typically have $L-C-L$ bending angles near 130° , have been synthesized with L = phosphine [carbodiphosphoranes, $C(PR_3)_2$]³ and L = carbene [carbodicarbenes, $C(CR_2)_2$].^{2a-f} Carbon suboxide (C_3O_2), which is usually rendered with cumulated double bonds ($O=C=C=O$),⁴ has also been considered a $OC \rightarrow C \leftarrow CO$ donor-acceptor species.^{1c-g} The carbone bonding model nicely explains why C_3O_2 has a bent gas-phase equilibrium geometry with $\angle(C-C-C) = 156^\circ$,⁵ the larger bending angle vis-à-vis carbodiphosphoranes and carbodicarbenes coming from the higher π -acceptor strength of CO.⁶

Theoretical searches for synthetically viable carbones have found that carbodiylides $C(ECp^*)_2$ ($E = Al-Tl$) are strongly bonded molecules with $E-C-E$ bending angles of 100° – 105° .⁷ In contrast to the heavier group-13 homologues, $C(BCp^*)_2$ was computed to have a linear $B-C-B$ arrangement. This finding was explained in terms of a $Cp^*B=C=BCp^*$ structure with electron-sharing bonds and boron in the formal oxidation state III, at variance with the carbodiylides $C(ECp^*)_2$ ($E = Al-Tl$) that possess donor-acceptor bonds $Cp^*E \rightarrow C \leftarrow ECp^*$ with the elements E in oxidation state I.

The theoretical studies of $C(ECp^*)_2$ also investigated the parent systems $C(EH)_2$.⁸ The heavier homologues of $C(EH)_2$ with $E = Al-Tl$ display equilibrium structures similar to

$\text{C}(\text{ECp}^*)_2$ with $\angle(\text{E}-\text{C}-\text{E}) = 100^\circ\text{--}110^\circ$. Thus, the electronic structure of $\text{C}(\text{ER})_2$ for $\text{E} = \text{Al--Ti}$ is mainly determined by the donor-acceptor interactions $\text{RE}\rightarrow\text{C}\leftarrow\text{ER}$, and the substituents R play only a minor (steric) role in the equilibrium geometry. However, a peculiar result was found for the boron homologue $\text{C}(\text{BH})_2$.⁸ Geometry optimizations of the linear form gave an $\text{HB}=\text{C}=\text{BH}$ equilibrium structure, but computations starting from a bent geometry yielded a second energy minimum with a very acute bending angle near 90° . A key question is whether the latter isomer might be considered a carbene $\text{HB}\rightarrow\text{C}\leftarrow\text{BH}$ rather than a carbene. A striking result of the computations was the near energetic equivalence of the linear and bent isomers of $\text{C}(\text{BH})_2$.⁸

In this work we report cutting-edge computations of the intriguing potential energy surface of $\text{C}(\text{BH})_2$. We analyze the bonding in the linear (**1a**) and bent (**1b**) isomers as well as the intervening reaction path, while making comparisons to several reference molecules (Figure 2.1). Furthermore, we pinpoint the energetic profile of the **1a** $\rightarrow$ **1b** isomerization and predict highly accurate vibrational spectra of the energy minima, in order to aid future experimental work. A linear $\text{C}(\text{BH})_2$ species was synthesized and spectroscopically identified in a low-temperature matrix by Hassanzadeh and Andrews in 1992.⁹ Low-level quantum chemical computations (RHF/DZP) of the equilibrium geometry, vibrational frequencies, and infrared intensities were compared with experimental spectra in order to identify the molecule. However, only the linear $\text{HB}=\text{C}=\text{BH}$ species was reported, and no assignments were made to the unconventional bent isomer. The present work reinvestigates the earlier findings in light of new, definitive computations on both isomers.

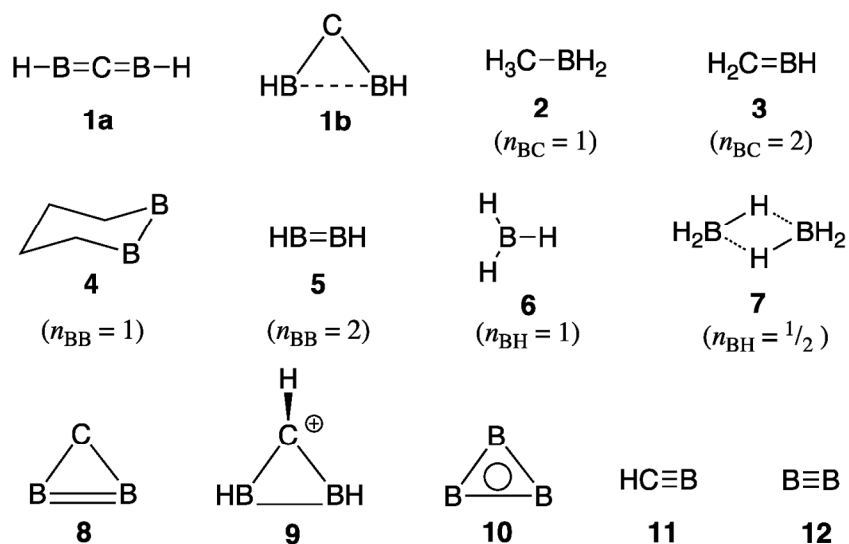


Figure 2.1 Linear (**1a**) and bent (**1b**) isomers of $C(BH)_2$ along with relevant reference molecules.

2.3 COMPUTATIONAL METHODS

High-level *ab initio* computations are crucial to accurately characterizing the nearly isoenergetic structural isomers of $C(BH)_2$. Equilibrium geometries and harmonic vibrational frequencies of the bent and linear isomers as well as the interconnecting transition state were determined using coupled cluster theory¹⁰ including full single and double excitations and a perturbative treatment of connected triple excitations [CCSD(T)].¹¹ Restricted Hartree-Fock reference wave functions were always employed. The computations were executed using the correlation-consistent polarized valence basis sets of the form cc-pVXZ ($X = D, T, Q$) and the associated core-valence cc-pCVXZ ($X = T, Q$) sets developed by Dunning and co-workers.¹²

The focal point analysis (FPA) scheme of Allen and co-workers¹³ was used to pinpoint relative energies by computing a hierarchical series of single-point energies at the CCSD(T)/cc-pVQZ reference geometries. Complete basis set (CBS) limits were found by extrapolating

cc-pV(Q,5,6)Z Hartree–Fock¹⁴ energies (E_{RHF}) and cc-pV(5,6)Z electron correlation energies (E_{corr}) by means of the functional forms¹⁵

$$E_{\text{RHF}}(X) = E_{\text{RHF}}^{\text{CBS}} + ae^{-bX} \quad (2.1)$$

and

$$E_{\text{corr}}(X) = E_{\text{corr}}^{\text{CBS}} + bX^{-3} \quad (2.2)$$

Total energies at the CBS limit for second-order Møller-Plesset perturbation (MP2) theory,¹⁶ the coupled cluster singles and doubles (CCSD)¹⁷ method, and CCSD(T)¹¹ theory were obtained by adding separate $E_{\text{RHF}}^{\text{CBS}}$ and $E_{\text{corr}}^{\text{CBS}}$ results from Eqs. (1) and (2). Our final coupled cluster electron correlation energies included full treatments of singles, doubles, and triples and a perturbative accounting of quadruple excitations [CCSDT(Q)].¹⁸ The following composite (c~) approximation was used to extract CCSDT(Q) results for the CBS limit:¹⁹

$$E_{\text{c-CCSDT(Q)}}^{\text{CBS}} = E_{\text{CCSD(T)}}^{\text{CBS}} + E_{\text{CCSDT(Q)}}^{\text{cc-pVTZ}} - E_{\text{CCSD(T)}}^{\text{cc-pVTZ}} \quad (2.3)$$

The effects of core electron correlation [$\Delta(\text{core})$], including the small shifts engendered in geometric structures, were evaluated with the cc-pCVQZ basis set^{12b} by differencing all-electron (AE) CCSD(T)/cc-pCVQZ//AE-CCSD(T)/cc-pCVQZ and frozen-core (FC) CCSD(T)/cc-pCVQZ//FC-CCSD(T)/cc-pVQZ energies, where // denotes “at the optimum geometry of”. The Diagonal Born-Oppenheimer Correction [ΔDBOC] was included at the RHF/cc-pVQZ level. A first-order relativistic correction [$\Delta(\text{rel})$] from the one-electron mass-velocity and Darwin terms was also incorporated from FC-CCSD(T)/cc-pVQZ computations. In total, the final FPA relative energies were computed as

$$\Delta E(\text{FPA}) = \Delta E_{\text{c-CCSDT(Q)}}^{\text{CBS}} + \Delta(\text{ZPVE}) + \Delta(\text{core}) + \Delta(\text{rel}) + \Delta(\text{DBOC}), \quad (2.4)$$

in which the zero-point vibrational energy (ZPVE) term was evaluated with FC-CCSD(T)/cc-pVQZ harmonic frequencies.

The CCSD(T) geometry optimizations and harmonic vibrational frequency computations were carried out using analytic gradient methods within the Mainz–Austin–Budapest (MAB) version of the ACESII program²⁰ or the successor CFOUR package.²¹ The MP2, CCSD, and CCSD(T) single-point computations for the focal point analyses were performed with the MOLPRO program.²² The CCSDT(Q) results were obtained with the string-based MRCC code of Kállay using integrals generated from MAB ACESII;^{18b,23} MRCC is a stand-alone program capable of carrying out arbitrary-order coupled cluster and configuration interaction energy computations.

Anharmonic vibrational frequencies were computed by application of second-order vibrational perturbation theory (VPT2)^{24,25,26,27} to FC-CCSD(T)/cc-pVTZ and c~CCSDT(Q)/cc-pCVQZ complete internal-coordinate quartic force fields, as obtained by the INTDIF numerical differentiation program²⁸ from an optimal grid of tightly-converged ($10^{-12} E_h$) energy points. The c~CCSDT(Q)/cc-pCVQZ force field was determined using the composite energy formula

$$E_{c\text{-CCSDT(Q)}}^{\text{cc-pCVQZ}} = E_{\text{AE-CCSD(T)}}^{\text{cc-pCVQZ}} + E_{\text{CCSDT(Q)}}^{\text{cc-pVDZ}} - E_{\text{CCSD(T)}}^{\text{cc-pVDZ}}, \quad (2.5)$$

and geometries were re-optimized at this level of theory before executing the numerical differentiation. By enforcing strict $D_{\infty/h}$ cylindrical symmetry²⁹ for **1a** and utilizing C_{2v} symmetry for **1b**, the full quartic force fields were accurately computed from only 239 and 568 points, respectively. The curvilinear force field transformations^{30,31} from internal to normal coordinates were executed with the INTDER program,^{32,33} after which vibrational anharmonicities and spectroscopic constants were extracted with ANHARM.³³ A Fermi resonance threshold of 25 cm^{-1} was chosen for the VPT2 treatment.

Diagnostics of multireference character were applied to the ground electronic state of the C(BH)₂ stationary points. At the FC-CCSD/cc-pVQZ level of theory, the (linear, bent, transition

state) structures displayed T_1 diagnostics³⁴ of (0.018, 0.016, 0.017) and D_1 diagnostics³⁵ of (0.042, 0.038, 0.038), in order, all of which are smaller than the recommended multireference thresholds of 0.02 (T_1) and 0.05 (D_1). Moreover, the (linear, bent, transition state) maximum absolute t_2 amplitudes were only (0.066, 0.080, 0.060) at the same level of theory. Finally, full-valence CASSCF/cc-pVQZ wave functions³⁶ (12 electrons in 14 molecular orbitals) were computed with MOLPRO to ascertain the leading configuration interaction (CI) coefficients (C_1 , C_2) for determinants constructed from CASSCF natural orbitals. The (linear, bent, transition state) structures exhibited $C_1 = (0.938, 0.938, 0.940)$ and $C_2 = (-0.100, -0.135, -0.098)$, revealing clear dominance of the ground-state Hartree-Fock configuration. In summary, $\text{C}(\text{BH})_2$ is predominantly a closed-shell system without substantial diradical character that can be accurately treated by the high-order single-reference coupled cluster methods employed here. This conclusion is particularly germane for the unusual bent isomer.

2.4 RESULTS AND DISCUSSION

2.4.1 Structures, energies and vibrational spectra

The geometric structures of the closed-shell ground electronic states of the linear and bent isomers of $\text{C}(\text{BH})_2$, as well as the transition state (**TS1**) for their interconversion, were optimized at the CCSD(T) level using basis sets ranging from cc-pVDZ to cc-pCVQZ. The resulting geometric parameters are collected in Tables 2.1–2.3. Figure 2.2 shows the AE-CCSD(T)/cc-pCVQZ structures in comparison with BP86/TZVPP³⁷ density functional results.

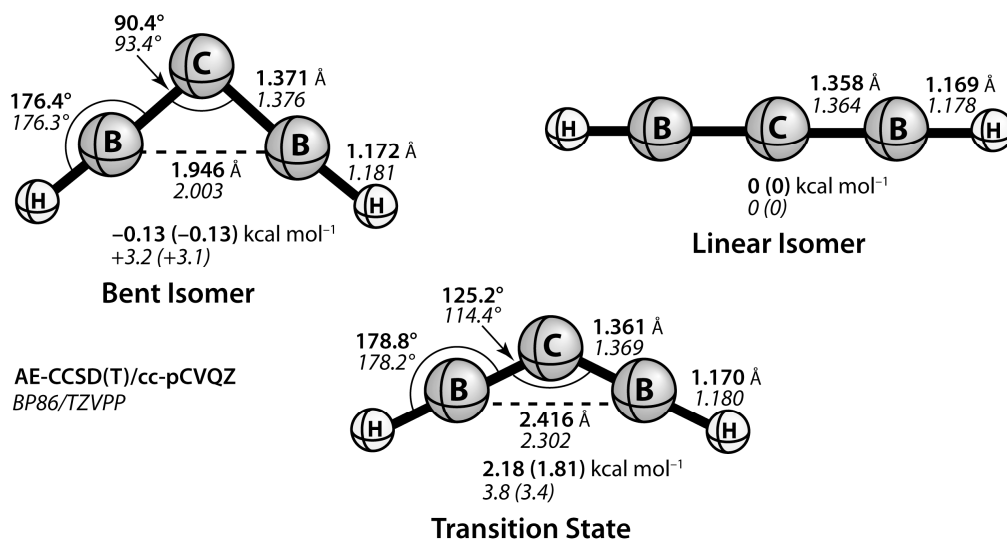


Figure 2.2 Optimum geometric parameters (Å, deg) and relative energies (ΔE_e , kcal mol⁻¹) for the linear (**1a**) and bent (**1b**) isomers of C(BH)₂ and the intervening transition state. AE-CCSD(T)/cc-pCVQZ values boldfaced; BP86/TZVPP results in italics; energies (ΔE_0) with zero-point vibrational corrections in parentheses.

As expected, the B–C and B–H distances decrease with both basis set enlargement and inclusion of core correlation, and the QZ basis sets provide results close to the CBS limit. Extrapolation of the bond distances with a bX^{-3} form as in Eq. (2.2) suggests that in all three C(BH)₂ structures the AE-CCSD(T)/cc-pCVQZ values for [$r_e(\text{B–C})$, $r_e(\text{B–H})$] lie about (0.003, 0.0014) Å above the CBS limit for this level of theory. The CCSD(T) bond angles in the bent and TS structures do not vary much as the basis set is improved, and convergence to about 0.2° is reached with the QZ basis sets. In Fig. 2.2 it is notable that BP86/TZVPP density functional theory gives substantial errors with respect to AE-CCSD(T)/cc-pCVQZ for the B–C–B angle, namely, (+3.0°, –10.8°) for the (bent, TS) forms.

From a chemical perspective, the carbon-boron bond length (1.355 Å) in **1a** is very short. This bond distance is much shorter than the standard value for a covalent C=B double bond (1.45

Å),³⁸ and it is only slightly longer than that for the C≡B triple bond (1.33 Å).³⁹ Note, however, that the genuine C≡B triple bond in the singlet ($^1\Sigma^+$) HCB molecule has an equilibrium distance of only 1.271 Å at the CCSD(T)/cc-pVTZ level.⁴⁰ In comparison, the boron-carbon triple bond length in HB≡CH[−] is predicted to be 1.319 Å at CISD/TZ2P and 1.325 Å at B3LYP/6-311++G**.⁴¹

Table 2.1 Linear C(BH)₂ isomer: optimized bond distances (r_e , Å) and relative energies (ΔE_0 , kcal mol^{−1})^a

	$r_e(\text{B-C})$	$r_e(\text{B-H})$	$\Delta E_0(\text{bent} - \text{linear})$	$\Delta E_0(\text{TS} - \text{linear})$	$r_e[\text{BH}(^1\Sigma^+)]^b$
CCSD(T)					
cc-pVDZ	1.3801	1.1870	−0.161	+1.889	1.2558
cc-pVTZ	1.3648	1.1726	+0.057	+1.910	1.2354
cc-pVQZ	1.3616	1.1714	−0.114	+1.775	1.2333
cc-pCVTZ (AE)	1.3613	1.1712	+0.036	+1.904	1.2332
cc-pCVQZ (AE)	1.3578	1.1692	−0.127	+1.805	1.2302
c~CCSDT(Q)					
cc-pCVQZ(AE)	1.3587	1.1693	+0.191	—	1.2302

^a All-electron, core-correlated results denoted by (AE); frozen-core otherwise. The ΔE_0 values include zero-point vibrational corrections. ^b Bond distances of diatomic BH fragment; the cc-pV(5,6)Z values are (1.2327, 1.2325) Å.

Table 2.2 Bent C(BH)₂ isomer: optimized bond distances (r_e , Å) and angles^a

	$r_e(\text{B-C})$	$r_e(\text{B-H})$	$\angle(\text{B-C-B})$	$\angle(\text{H-B-C})$	$r_e(\text{B-B})$	$\angle(\text{C-B-B})$
CCSD(T)						
cc-pVDZ	1.3987	1.1911	90.99°	175.82°	1.9951	44.50°
cc-pVTZ	1.3803	1.1749	90.64°	176.03°	1.9629	44.68°
cc-pVQZ	1.3756	1.1739	90.56°	176.24°	1.9549	44.72°
cc-pCVTZ (AE)	1.3761	1.1735	90.57°	176.14°	1.9556	44.72°
cc-pCVQZ (AE)	1.3712	1.1717	90.42°	176.35°	1.9464	44.79°
c~CCSDT(Q)						
cc-pCVQZ(AE)	1.3721	1.1718	90.36°	176.32°	1.9467	44.82°

^a See footnote a of Table 2.1.

Table 2.3 Transition state for C(BH)₂ isomerization: CCSD(T) optimized bond distances (r_e , Å) and angles^a

CCSD(T)/basis	$r_e(\text{B-C})$	$r_e(\text{B-H})$	$\angle(\text{B-C-B})$	$\angle(\text{H-B-C})$	$r_e(\text{B-B})$
cc-pVDZ	1.3853	1.1889	125.84°	178.48°	2.4668
cc-pVTZ	1.3689	1.1735	124.83°	178.49°	2.4266
cc-pVQZ	1.3649	1.1725	125.22°	178.71°	2.4238
cc-pCVTZ (AE)	1.3650	1.1722	124.80°	178.62°	2.4193
cc-pCVQZ (AE)	1.3608	1.1703	125.17°	178.82°	2.4160

^a See footnote a of Table 2.1.

Our computations show that **1b** has a remarkably acute B–C–B bending angle close to 90°, the most reliable prediction being 90.4°[AE-CCSD(T)/cc-pCVQZ]. The large change in the B–C–B angle from 180° in **1a** to 90° in **1b** is accompanied by a surprisingly small elongation (≈ 0.013 Å) of the carbon-boron bond length. Even in the isomerization transition state, the B–C length differs by no more than 0.01 Å from the corresponding reactant and product distances. In addition, the B–H bond varies by less than 0.003 Å during the isomerization process, always maintaining a distance about 0.06 Å longer than that in diatomic BH(¹Σ⁺) (Table 2.1). Finally, **1b** exhibits an H–B–C angle that is removed from linearity by less than 4°.

The bent isomer does not exhibit a true B–B bond, although some boron-boron covalent interaction can be expected. The B–B interatomic distance of 1.946 Å (AE-CCSD(T)/cc-pCVQZ) in **1b** is much longer than the standard value for a B–B single bond (1.70 Å).⁴² Moreover, BP86/TZ2P theory yields a B–B distance in **1b** that is 0.25 Å longer than that in planar H₂B–BH₂ (1.752 Å).⁴³ More discussion on this topic appears in the bonding analysis section below. Our searches did not find an energy minimum for a genuine cyclic form of C(BH)₂ exhibiting a B–B single bond.

The relative energies of the linear, bent, and TS structures of C(BH)₂ are also given in Table 2.1 and Fig. 2.2. At the BP86/TZVPP level, **1b** is 3.1 kcal mol^{−1} higher than **1a**, and the

barrier for collapsing to **1a** is merely 0.3 kcal mol⁻¹. However, the CCSD(T) results show that BP86/TZVPP significantly underestimates both the thermodynamic and kinetic stability of **1b**. All of the CCSD(T) data in Table 2.1 place **1b** within 0.2 kcal mol⁻¹ of **1a**. In particular, AE-CCSD(T)/cc-pCVQZ theory predicts that the bent isomer is 0.13 kcal mol⁻¹ lower in energy.

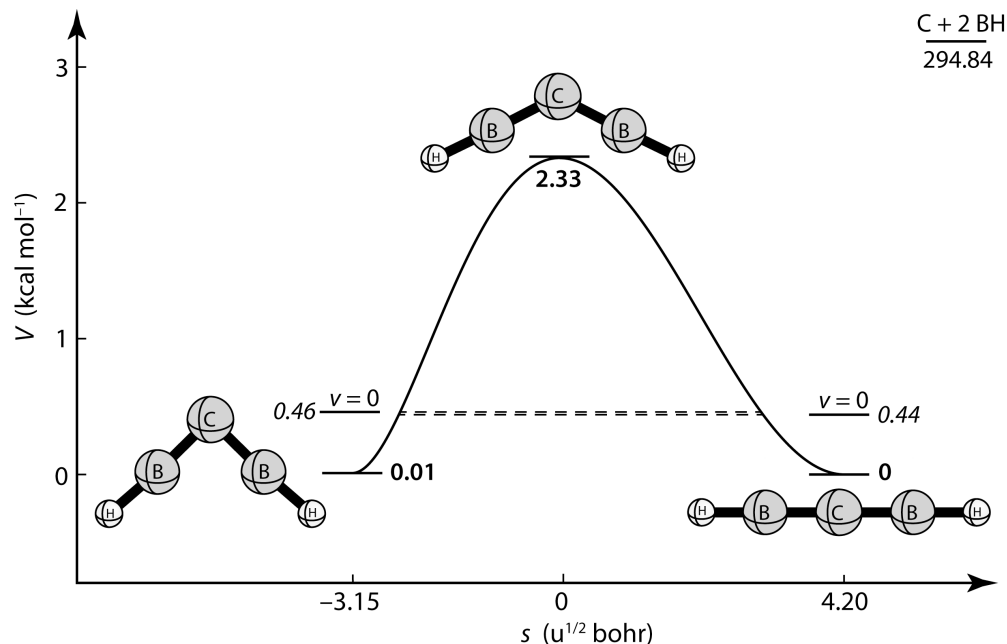


Figure 2.3 Final FPA energy profile $[V(s)]$ vs. arc length (s) along the $C(BH)_2$ isomerization path, in comparison to the energy of the separated fragments $C(^3P) + 2 BH(^1\Sigma^+)$ (not drawn to scale). The boldfaced values correspond to the vibrationally adiabatic potential energy curve that includes ZPVE for all modes complementary to the reaction coordinate. The ground vibrational levels of the two isomers, containing the ZPVE available to the reaction coordinate, are shown in italics. The abscissa is the arc length in mass-weighted Cartesian coordinate space along the intrinsic reaction path (IRP).

The linear $\rightarrow$ bent isomerization energy is pinpointed by the FPA results in Table 2.4. Therein, full convergence to the CBS limit is achieved, as demonstrated by the nearly exact agreement between the explicitly computed cc-pV6Z increments and the extrapolated values. The convergence toward the electron correlation limit is also excellent; systematic reduction is

witnessed in the successive correlation increments, and the final $\delta[\text{CCSDT(Q)}]$ contribution is only $0.33 \text{ kcal mol}^{-1}$. With inclusion of the auxiliary terms, we find a final FPA isomerization energy of $0.02 \text{ kcal mol}^{-1}$, favoring the linear form by a minuscule amount. In fact, this energy difference is less than our estimated uncertainty of $\pm 0.10 \text{ kcal mol}^{-1}$. In essence, *the two angle-deformation isomers of C(BH)_2 are energetically degenerate.*

Table 2.4 Focal point analysis^a of the linear $\rightarrow$ bent isomerization energy (kcal mol^{-1}) of C(BH)_2

	$\Delta E_e(\text{RHF})$	$+\delta[\text{MP2}]$	$+\delta[\text{CCSD}]$	$+\delta[\text{CCSD(T)}]$	$+\delta[\text{CCSDT(Q)}]$	NET
cc-pVDZ	+3.41	-2.71	-1.36	+0.83	+0.32	+0.48
cc-pVTZ	+3.97	-3.52	-1.02	+0.71	+0.33	+0.47
cc-pVQZ	+3.90	-3.70	-1.01	+0.70	[+0.33]	[+0.23]
cc-pV5Z	+3.90	-3.85	-0.99	+0.69	[+0.33]	[+0.07]
cc-pV6Z	+3.89	-3.88	-0.99	+0.69	[+0.33]	[+0.04]
CBS LIMIT	[+3.89]	[-3.91]	[-0.99]	[+0.69]	[+0.33]	[+0.01]
Function	$a+be^{-cX}$	$a+bX^{-3}$	$a+bX^{-3}$	$a+bX^{-3}$	addition	
X (fit points) =	(4,5,6)	(5,6)	(5,6)	(5,6)		

FC-CCSD(T)/cc-pVQZ reference geometries

$\Delta(\text{ZPVE}) = -0.011$; $\Delta(\text{core}) = +0.020$; $\Delta(\text{DBOC}) = +0.005$; $\Delta(\text{rel}) = -0.005$.

$\Delta E_0(\text{FPA}) = +0.01 - 0.011 + 0.005 - 0.005 + 0.020 = \mathbf{+0.02 \text{ kcal mol}^{-1}}$

^a The symbol δ denotes the *increment* in the energy difference (ΔE_e) with respect to the previous level of theory in the hierarchy $\text{RHF} \rightarrow \text{MP2} \rightarrow \text{CCSD} \rightarrow \text{CCSD(T)} \rightarrow \text{CCSDT(Q)}$. Bracketed numbers result from basis set extrapolations (using the specified functions and fit points) or additivity approximations, while unbracketed numbers were explicitly computed. The main table targets $\Delta E_e[\text{FC-CCSDT(Q)}]$ in the complete basis set limit (NET/CBS LIMIT). Auxiliary energy terms are appended for zero-point vibrational energy (ZPVE), core electron correlation [$\Delta(\text{core})$], the diagonal Born-Oppenheimer correction [$\Delta(\text{DBOC})$], and special relativity [$\Delta(\text{rel})$]. The final energy difference $\Delta E_0(\text{FPA})$ is boldfaced.

Figure 2.3 shows the FPA reaction profile for the rearrangement between **1a** and **1b**. In this diagram, the ZPVE of the low-frequency B–C–B bending mode has been removed from the relative energies to expose the one-dimensional vibrationally adiabatic potential energy curve on which isomerization occurs. In this representation, **1b** lies $0.01 \text{ kcal mol}^{-1}$ above **1a**, and its

ground vibrational state ($\nu = 0$) is 0.02 kcal mol⁻¹ higher than its linear counterpart. The B–C–B bending angle distorts to 125.2° [AE-CCSD(T)/cc-pCVQZ] in the transition state, resulting in a barrier of 2.33 kcal mol⁻¹ with respect to the linear form. With inclusion of ZPVE for the reaction mode, the activation barrier is reduced to 1.89 kcal mol⁻¹. The FPA that arrives at this result is laid out in Table 2.5, wherein the basis set and electron correlation series are converged even better than for the isomerization energy in Table 2.4. Because the barrier separating **1a** and **1b** is so small, these two isomers should rapidly interconvert even at low temperatures.

The thermodynamic stability of C(BH)₂ was assessed by computing the total dissociation energy (TDE) for breaking both carbon-boron bonds in **1a** yielding ground-state fragments:

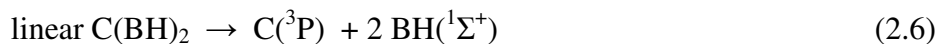


Table 2.6 details the FPA for reaction (2.6). Because multiple bonds are being homolytically cleaved, the basis set and electron correlation requirements for computing an accurate TDE are severe. Nonetheless, our FPA is able to arrive at a result, TDE = 294.8 kcal mol⁻¹, that is accurate to better than 1 kcal mol⁻¹. Therefore, we confidently conclude that the mean C–B bond dissociation energy (D_0) in both C(BH)₂ isomers is very large, 147 kcal mol⁻¹. This value is much larger than in the case of HC≡B(¹Σ⁺) → CH(²Π) + B(²P), for which we computed a precise $D_0[\text{HCB}({}^1\Sigma^+)] = 84.9$ kcal mol⁻¹ using our FPA method. However, the excitation energies for atomic B(²P→²D) (136.7 kcal mol⁻¹)⁴⁴ and diatomic CH(²Π→⁴Σ⁻) (16.7 kcal mol⁻¹),⁴⁵ which are required to obtain the electronic reference state for HC≡B, are much higher than the excitation energy for 2 BH(¹Σ⁺→³Π) (2 × 30.3 = 60.6 kcal mol⁻¹),⁴⁶ which provides the electronic reference state of C(BH)₂. The mean intrinsic interaction energy of the carbon-boron bonds in **1a** becomes 178 kcal mol⁻¹ when the reference state C(³P) + BH(³Π) is considered. In comparison, the intrinsic interaction energy for the triple bond in HC≡B with respect to CH(⁴Σ⁻) + B(²D) is 238.3

kcal mol⁻¹, obtained by correcting our aforementioned $D_0[\text{HCB}(^1\Sigma^+)]$ computed with the FPA method.

Table 2.5 Focal point analysis^a of the barrier height (kcal mol⁻¹) for linear $\rightarrow$ bent isomerization of $\text{C}(\text{BH})_2$

	$\Delta E_e(\text{RHF})$	$+\delta[\text{MP2}]$	$+\delta[\text{CCSD}]+\delta[\text{CCSD(T)}]$	$+\delta[\text{CCSDT(Q)}]$	NET	
cc-pVDZ	+1.91	+0.91	-0.99	+0.61	+0.18	+2.61
cc-pVTZ	+2.18	+0.46	-0.85	+0.56	+0.20	+2.56
cc-pVQZ	+2.10	+0.36	-0.88	+0.57	[+0.20]	[+2.35]
cc-pV5Z	+2.10	+0.26	-0.88	+0.57	[+0.20]	[+2.26]
cc-pV6Z	+2.10	+0.24	-0.88	+0.57	[+0.20]	[+2.24]
CBS LIMIT	[+2.10]	[+0.22]	[-0.88]	[+0.57]	[+0.20]	[+2.21]
Function	$a+be^{-cX}$	$a+bX^{-3}$	$a+bX^{-3}$	$a+bX^{-3}$	addition	
X (fit points) =	(4,5,6)	(5,6)	(5,6)	(5,6)		

FC-CCSD(T)/cc-pVQZ reference geometries

$\Delta(\text{ZPVE}) = -0.378$; $\Delta(\text{core}) = +0.054$; $\Delta(\text{DBOC}) = +0.002$; $\Delta(\text{rel}) = -0.003$.

$\Delta E_0(\text{FPA}) = +2.21 - 0.378 + 0.002 - 0.003 + 0.054 = \mathbf{+1.89 \text{ kcal mol}^{-1}}$

^a See footnote of Table 2.4 for notation.

Table 2.6 Focal point analysis^a of the reaction energy (kcal mol⁻¹) for linear $\text{C}(\text{BH})_2 \rightarrow \text{C}(^3\text{P}) + 2 \text{BH}(^1\Sigma^+)$

	$\Delta E_e(\text{RHF})$	$+\delta[\text{CCSD}]+\delta[\text{CCSD(T)}]$	$+\delta[\text{CCSDT(Q)}]$	NET	
cc-pVDZ	+235.96	+31.70	+8.59	+0.72	+276.97
cc-pVTZ	+240.84	+41.87	+10.27	+0.54	+293.52
cc-pVQZ	+241.50	+46.05	+10.71	[+0.54]	[+298.79]
cc-pV5Z	+241.59	+47.35	+10.85	[+0.54]	[+300.32]
cc-pV6Z	+241.56	+47.91	+10.90	[+0.54]	[+300.91]
CBS LIMIT	[+241.55]	[+48.67]	[+10.97]	[+0.54]	[+301.73]
Function	$a+be^{-cX}$	$a+bX^{-3}$	$a+bX^{-3}$	addition	
X (fit points) =	(4,5,6)	(5,6)	(5,6)		
FC-CCSD(T)/cc-pVQZ reference geometries					
$\Delta(\text{ZPVE}) = -10.413$; $\Delta(\text{core}) = +3.019$; $\Delta(\text{DBOC}) = +0.276$; $\Delta(\text{rel}) = -0.214$.					
$\Delta E_0(\text{FPA}) = +301.73 - 10.413 - 0.765 - 0.214 + 3.019 = \mathbf{+294.84 \text{ kcal mol}^{-1}}$					

^a See footnote of Table 2.4 for notation.

The matrix isolation investigation⁹ that produced C(BH)₂ and identified it as a linear molecule codeposited methane molecules with pulsed laser evaporated boron atoms to create numerous new species. Attention was focused on the 1700–1900 cm⁻¹ infrared region because it contained only one new product. Scaled vibrational frequencies computed from a low level of theory (RHF/DZP) aided the assignment of a limited set of experimental IR spectral bands arising from ¹¹B/¹⁰B, H/D, and ¹²C/¹³C isotopologues. The possibility of a bent C(BH)₂ isomer was apparently not considered. The experimental spectra showed three strong IR bands at (1895.2, 1883.9, 1872.0) cm⁻¹ that were assigned to the $\nu_4(\sigma_u^+)$ antisymmetric B=C=B stretching mode of the (H¹⁰BC¹⁰BH, H¹¹BC¹⁰BH, H¹¹BC¹¹BH) species. Corresponding $\nu_4(\sigma_u^+)$ assignments of (1849.7, 1837.9, 1825.4) cm⁻¹ $\leftrightarrow$ (H¹⁰B¹³C¹⁰BH, H¹¹B¹³C¹⁰BH, H¹¹B¹³C¹¹BH) and (1732.2, 1729.8, 1727.4) cm⁻¹ $\leftrightarrow$ (D¹⁰BC¹⁰BD, D¹¹BC¹⁰BD, D¹¹BC¹¹BD) were also made. Finally, a (2230.7, 2213.1, 2190.9) cm⁻¹ set of bands was assigned to the $\nu_3(\sigma_u^+)$ antisymmetric B–D stretching mode of (D¹⁰BC¹⁰BD, D¹¹BC¹⁰BD, D¹¹BC¹¹BD). No additional bands of linear C(BH)₂ were assigned to other regions of the IR spectrum.

The CCSD(T) and c~CCSDT(Q) harmonic (ω_i) and anharmonic (ν_i) vibrational frequencies of the parent ¹²C/¹¹B/H isotopologue computed in this study for the linear, bent, and transition state structures of C(BH)₂ are collected in Table 2.7, where good convergence is seen with respect to level of theory. In Tables A3–A12 of Appendix A, harmonic and anharmonic frequencies for the CCSD(T)/cc-pVTZ, CCSD(T)/cc-pCVQZ, and c~CCSDT(Q)/cc-pCVQZ levels of theory are tabulated for a full set of 12 isotopologues arising from ¹³C, ¹⁰B, and D substitutions. Figure 2.4 illustrates the c~CCSDT(Q)/cc-pCVQZ infrared spectrum corresponding to natural isotopic abundances and an equimolar mixture of the linear and bent isomers.

Table 2.7 Harmonic (ω_i) and anharmonic (ν_i) vibrational frequencies (cm^{-1}) and IR intensities (km mol^{-1} , in parentheses) of stationary points of $\text{C}(\text{BH})_2$ computed with several basis sets^a

Mode (sym)	Description ^b	cc-pVTZ CCSD(T)	cc-pVQZ CCSD(T)	cc-pCVQZ CCSD(T)	cc-pCVQZ c~CCSDT(Q)	cc-pVTZ CCSD(T)	cc-pCVQZ c~CCSDT(Q)
		ω_i	ω_i	ω_i	ω_i	ν_i	ν_i
Linear $\text{C}(\text{BH})_2$							
1 (σ_g^+)	sym B–H stretch	2834 (0)	2839 (0)	2846 (0)	2844	2734	2743
2 (σ_g^+)	sym B–C stretch	1118 (0)	1121 (0)	1126 (0)	1122	1113	1119
3 (σ_u^+)	asym B–H stretch	2843 (141)	2851 (141)	2858 (140)	2857	2744	2752
4 (σ_u^+)	asym B–C stretch	1902 (427)	1905 (437)	1913 (440)	1905	1874	1875
5 (π_g)	asym H–B–C bend	751 (0)	754 (0)	756 (0)	752	746	751
6 (π_u)	sym H–B–C bend	727 (28)	734 (29)	738 (29)	733	723	732
7 (π_u)	B–C–B bend	166 (36)	154 (37)	154 (37)	158	151	153
Bent $\text{C}(\text{BH})_2$							
1 (a_1)	sym B–H stretch	2811 (13)	2816 (12)	2824 (12)	2822	2708	2714
2 (a_1)	sym B–C stretch	1414 (11)	1423 (12)	1432 (12)	1428	1386	1395
3 (a_1)	sym H–B–C ip bend	769 (3)	772 (3)	775 (3)	772	766	768
4 (a_1)	B–C–B bend	315 (0.02)	317 (0.02)	320 (0.03)	318	287	289
5 (a_2)	asym H–B–C oop bend	774 (0)	783 (0)	786 (0)	784	769	775
6 (b_1)	sym H–B–C oop bend	719 (3)	729 (3)	732 (3)	729	716	722
7 (b_2)	asym B–H stretch	2809 (57)	2815 (54)	2823 (52)	2821	2704	2715
8 (b_2)	asym B–C stretch	1536 (84)	1543 (85)	1551 (85)	1545	1525	1537
9 (b_2)	asym H–B–C ip bend	791 (12)	796 (12)	799 (11)	797	785	788
$\text{C}(\text{BH})_2$ transition state							
1 (a_1)	sym B–H stretch	2824	2831	2838			
2 (a_1)	sym B–C stretch	1275	1280	1288			
3 (a_1)	sym H–B–C ip bend	743	751	754			
4 (a_1)	B–C–B bend	176 <i>i</i>	173 <i>i</i>	175 <i>i</i>			
5 (a_2)	asym H–B–C oop bend	748	757	759			
6 (b_1)	sym H–B–C oop bend	721	732	736			
7 (b_2)	asym B–H stretch	2832	2839	2846			
8 (b_2)	asym B–C stretch	1770	1777	1785			
9 (b_2)	asym H–B–C ip bend	762	770	772			

^a (FC, AE) CCSD(T) for the (cc-pVXZ, cc-pCVXZ) basis sets; IR intensities are double-harmonic values.

^b Abbreviations: sym = symmetric; asym = antisymmetric; ip = in-plane; oop = out-of-plane.

The linear and bent isomers exhibit characteristic differences in their vibrational spectra that could make it possible to identify both species through IR spectroscopy. The anharmonic c~CCSDT(Q)/cc-pCVQZ spectrum for linear $\text{H}^{11}\text{B}^{12}\text{C}^{11}\text{BH}$ shows strong signals at (1875, 2752) cm^{-1} for the antisymmetric (B=C=B, B–H) stretches, in order; the corresponding absorption frequencies for $\text{D}^{11}\text{B}^{12}\text{C}^{11}\text{BD}$ are (1730, 2193) cm^{-1} . These results are in very close agreement with the recorded IR spectrum of Hassanzadeh and Andrews,⁹ deviating by only 2–3 cm^{-1} ! In Table 2.8, CCSD(T)/cc-pVTZ and c~CCSDT(Q)/cc-pCVQZ isotopic shifts of the ν_3 and ν_4

fundamental frequencies of linear $\text{C}(\text{BH})_2$ are listed alongside the observed values.⁹ The agreement between theory and experiment is spectacular, further confirming the matrix isolation assignments.

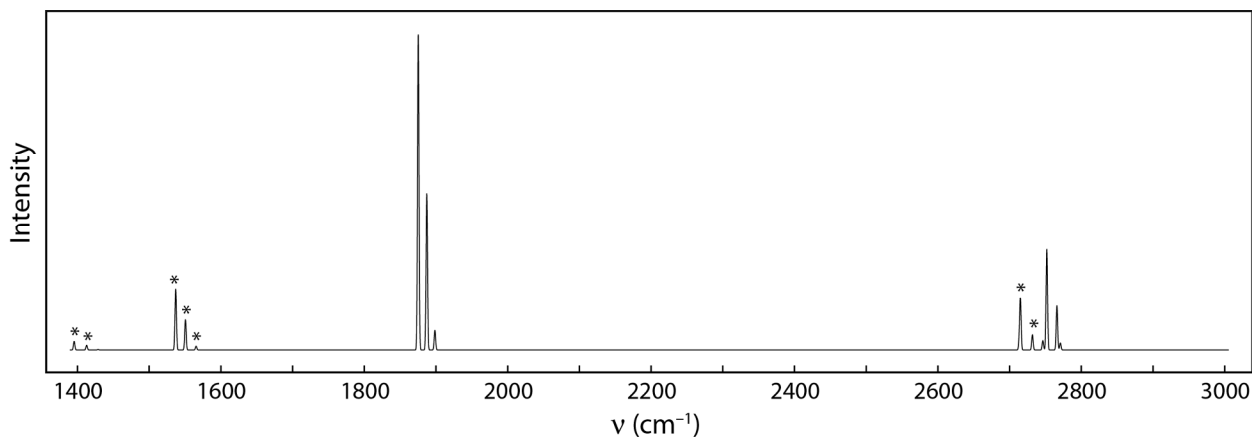


Figure 2.4 Simulated IR spectrum in the 1400–3000 cm^{-1} region of an equimolar mixture of linear and bent $\text{C}(\text{BH})_2$ in natural isotopic abundances, based on $\text{c}\sim\text{CCSDT}(\text{Q})/\text{cc-pCVQZ}$ anharmonic frequencies and $\text{AE-CCSD}(\text{T})/\text{cc-pCVQZ}$ harmonic intensities. Asterisks denote absorptions of the bent isomer.

Table 2.8 Isotopic shifts ($\Delta\nu$, cm^{-1}) of anharmonic vibrational frequencies of linear HBCBH

		$\Delta\nu$ [$\text{CCSD}(\text{T})/\text{cc-pVTZ}$, $\text{c}\sim\text{CCSDT}(\text{Q})/\text{cc-pCVQZ}$, Matrix isolation ⁹]		
		$^{11}\text{B}/^{11}\text{B}$	$^{11}\text{B}/^{10}\text{B}$	$^{10}\text{B}/^{10}\text{B}$
$\nu_3(\sigma_u^+)$	DB=C=BD	(0, 0, 0)	(22.4, 22.4, 22.2)	(39.7, 39.5, 39.8)
$\nu_4(\sigma_u^+)$	HB=C=BH	(0, 0, 0)	(11.9, 11.9, 11.9)	(23.2, 23.2, 23.2)
	HB= ^{13}C =BH	(−46.6, −46.7, −46.6)	(−34.1, −34.1, −34.1)	(−22.3, −22.3, −22.3)
	DB=C=BD	(−146.9, −145.4, −144.6)	(−144.5, −143.0, −142.2)	(−142.2, −140.7, −139.8)

The theoretical IR spectrum of **1b** contains only two fundamental frequencies with substantial intensity, $\nu_7(\text{asym B-H str}) = 2715 \text{ cm}^{-1}$ and $\nu_8(\text{asym B-C str}) = 1537 \text{ cm}^{-1}$ [$\text{c}\sim\text{CCSDT}(\text{Q})/\text{cc-pCVQZ}$, Table 2.7]. The ν_8 frequency is considerably downshifted by 338 cm^{-1} compared to the antisymmetric B–C stretch of the linear isomer, whereas the corresponding

downshift for ν_7 is 37 cm^{-1} . While certainly observable, the ν_7 and ν_8 absorptions of **1b** are predicted to have only 37% and 19%, respectively, of the intensity of their **1a** counterparts. Thus, a critical question regarding the spectroscopic identification of **1b** is whether this isomer can be produced in sufficient quantities. This question must now be addressed.

Quantum tunneling of the heavy-atom framework of $\text{C}(\text{BH})_2$ is responsible for rapid interconversion between the linear and bent isomers, even at cryogenic temperatures. To establish this isomerization mechanism, the FC-CCSD(T)/cc-pVTZ method was employed to precisely map out the associated intrinsic reaction path (IRP) and to determine zero-point vibrational energies (ZPVEs) along this steepest-descent route. The potential energy curve $V(s)$ along the IRP was constructed as a function of arc length (s) in mass-weighted Cartesian coordinates by computing AE-CCSD(T)/cc-pCVQZ energy points appended with the aforementioned ZPVEs. Finally, a hyperbolic tangent switching function was used to slightly adjust the barrier height and reaction energy by 0.046 and $0.148\text{ kcal mol}^{-1}$, respectively, in order to match the key features of $V(s)$ with the FPA energetics. Figure 2.3 shows a quantitative plot of the final $V(s)$ function.

Exact probabilities (κ_{exact}) for tunneling through the $V(s)$ barrier profile were evaluated by numerically integrating time-independent, complex-valued wave functions through the barrier and applying the proper boundary conditions for incoming, reflected, and transmitted waves. In addition, WKB (Wentzel-Kramers-Brillouin) tunneling probabilities (κ_{WKB}) were obtained by numerically evaluating barrier penetration integrals (θ) over the final $V(s)$ function.⁴⁷ This first-principles approach to quantifying tunneling rates has proved very effective in recent studies of hydroxycarbenes.^{48,49,50}

The reactant normal mode leading from bent to linear $\text{C}(\text{BH})_2$ has the harmonic vibrational frequency $\omega_4(\text{B-C-B bend}) = 320 \text{ cm}^{-1}$ [AE-CCSD(T)/cc-pCVQZ, Table 2.7]. Therefore, collisions of **1b** with the isomerization barrier occur with a 0 K energy $\varepsilon = \omega_4/2 = 160 \text{ cm}^{-1}$ in the reaction coordinate. The tunneling rate for isomerization can be computed as the product of the transmission coefficient $[\kappa(\varepsilon)]$ and the classical rate (ω_4) at which the reactant hits the barrier. Employing $(\kappa_{\text{exact}}, \kappa_{\text{WKB}})$ reveals a half-life ($t_{1/2}$) of only (0.010, 0.012) s for tunneling from the ground vibrational state of the bent isomer to the linear form. Performing the same analysis for reverse tunneling of **1a** back to **1b** yields $t_{1/2} = (0.016, 0.021) \text{ s}$ based on $(\kappa_{\text{exact}}, \kappa_{\text{WKB}})$. If the AE-CCSD(T)/cc-pCVQZ curve for the IRP is used without final adjustment to match the FPA energetics, the same linear $\leftrightarrow$ bent interconversion half-lives range only from 0.005 s to 0.050 s. The picture that emerges, regardless of the details of the theoretical analysis, is that the two isomers of $\text{C}(\text{BH})_2$ can interconvert by heavy-atom tunneling on a time scale much less than 1 s even in the complete absence of thermal energy.

To discern the longest possible period over which a viable isotopologue of the bent form could persist in isolation prior to isomerization, we applied our tunneling analysis to $^{13}\text{C}(^{11}\text{BD})_2$. The IRP was explicitly mapped out again with the heavier masses, and the $V(s)$ curve was reconstructed with new energy points. The WKB tunneling result was $t_{1/2} = 3.8 \text{ s}$, which highlights the inherent evanescent nature of the bent species.

Rapid tunneling between the linear and bent isomers may allow an equilibrium to be reached between these species in cryogenic matrices. At the temperature (12 K) of the matrix-isolation experiments of Refs. 9 and 51, the Boltzmann factor (f_{B}) representing the bent:linear population ratio is 0.55 based on the FPA energy difference ($\Delta E_0 = +0.014 \text{ kcal mol}^{-1}$). The ratio of the greatest IR intensities in the vibrational spectra of these isomers is $f_{\text{IR}} = 0.19$

[$I(\omega_8 \text{ bent})$: $I(\omega_4 \text{ linear})$, AE-CCSD(T)/ cc-pCVQZ, Table 2.7]. Therefore, in an equilibrium mixture at 12 K, the signal of the strongest IR band of the bent isomer would be only a fraction $f = f_B f_{\text{IR}} = 0.11$ of the signal coming from the linear species. If matrix effects and residual errors in the FPA energy predictions were to shift ΔE_0 by (+0.05, -0.05) kcal mol⁻¹, very reasonable scenarios, f would be (reduced, increased) to (0.01, 0.86). These rough estimates assist in the interpretation of the matrix-isolation experiments. The comprehensive 1993 paper that followed the preliminary report of Hassanzadeh and Andrews⁹ showed the entire 500–1900 cm⁻¹ region of the infrared spectrum obtained after codepositing laser ablated boron atoms with Ar/CH₄. A broad, weak feature in the vicinity of 1550 cm⁻¹ is unassigned. Because the intensity of this band does not correlate well with changes in the **1a** signals upon either UV radiation or annealing of the matrix, the absorption probably does not arise primarily from **1b** and serves to mask any signal from this isomer. In summary, our computations show that it is quite possible that a significant fraction of C(BH)₂ exists in the Ar matrix as the bent isomer, but the associated IR signals are inherently more difficult to detect and are obscured by other species.

2.4.2 Bonding Analysis

The bonding in **1a** and **1b** was analyzed with various methods to explain the unusual occurrence of two nearly isoenergetic angle-deformation isomers. The investigation tested the hypothesis that the linear form exhibits C–B electron sharing bonds while the bent isomer is characterized by HB→C←BH coordinate covalent, donor-acceptor interactions wherein the carbon atom retains two lone pairs. An AIM (Atoms-In-Molecules)⁵¹ analysis of the electronic structure was carried out first. Figure 2.5 shows the contours of the Laplacian $\nabla^2\rho(\mathbf{r})$ of the electron density of the two isomers in the molecular plane.

In both **1a** and **1b**, C–B and B–H bond paths exist as expected, but no B–B bond path is observed in the bent isomer. The Laplacian of both isomers exhibits large areas of internuclear charge concentration ($\nabla^2\rho < 0$, solid lines) indicative of C–B electron sharing bonds. The area of charge concentration below the carbon atom and between the boron atoms in **1b** suggests a weak covalent B–B interaction, but not strong enough to yield a bond path. The possible strength of the B–B interaction was gauged by computing the energy difference between the (BH)₂ system at the frozen geometry of **1b** and two separated BH diatomics. This measure yields significant boron-boron attraction in bent C(BH)₂, 54.1 and 48.9 kcal mol^{−1} at BP86/TZVPP and CCSD(T)/TZVPP//BP86/TZVPP, respectively.

The position of the C–B bond critical point (bcp) evidences strong polarization towards carbon in both isomers (Figure 2.5). Likewise, NBO analysis gives a large negative charge on carbon in the linear form (−1.49 *e*) and the bent isomer (−0.98 *e*). The charge density, Laplacian $\nabla^2\rho$, and energy *H* at the bcp of the C–B bonds are all similar in the two isomers. Moreover, the shape of the Laplacian distribution at the carbon atom in bent C(BH)₂ is not typical for lone-pair electrons. Collectively, these results show that the C–B bonding is not very different in **1a** and **1b**, and the donor-acceptor interpretation of the bonding in bent C(BH)₂ is not supported.

Figure 2.5 depicts the valence orbitals of the two isomers. The degenerate π HOMO of **1a** is split into the energetically similar π HOMO(*b*₁) and σ HOMO−1(*a*₁) of **1b**. The π HOMO of **1b** has the same shape as the lowest-lying π molecular orbital of the allyl system. The σ HOMO−1 has the largest contribution from the *p*(σ) AO of carbon, whose backside lobe overlaps in-phase with the in-plane *sp* hybridized AOs of boron. Thus, the HOMO−1 further strengthens the B–C bonds and also contributes some B–B bonding. A similar shape was found for the HOMO−1 of the substituted homologues C(ECp^{*})₂ (Al – Tl), attesting to some E–E attraction.⁷

The electron density profile of the HOMO–1 accounts for the rather acute central bond angles in $\text{C}(\text{ECp}^*)_2$ (Al – Tl) and **1b**. This density is visible in the area of charge concentration between the boron atoms in the Laplacian distribution of bent $\text{C}(\text{BH})_2$ (Figure 2.5b). The lower-lying valence orbitals of **1b** directly correlate with the associated valence orbitals of **1a**.

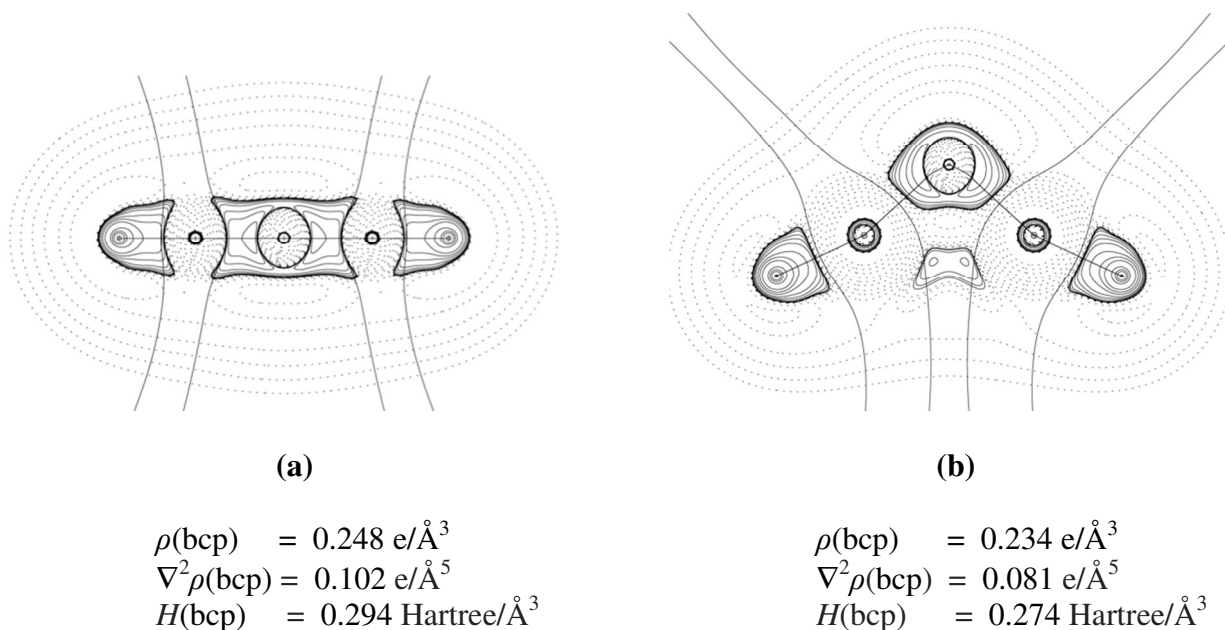
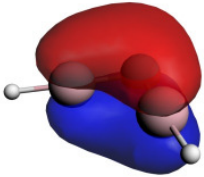
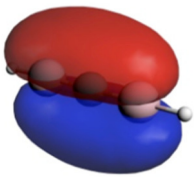
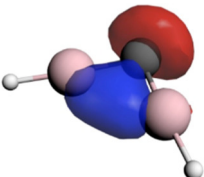
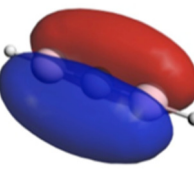
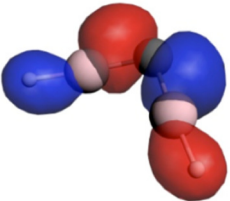
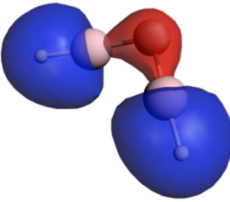
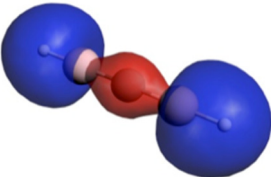
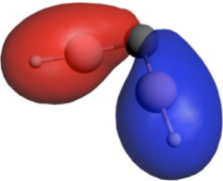
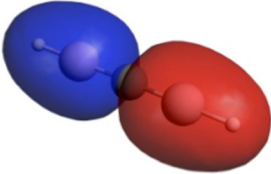
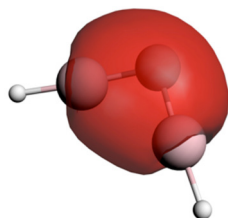


Figure 2.5 Contour line diagrams $\nabla^2\rho(\mathbf{r})$ of (a) linear $\text{C}(\text{BH})_2$ and (b) bent $\text{C}(\text{BH})_2$. Solid lines indicate areas of charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$) while dashed lines show areas of charge depletion ($\nabla^2\rho(\mathbf{r}) > 0$). The thick solid lines connecting the atomic nuclei are the bond paths. The thick solid lines separating the atomic basins indicate the zero-flux surfaces crossing the molecular plane. Electron density $\rho(\mathbf{r}_c)$, Laplacian $\nabla^2\rho(\mathbf{r}_c)$ and total energy density $H(\mathbf{r}_c)$ at the C-B bond critical points.

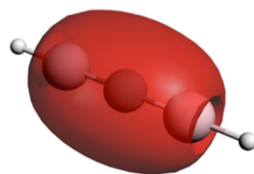
The bonding in linear and bent $\text{C}(\text{BH})_2$ may thus become interpreted as follows. The linear isomer is a cumulene $\text{HB}=\text{C}=\text{BH}$ with classical electron-sharing σ/π double bonds (Figure 2.5a) in which the π -bonding comes from two three-center two-electron bonds. Thus, each C–B π bond extends over the entire B–C–B framework, explaining why the C–B bond distance in the linear form is shorter than that of a standard double bond. However, from the traditional bonding

	bent C(BH) ₂	linear C(BH) ₂
HOMO	 -0.264 eV (b_1)	 -0.240 eV (π_u)
HOMO-1	 -0.279 eV (a_1)	 -0.245 eV (π_u)
HOMO-2	 -0.330 eV (b_2)	 -0.374 eV (σ_u^+)
HOMO-3	 -0.416 eV (a_1)	 -0.412 eV (σ_g^+)
HOMO-4	 -0.430 eV (b_2)	 -0.460 eV (σ_u^+)

HOMO-5

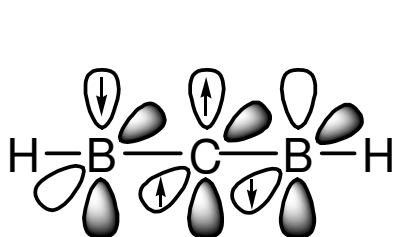


$-0.648 \text{ eV } (a_1)$

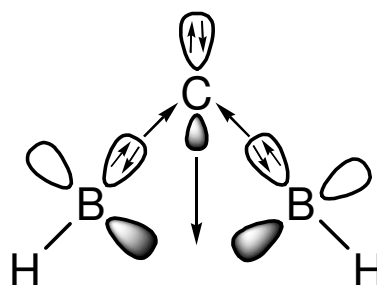


$-0.597 \text{ eV } (\sigma_g^+)$

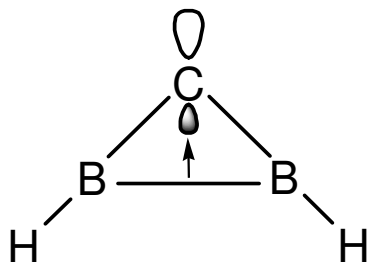
Figure 2.6 Shape and eigenvalues of the valence orbitals of linear and bent $\text{C}(\text{BH})_2$.



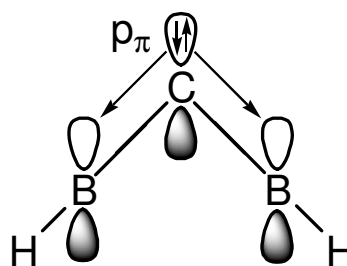
(a)



(b)



(c)



(d)

Figure 2.7 Qualitative model for explaining the shape of the HOMO and HOMO-1 of bent $\text{C}(\text{BH})_2$. Two different perspectives are shown for the intramolecular orbital interactions that lead to the HOMO-1. Depiction (b) starts from a carbone reference point but is not meant to imply that the final electronic structure of bent $\text{C}(\text{BH})_2$ has substantial carbone character.

perspective the boron atoms in **1a** have only six electrons in their valence shells. This viewpoint suggests that partially gaining an electron octet around the boron atoms might be a driving force for forming the bent isomer. The process is shown schematically in Figure 2.7b, which depicts an initial carbene $\text{HB}\rightarrow\text{C}\leftarrow\text{BH}$ reference structure whose carbon σ lone-pair is subsequently donated into the empty in-plane p -AOs of boron. An alternative view is provided by a cyclic $\text{C}(\text{BH})_2$ reference structure with an “inverted” carbene⁵² configuration that donates charge into the vacant carbon σ lone-pair orbital (Figure 2.7c).⁵³ Both perspectives come to the same conclusion: the HOMO–1 in bent $\text{C}(\text{BH})_2$ enhances carbon-boron bonding, it yields partial boron-boron bonding, and it has some (reduced) σ lone-pair character. Finally, Figure 2.7d shows the π -backdonation from the occupied $p(\pi)$ AO of carbon into the empty $p(\pi)$ AOs of boron. The shape of the HOMO (Figure 2.7) suggests that the $\text{C}\rightarrow\text{BH}$ π -backdonation is very strong, which considerably weakens the lone-pair character at carbon.

The lack of strong carbene character in bent $\text{C}(\text{BH})_2$ is revealed by computing first and the second proton affinities (PAs). It has been shown before that carbenes have exceptionally high second PAs, because they have two lone pairs available for protonation in contrast to carbones.¹ Typical carbones CL_2 with $\text{L} = \text{PR}_3$ (carbodiphosphoranes) and $\text{L} = \text{NHC}$ (carbodicarbenes; $\text{NHC} = \text{N-heterocyclic carbene}$) have a first PA of 280–300 kcal mol^{-1} while the second PA is 150–190 kcal mol^{-1} .⁵⁴ With CCSD(T)/TZVPP, the first PA of bent $\text{C}(\text{BH})_2$ is 190.9 kcal mol^{-1} while the second PA is only 35.4 kcal mol^{-1} . These results are more characteristic of a carbene than a carbene.

2.4.3 URVA analysis of isomers via local vibration modes and force constants

Information on the electronic structure of a molecule and its bonding is encoded in the normal vibrational modes. However, normal modes tend to be delocalized as a result of coupling

of local modes. Therefore, only the latter can provide detailed insight into the different bonding and electronic structure of isomers such as **1a** and **1b**. Recent work^{55,56} has proved that the local vibrational modes of Konkoli and Cremer⁵⁷ represent a unique set of local modes directly related to the normal vibrational modes via an adiabatic connection scheme (ACS). The change of a local mode frequency ω_a from the corresponding normal mode frequency ω_μ in an ACS is measured by the coupling frequency

$$\omega_{\text{coup}} = \omega_a - \omega_\mu, \quad (2.7)$$

which absorbs all mass-coupling effects with all other $N_{\text{vib}} - 1$ local modes. The sum of all $|\omega_{\text{coup}}|$ adopts a minimum if the set of local vibrational modes is unique.⁵⁵

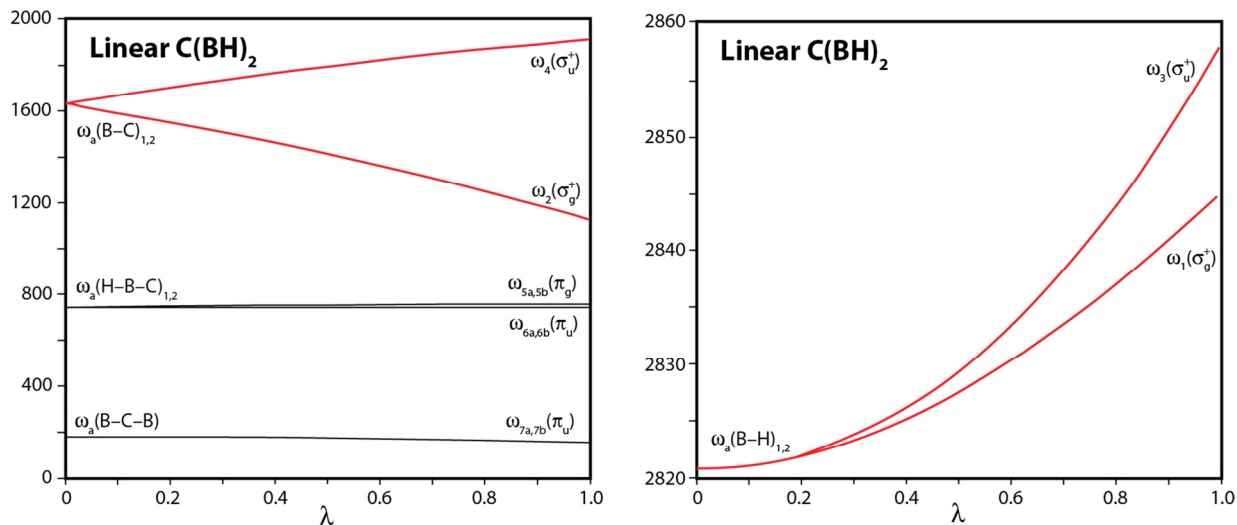


Figure 2.8 Adiabatic connection scheme for **1a** showing the transformation of local (ω_a) to normal (ω_μ) mode vibrational frequencies [AE-CCSD(T)/cc-pCVQZ, in cm⁻¹] as the scale factor λ varies from 0 to 1.

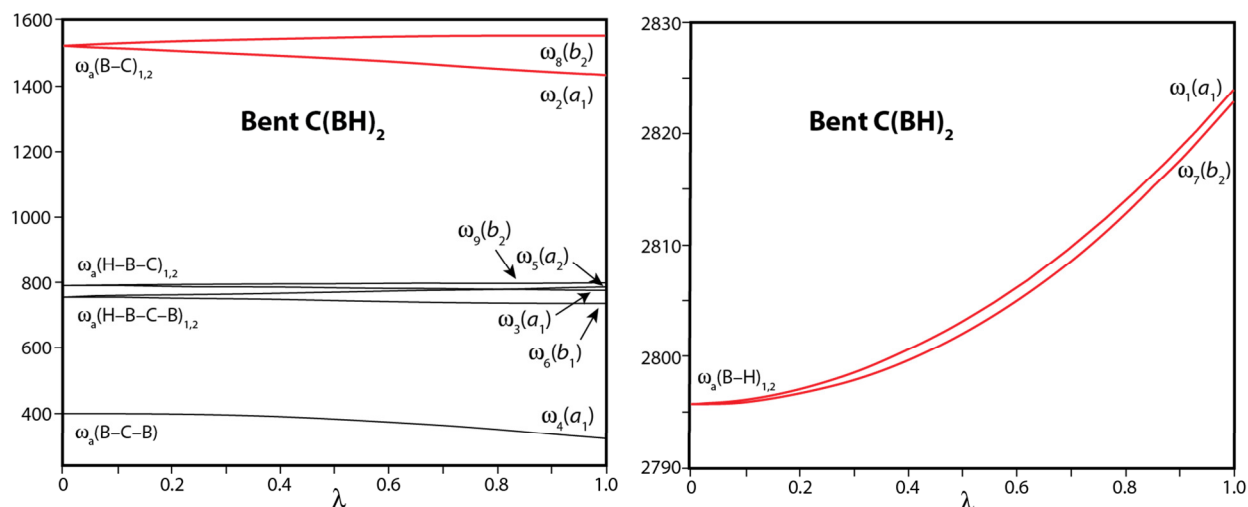


Figure 2.9 Adiabatic connection scheme for **1b** showing the transformation of local (ω_a) to normal (ω_μ) mode vibrational frequencies [AE-CCSD(T)/cc-pCVQZ, in cm^{-1}] as the scale factor λ varies from 0 to 1.

In Figures 2.8 and 2.9 the adiabatic connection scheme for **1a** and **1b**, respectively, is shown as the fractional coupling parameter (λ) varies from 0 to 1. For **1a**, four bond lengths [(B-H)_{1,2}, (B-C)_{1,2}] and three pairs of linear bending angles [(H-B-C)_{1a,1b}, (H-B-C)_{2a,2b}, (B-C-B)_{ab}] give the best match between normal and local vibrational modes. For **1b**, four bond lengths [(B-H)_{1,2}, (B-C)_{1,2}], three bond angles [(H-B-C)_{1,2}, (B-C-B)], and two torsional angles [(H-B-C-B)_{1,2}] lead to the lowest coupling frequencies. In Table 2.9 AE-CCSD(T)/cc-pCVQZ local-mode, normal-mode and coupling frequencies (ω_a , ω_μ , ω_{coup}) are given for **1a** and **1b** along with the local-mode decomposition of the normal modes according to Konkoli and Cremer.⁵⁸ The ACSs reveal that for both **1a** and **1b** the mass coupling is small for all bending motions and the B-H stretching motions. There is however a significant difference between the isomers for the B-C stretching modes. In general, a central bond angle of 90° suppresses couplings between neighboring stretches, whereas a bond angle of 0° or 180° leads to the strongest coupling.⁵⁵ Because the B-C-B angle in **1b** is very close to 90°, the local B-C stretches are only weakly

coupled. The local $\omega_a(\text{B-C})_{1,2}$ stretching frequencies of 1522 cm^{-1} transform into the symmetric and antisymmetric B-C normal mode frequencies [$\omega_2(a_1) = 1432\text{ cm}^{-1}$, $\omega_8(b_2) = 1551\text{ cm}^{-1}$] as a result of $\omega_{\text{coup}} = -90$ and 29 cm^{-1} . In contrast, for **1a** the B-C-B angle of 180° should lead to strong coupling, as fully confirmed by the ACS. Considerably larger **1a** coupling frequencies of -504 and 283 cm^{-1} transform the local $\omega_a(\text{B-C})_{1,2}$ stretching frequencies of 1630 cm^{-1} into the symmetric and antisymmetric B-C normal mode frequencies [$\omega_2(\sigma_g^+) = 1126\text{ cm}^{-1}$, $\omega_4(\sigma_u^+) = 1913\text{ cm}^{-1}$].

Measures of the B-C and B-H bond strengths in **1a** and **1b** must be obtained from local mode rather than normal mode properties. Local mode adiabatic stretching force constants (k_a) provide a direct measure of bond strengths⁵⁸ devoid of the mass effects. These force constants can be converted into more interpretable bond-order parameters (n) with the help of suitable reference molecules (Figure 2.1).^{59,60,61,62} For this purpose we assume the reference bond orders $n_{\text{BC}} = 1$ for CH_3BH_2 (**2**), $n_{\text{BC}} = 2$ for $\text{H}_2\text{C}=\text{BH}$ (**3**), $n_{\text{BB}} = 1$ for $\text{C}_4\text{B}_2\text{H}_{10}$ (**4**) (diborocyclohexane), $n_{\text{BB}} = 2$ for $\text{HB}=\text{BH}$ (**5**), $n_{\text{BH}} = 1$ for BH_3 (**6**), and $n_{\text{BH}} = \frac{1}{2}$ for B_2H_6 (**7**) (electron deficient bonding in H-B-H bridges). Accordingly, the following power relationships are obtained from the B3LYP/6-31G(d,p) data in Table 2.10:

$$n_{\text{BC}} = 0.297 k_a(\text{B-C})^{0.907} \quad (2.8)$$

$$n_{\text{BB}} = 0.363 k_a(\text{B-B})^{0.984} \quad (2.9)$$

$$n_{\text{BH}} = 0.286 k_a(\text{B-H})^{0.921} . \quad (2.10)$$

As discussed in Section 2.4.2, the π bonding in **1a** results for two 2-electron-3-center B-C bonds, which together with the σ bonding should lead to a bond order significantly larger than 2. In **1b** the loss of π -bonding is balanced to a large extent by $\text{C} \rightarrow \text{B}$ π -backdonation, but the B-C bond order should be somewhat smaller than in **1a**. These expectations are confirmed in Table

2.10, wherein $n_{\text{BC}} = 2.25$ for **1a** and $n_{\text{BC}} = 2.03$ for **1b**. The bond order $n_{\text{BC}} = 2.18$ for **TS1** is closer to **1a** than **1b**, consistent with the bond distances in Fig. 2.2. The B–C bond orders for molecules **8–12** (Table 2.10) further demonstrate the usefulness of relation (8).

The B–H bond orders n_{BH} for **1a** (1.12), **1b** (1.10), and **TS1** (1.11) are quite similar, and greater than in BH_3 . It is particularly interesting is to derive a bond order for the B–B interaction. As reflected by the values $n_{\text{BB}} = 0.085$ for **TS1** and 0.123 for **1b** in Table 2.10, the bent form has a stabilizing B–B interaction, which will be further quantified in the next section.

Table 2.9 Vibrational analysis of **1a** and **1b** applied to CCSD(T)/cc-pCVQZ harmonic vibrational normal mode frequencies ω_μ

Type	ω_a (cm^{-1})	μ	ω_μ (cm^{-1})	ω_{coup} (cm^{-1})	Local mode contributions to normal mode (%)
1a					
$\omega_a(\text{B-H})_1$	2821	3	2858	37	48 (B-H) ₁ + 48 (B-H) ₂
$\omega_a(\text{B-H})_2$	2821	1	2846	24	49 (B-H) ₁ + 49 (B-H) ₂
$\omega_a(\text{B-C})_1$	1630	4	1913	282	48 (B-C) ₁ + 48 (B-C) ₂
$\omega_a(\text{B-C})_2$	1630	2	1126	−504	49 (B-C) ₁ + 49 (B-C) ₂
$\omega_a(\text{H-B-C})_1$	746	5a,5b	756	10	50 (H-B-C) ₁ + 50 (H-B-C) ₂
$\omega_a(\text{H-B-C})_2$	746	6a,6b	738	−8	49 (H-B-C) ₁ + 49 (H-B-C) ₂
$\omega_a(\text{B-C-B})$	178	7a,7b	154	−24	100 (B-C-B)
ZPVE	17.50		17.21	−0.29	
1b					
$\omega_a(\text{B-H})_1$	2796	1	2824	28	49 (B-H) ₁ + 49 (B-H) ₂
$\omega_a(\text{B-H})_2$	2796	7	2823	27	49 (B-H) ₁ + 49 (B-H) ₂
$\omega_a(\text{B-C})_1$	1522	8	1551	29	48 (B-C) ₁ + 48 (B-C) ₂
$\omega_a(\text{B-C})_2$	1522	2	1432	−90	48 (B-C) ₁ + 48 (B-C) ₂
$\omega_a(\text{H-B-C})_1$	791	9	799	8	50 (H-B-C) ₁ + 50 (H-B-C) ₂
$\omega_a(\text{H-B-C-B})_1$	757	5	786	29	50 (HBCB) ₁ + 50 (HBCB) ₂
$\omega_a(\text{H-B-C})_2$	791	3	775	−16	47 (H-B-C) ₁ + 47 (H-B-C) ₂ + 5 (B-C-B)
$\omega_a(\text{H-B-C-B})_2$	757	6	732	−25	50 (HBCB) ₁ + 50 (HBCB) ₂
$\omega_a(\text{B-C-B})$	401	4	320	−81	97 (B-C-B)
ZPVE	17.34		17.21	−0.13	

^a The zero-point vibrational energy (ZPVE, kcal mol^{-1}) is added to verify that the sum of local mode frequencies plus the sum of coupling frequencies equals the sum of normal mode frequencies.

2.4.4 URVA analysis of the isomerization mechanism

The Unified Reaction Valley Analysis (URVA)^{63,64} was applied to elucidate the **1a** → **1b** isomerization. Curvature $\mathbf{k}(s)$ and direction $\mathbf{t}(s)$ vectors of the isomerization path as a function of the arc length s were computed using both MP2 and B3LYP theory with the 6-31G(d,p) basis set. According to the *reaction phase* concept of Kraka and Cremer,⁶⁰ chemical processes such as bond cleavage/formation are indicated by curvature maxima along the reaction path. The generation of a new (transient) electronic structure is finished when the reaction path curvature adopts a minimum (low chemical activity) after having passed through a curvature maximum (high chemical activity). Hence, a reaction phase is defined as the reaction path range from one curvature minimum (start of the chemical process) to the next (end of a chemical process), being characterized by an intervening curvature peak. Different chemical reactions possess different curvature patterns and numbers of reaction phases, which can be used as fingerprints.

Further insight into the transformation from **1a** to **1b** can be gained by decomposition of the scalar reaction path curvature and direction into contributions $A_{n,s}(\mathbf{k};s)$ and $A_{n,s}(\mathbf{t};s)$, respectively, from each local mode n . Figure 2.10 shows the $\mathbf{k}(s)$ decomposition for the **1a** → **1b** reaction path, while Figure A1 provides the corresponding $\mathbf{t}(s)$ plot. The local mode coupling coefficients identify the internal coordinates that dominate the chemical reaction at a given point and reveal the associated chemical changes, such as bond cleavage/formation or rehybridization. Furthermore, the sign of $A_{n,s}(\mathbf{k};s)$ determines whether changes in the structural parameter in question are promoting (positive sign) or hindering (negative sign) the reaction. Because curvature $\mathbf{k}(s)$ and direction $\mathbf{t}(s)$ are orthogonal to each other, their decomposition into local vibrational modes is complementary. Generally, an internal coordinate dominating $\mathbf{t}(s)$ has only a small influence on $\mathbf{k}(s)$ at that point, and vice versa.

The curvature diagram (Fig. 2.10, with s in $\text{u}^{1/2}\text{bohr}$) reveals two phases for the **1a** $\rightarrow$ **1b** isomerization: Phase 1 starts with maximum total curvature near the reactant ($s = -3.5$), decreases smoothly over a long range, and ends at the curvature minimum M1 ($s = 2.85$). A short Phase 2 follows that is completed at $s = 3.8$ with the second curvature maximum. The curvature changes in Fig. 2.10 are small, being typical of partial cleavage of a multiple bond while a single bond is preserved, as for internal rotation in ethylene. **TS1** is located in the middle of Phase 1 and does not play a special role in the transformation of the electronic structure, as seen from the lack of features in the curvature diagram. Phases 1 and 2 correspond to two forms of **1** that can be distinguished by their electronic structures.

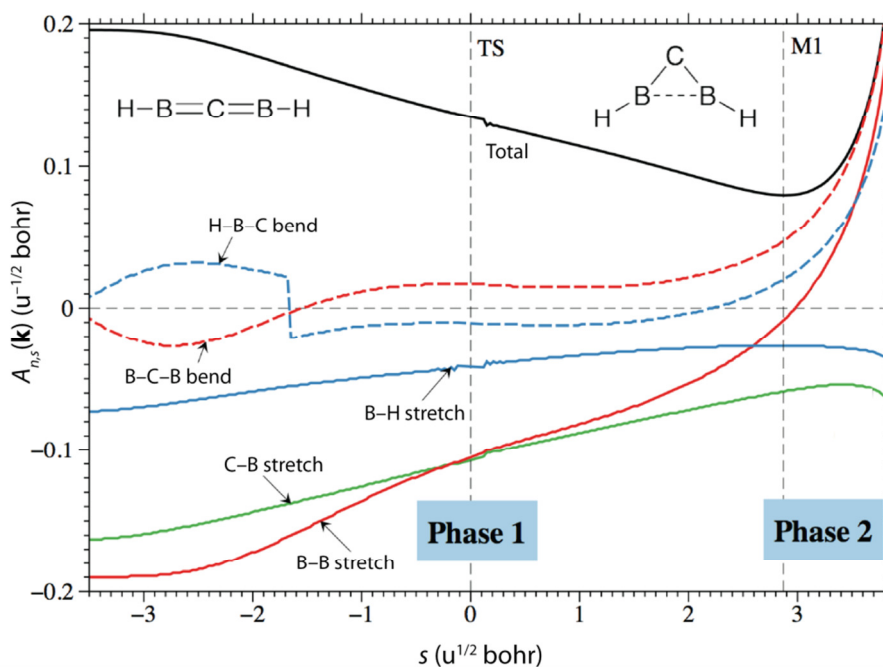


Figure 2.10 Total curvature and coupling coefficients $A_{n,s}(\mathbf{k};s)$ for each local mode n as a function of arc length s along the $\text{C}(\text{BH})_2$ isomerization path, MP2/6-31G(d,p) level of theory.

The local mode decomposition of the curvature is unusual in that it requires two seemingly redundant parameters, namely the B–B distance and the B–C–B bending angle, to

describe all electronic effects taking place during the **1a** $\rightarrow$ **1b** isomerization. The B–C–B angle probes electronic reorganization at the carbon atom, e.g. rehybridization from sp to sp^2 , while the B–B distance is necessary to account for charge reorganization in the boron sp -hybridized σ orbitals and the through-space 1,3-boron-boron interactions. At the beginning of the reaction, the negative B–C–B and C–B curvature coupling coefficients in Fig. 2.10 signal resistance to the associated linear bending and bond weakening. Bending requires rehybridization at the C atom, which is opposed by the allenic B–C–B unit. Reflecting exchange repulsion between the two boron atoms, the B–B distance exhibits the largest $A_{n,s}(\mathbf{k};s)$ coefficient and strongest resistance to bending until the transition state is reached. Only the H–B–C angle is supportive at the early stages of the isomerization.

In Phase 1 a critical point in the chemical transformation occurs at $s = -1.62$, where the coupling coefficient for B–C–B bending changes from negative to positive. At this point carbon rehybridization is no longer resistive but supportive, i.e., the molecule leaves a distorted allenic form to adopt a bent form with different electronic structure and bonding. Concomitantly, $A_{n,s}(\mathbf{k};s)$ for the resisting B–B mode becomes smaller in size, while the H–B–C angle decreases from 182° to 178° with a corresponding jump in its curvature coupling coefficient.

The transition state for the isomerization does not result from any particular chemical change. As the linear allenic 4π -system changes into a bent form with just two π -electrons, the C–B bond order decreases, coupled to a smaller weakening of the B–H bond. The collective increase of these and other energy contributions, such as repulsive 1,3 B–B interactions, gives rise to the transition state. Afterwards at M1, the B–B interactions switch from repulsive to attractive, as revealed by the sign change of the corresponding curvature coupling coefficient. This transformation plays the key role in moving from carbon reorganization Phase 1 to Phase 2,

in which the bent form of **1** is finalized. At the final reaction path point ($s = 3.8$), the supportive B–B, B–C–B, and H–B–C curvature coupling coefficients all reach maximum values.

Table 2.10 Comparative B3LYP/6-31G(d,p) bond distances $r(\text{\AA})$, associated frequencies ω_μ (cm^{-1}) and adiabatic stretching force constants k_a ($\text{mdyn \AA}^{-1}$), and bond orders n of species **1–12**^a

Species	B–C bond				B–B bond				B–H bond			
	r	ω_μ	k_a	n	r	ω_μ	k_a	n	r	ω_μ	k_a	n
1a	1.358	–	9.352	2.25	–	–	–	–	1.171	–	4.399	1.12
TS1	1.363	1631	8.999	2.18	2.335	266	0.229	0.085	1.173	2830	4.358	1.11
1b	1.370	1567	8.307	2.03	2.031	321	0.334	0.123	1.174	2817	4.318	1.10
2	1.558	1063	3.820	1	–	–	–	–	1.197	2626	3.752	–
3	1.381	1557	8.205	2	–	–	–	–	1.174	2825	4.343	–
4	1.527	1058	3.789	–	1.517	1010	3.305	1	–	–	–	–
5	–	–	–	–	1.525	1322	5.667	2	1.174	–	4.319	–
6	–	–	–	–	–	–	–	–	1.192	2673	3.886	1
7	–	–	–	–	1.769	844	2.312	–	1.316	1834	1.831	0.5
8	1.405	1349	6.160	–	1.588	999	3.235	–	–	–	–	–
9	1.416	1429	6.905	–	2.499	386	0.483	–	1.171	2859	4.445	–
10	–	–	–	–	1.495	1232	4.923	–	1.182	2747	4.104	–
					1.604 ^c	985	3.147	–	–	–	–	–
11^b	1.359	1665	9.379		–	–	–	–	–	–	–	–
12^b	–	–	–	–	1.618	1014	3.278	–	–	–	–	–

^a Bond orders n calculated according to Eqs. (8), (9) and (10) using references (**2**, **3**) for B–C bonds, (**6**, **7**) for B–B bonds, and (**4**, **5**) for B–H bonds. ^b Triplet ground state. ^c BH-B bonds.

The evolution of NBO charges along the reaction path is shown in Figure 2.11. Reactant **1a** has an sp -hybridized carbon with a large negative charge $q(\text{C}) = -1.18 e$, whereas in product **1b** the charge on carbon is only $-0.72 e$. The change in $q(\text{C})$ is monotonic, starting slowly in the entrance channel and accelerating in Phase 2. Overall the carbon atom loses 0.46 electrons, each boron atom gains 0.26 electrons, and the hydrogen atom charges hardly change. As shown in

Figure A2, the redistribution of the π -electrons along the reaction path follows the same trends. The carbon π_x occupation perpendicular to the plane of bending is 1.22 in **1a** but only 1.05 in **1b**; simultaneously, the π_x occupation of each B atom increases from 0.38 to 0.47. In contrast, the σ charge between the two boron atoms decreases, as reflected by the total boron p_y orbital populations of 1.54 in **1a** and 1.25 in **1b** (Figure A3).

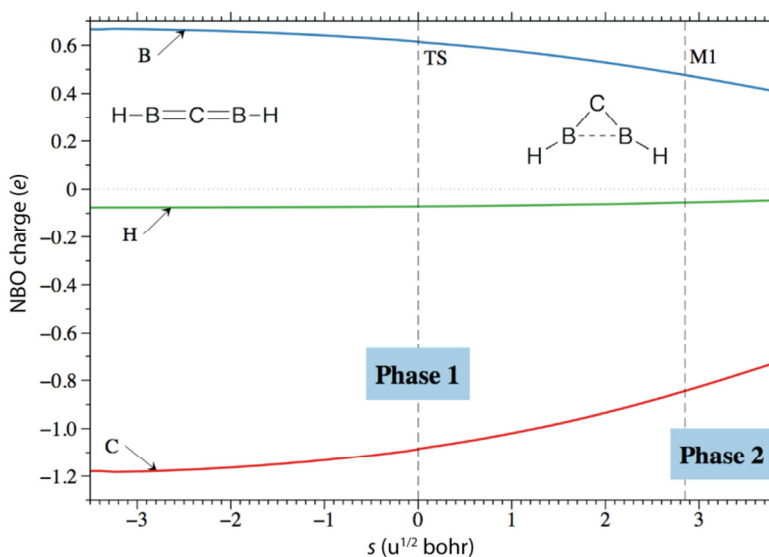


Figure 2.11 Natural bond orbital (NBO) atomic charges as a function of arc length s along the $\text{C}(\text{BH})_2$ isomerization path, MP2/6-31G(d,p) level of theory.

In the entrance channel this decrease parallels the reduction of the B–B distance, while in Phase 2 it levels out. Obviously, there is enough overall charge between the boron atoms to create stabilizing B–B interactions, in line with the B–B bond order of 0.123, but not enough to form a full bond and three-membered ring.

2.5 THE ALUMINUM ANALOGUE, C(AlH)₂

2.5.1 Computational Methods

Our computational endeavor was extended to include a thorough investigation of the aluminum analogue, C(AlH)₂. High-accuracy coupled-cluster theory in association with the correlation-consistent cc-pVXZ ($X = D, T, Q, 5$) and the weighted core-valence cc-pwCVXZ ($X = D, T, Q$) basis sets⁶⁵ was employed. Additionally, in all the computations involving the cc-pVXZ basis sets, the aluminum atom was exclusively treated with the cc-pV($X+d$)Z sets that include extra tight d functions.⁶⁶ Henceforth, references will be made to the cc-pV($X+d$)Z sets while describing those computations. The reference geometries for the FPA treatment were optimized at the AE-CCSD(T)/cc-pwCVQZ level. Energy extrapolations to the CBS limit for Hartree-Fock theory and the electron correlation methods were performed using the same techniques employed for C(BH)₂ (cf. Section 2.3). Auxiliary corrections were added to obtain the final FPA relative energies using Eq. (2.4). Geometry optimizations, harmonic vibrational frequencies, and anharmonicities were obtained using similar computational techniques and software packages as employed for C(BH)₂.

The ground electronic state at the C(AlH)₂ stationary points was carefully investigated using the diagnostics of multireference character. At the AE-CCSD/cc-pwCVQZ level of theory, the bent minimum and the linear transition state (TS) structures displayed T_1 diagnostics⁶⁷ of 0.015 and 0.012 respectively, and D_1 diagnostics⁶⁸ of 0.053 and 0.039, in order. Both the T_1 diagnostics were well below the recommended multireference threshold of 0.02,⁶⁷ but the D_1 value for the bent minimum turned out to be slightly above the suggested threshold of 0.05.⁶⁸ Nevertheless, the maximum absolute t_1 and t_2 amplitudes for the (minimum, TS) were only (0.024, 0.026) and (0.085, 0.041) respectively at the same level of theory, which were well

within the recommended thresholds of 0.05 and 0.1, in order. Finally, full-valence (12 electrons in 14 molecular orbitals) complete active space self-consistent-field (CASSCF) wave functions⁶⁹ computed with cc-pwCVQZ basis set were obtained to ascertain the leading configuration interaction (CI) coefficients (C_1 , C_2) for determinants constructed from CASSCF natural orbitals. The computations were performed with MOLPRO at the respective optimized AE-CCSD(T)/cc-pwCVQZ structures. A clear dominance of the ground-state Hartree-Fock configuration was revealed as the (minimum, TS) structures exhibited $C_1 = (0.925, 0.932)$ and $C_2 = (-0.164, -0.083)$. Hence, $C(\text{AlH})_2$ is predominantly a closed-shell system without any significant diradical character, and can be accurately treated by the high-order single-reference coupled cluster methods.

A similar investigation of the CASSCF/cc-pV(Q+d)Z leading CI coefficients for the closed-shell singlet ($^1A_1$) state of Al_2C indicated the presence of two dominant closed-shell electronic configurations ($C_1=+0.817$, $C_2=-0.419$), thus confirming the need for a multireference approach for this electronic state. Consequently, the absolute energies for the lowest singlet ($^1A_1$) and triplet ($^3B_1$) states of Al_2C were compared using state-specific multiconfigurational methods in the form of CASSCF,²⁵ complete active space second-order perturbation theory (CASPT2),⁷⁰ and internally contracted multiconfiguration reference configuration interaction (MRCI),⁷¹ accompanied by the cc-pV(X+d)Z ($X = \text{D, T, Q}$) basis sets at the respective optimized geometries. Geometry optimizations were carried out using the quadratic steepest descent technique⁷² in MOLPRO. Full-valence (10 electrons/12 MOs) CASSCF(10,12) reference wavefunctions were always used.

The FPA treatment was employed to evaluate the most accurate relative energy between the $^1A_1$ and $^3B_1$ electronic states at the FC-MRCI/cc-pV(T+d)Z(CAS 2,2) reference geometries

optimized in MOLPRO. The dominance of two closed-shell electronic configurations in the $^1A_1$ wavefunction led to the choice of CASSCF(2,2) references in optimizing the structures. The hierarchical series of single-point energies were computed using two configuration self-consistent-field (TCSCF),⁷³ which is mathematically identical to CASSCF(2,2) here, and restricted open-shell Hartree-Fock (ROHF)⁷⁴ reference wavefunctions for $^1A_1$ and $^3B_1$ states, respectively. State-specific multireference electron correlation methods⁷⁵ in the form of Mukherjee multireference second-order perturbation theory (Mk-MRPT2),⁷⁶ Mukherjee multireference coupled cluster singles and doubles (Mk-MRCCSD),⁷⁷ and Mukherjee multireference coupled cluster singles and doubles with perturbative triples [Mk-MRCCSD(T)]⁷⁸ were employed to compute the single-point energies using the production-level code PSIMRCC⁷⁹ within the PSI 3.3 package.⁸⁰ Molecular orbital symmetry was turned off, and the active orbitals were localized.⁸¹ The Tikhonov regularization procedure ($\omega = 0.001$ to 0.004) was introduced to avoid singularities,⁸² and the final result was obtained by extrapolation of the four different energy values to $\omega = 0$. The CBS limits were found by extrapolating cc-pV(T,Q,5+d)Z TCSCF/ROHF energies using Eq. (2.1), and cc-pV(Q,5+d)Z electron correlation energies using Eq. (2.2), and the total energies were obtained by adding separate $E_{\text{TCSCF/ROHF}}^{\text{CBS}}$ and $E_{\text{corr}}^{\text{CBS}}$ results. Core-correlation effects [$\Delta(\text{core})$] were computed by differencing AE-MRCI/cc-pwCVTZ(2,2) and FC-MRCI/cc-pwCVTZ(2,2) energies at the FC-MRCI/cc-pV(T+d)Z(2,2) reference geometries. Relativistic corrections [$\Delta(\text{rel})$] and ZPVEs were obtained using the same reference structures, and the final FPA relative energy is calculated according to the following equation:

$$\Delta E(\text{FPA}) = \Delta E_{\text{Mk-MRCCSD(T)}}^{\text{CBS}} + \Delta(\text{ZPVE}) + \Delta(\text{core}) + \Delta(\text{rel}). \quad (2.11)$$

2.5.2 Structures, Energies, and Vibrational Spectra of C(AlH)₂

The closed-shell singlet state, $^1A_1$, of bent C(AlH)₂ lies 37.5 kcal mol⁻¹ below the lowest triplet state, $^3B_1$, at the FC-CCSD(T)/cc-pV(Q+d)Z level. Subsequently, the geometries of the closed-shell ground electronic state and the corresponding linear stationary point of C(AlH)₂ were optimized using the CCSD(T) level of theory accompanied by the series of correlation consistent basis sets ranging from cc-pV(D+d)Z to cc-pwCVQZ, as detailed in Tables 2.11 and 2.12. The best geometric structures at the AE-CCSD(T)/cc-pwCVQZ level are presented in Figure 2.12. Systematic convergence in the Al–C and Al–H bond lengths was achieved as expected with the enlargement of the basis sets and the inclusion of core correlation. Extrapolation of the bond lengths using the bX^{-3} form in Eq. (2.2) indicated that the AE-CCSD(T)/CBS limits for $r_e(\text{Al–C})$ and $r_e(\text{Al–H})$ bonds lie within 0.0046 and 0.0010 Å, respectively, of the AE-CCSD(T)/cc-pwCVQZ values for both the bent minimum and the linear TS. Basis set improvement effected a very small change in the Al–C–Al and H–Al–C bond angles of the bent minimum, and the extrapolated CBS limits lie just 0.3 and 0.4 degrees, in order, above the cc-pwCVQZ values.

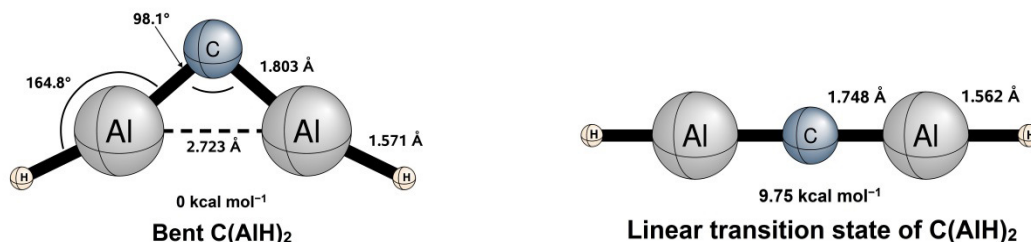


Figure 2.12 AE-CCSD(T)/cc-pwCVQZ optimized geometric parameters (Å, °) and relative energies (ΔE_e in kcal mol⁻¹) for the bent minimum and the linear transition state of C(AlH)₂.

Table 2.11 CCSD(T) optimized bond lengths (r_e , Å) and angles ($^\circ$) for $\text{C}(\text{AlH})_2$.^[a, b]

Basis Set	$r_e(\text{Al}-\text{C})$	$r_e(\text{Al}-\text{H})$	$\angle(\text{Al}-\text{C}-\text{Al})$	$\angle(\text{H}-\text{Al}-\text{C})$	$r_e(\text{Al}-\text{Al})$	$\angle(\text{C}-\text{Al}-\text{Al})$
cc-pV(D+d)Z	1.8318	1.5811	97.15	164.61	2.7470	41.43
cc-pV(T+d)Z	1.8200	1.5797	97.61	164.44	2.7390	41.20
cc-pV(Q+d)Z	1.8137	1.5781	98.14	164.75	2.7407	40.93
cc-pV(5+d)Z	1.8120	1.5779	98.23	164.90	2.7398	40.89
cc-pwCVDZ (AE)	1.8296	1.5792	97.22	164.73	2.7452	41.39
cc-pwCVTZ (AE)	1.8091	1.5719	97.68	164.27	2.7241	41.16
cc-pwCVQZ (AE)	1.8028	1.5709	98.08	164.81	2.7229	40.96

^[a] All-electron, core-correlated results denoted by (AE); frozen-core otherwise.^[b] cc-pVXZ and cc-pV(X+d)Z sets ($X = \text{D through 5}$) for carbon/hydrogen and aluminum respectively.**Table 2.12** CCSD(T) optimized bond lengths (r_e , Å) and relative energies (ΔE_0 , kcal mol⁻¹) for the linear transition state (TS) of $\text{C}(\text{AlH})_2$.^[a, b]

Basis Set	$r_e(\text{Al}-\text{C})$	$r_e(\text{Al}-\text{H})$	ΔE_0	$r_e[\text{AlH}(^1\Sigma^+)]^{[c]}$
cc-pV(D+d)Z	1.7714	1.5709	+10.815	1.6526
cc-pV(T+d)Z	1.7599	1.5707	+10.088	1.6522
cc-pV(Q+d)Z	1.7577	1.5690	+9.823	1.6500
cc-pV(5+d)Z	1.7565	1.5689	+9.767	1.6501
cc-pwCVDZ (AE)	1.7679	1.5687	+10.835	1.6556
cc-pwCVTZ (AE)	1.7501	1.5631	+9.964	1.6462
cc-pwCVQZ (AE)	1.7475	1.5617	+9.753	1.6447

^[a] See footnotes [a, b] of Table 2.11.^[b] The ΔE_0 values include zero-point vibrational corrections.^[c] Bond lengths of the dissociated product AlH from $\text{C}(\text{AlH})_2 \rightarrow \text{C}(^3\text{P}) + 2\text{AlH}(^1\Sigma^+)$.

The relative energies between the bent minimum and the linear TS of $\text{C}(\text{AlH})_2$ are outlined in Table 2.12. Zero-point vibrational corrections were included in each case. The energy barrier, $\Delta E_0(\text{TS}-\text{bent})$, was relatively consistent in all the CCSD(T) values, the cc-pwCVQZ prediction being +9.75 kcal mol⁻¹. The most accurate prediction was extracted from the FPA of the relative energies performed on the AE-CCSD(T)/cc-pwCVQZ optimized geometries, as delineated in Table 2.13. Full convergence to the CBS limit was achieved at each level of theory demonstrated by the nearly exact agreement between the explicitly computed cc-pV(6+d)Z increments and the extrapolated values. Furthermore, systematic reduction in the successive electron correlation increments ensured excellent convergence to the electron correlation limit, as highlighted by the final $\delta[\text{CCSDT}(\text{Q})]$ contribution of 0.0 kcal mol⁻¹. With the auxiliary corrections included, the final FPA energy at the FC-CCSDT(Q)/CBS limit placed the linear

transition state at 9.60 kcal mol⁻¹ higher than the bent minimum, with an estimated uncertainty of ± 0.10 kcal mol⁻¹.

Table 2.13 Focal point analysis of the relative energy (kcal mol⁻¹) between C(AIH)₂ and its linear TS.^[a]

	$\Delta E_e(\text{RHF})$	$+\delta[\text{MP2}]$	$+\delta[\text{CCSD}]$	$+\delta[\text{CCSD(T)}]$	$+\delta[\text{CCSDT(Q)}]$	NET
cc-pV(D+d)Z	+4.90	+4.15	+1.37	+0.72	+0.00	+11.14
cc-pV(T+d)Z	+4.30	+3.81	+1.39	+0.86	[+0.00]	[+10.36]
cc-pV(Q+d)Z	+4.41	+3.52	+1.35	+0.86	[+0.00]	[+10.13]
cc-pV(5+d)Z	+4.36	+3.53	+1.32	+0.86	[+0.00]	[+10.06]
cc-pV(6+d)Z	+4.35	+3.49	+1.31	+0.86	[+0.00]	[+10.01]
CBS LIMIT	[+4.34]	[+3.45]	[+1.31]	[+0.86]	[+0.00]	[+9.96]
Function	$a+be^{-cX}$	$a+bX^{-3}$	$a+bX^{-3}$	$a+bX^{-3}$	addition	
X (fit points) =	(4,5,6)	(5,6)	(5,6)	(5,6)		

AE-CCSD(T)/cc-pwCVQZ reference geometries.

$\Delta(\text{ZPVE}) = -0.303$; $\Delta(\text{core}) = -0.087$; $\Delta(\text{rel}) = +0.052$; $\Delta(\text{DBOC}) = -0.020$.

$\Delta E_0(\text{FPA}) = +9.96 - 0.303 - 0.087 + 0.052 - 0.020 = \mathbf{+9.60 \text{ kcal mol}^{-1}}$.

^[a] The symbol δ denotes the *increment* in the energy difference (ΔE_e) with respect to the previous level of theory in the hierarchy RHF $\rightarrow$ MP2 $\rightarrow$ CCSD $\rightarrow$ CCSD(T) $\rightarrow$ CCSDT(Q). Bracketed numbers result from basis set extrapolations (using the specified functions and fit points) or additivity approximations, while unbracketed numbers were explicitly computed. The main table targets $\Delta E_e[\text{FC-CCSDT(Q)}]$ in the complete basis set limit (NET/CBS LIMIT). Auxiliary energy terms are appended for zero-point vibrational energy (ZPVE), core electron correlation [$\Delta(\text{core})$], the diagonal Born-Oppenheimer correction [$\Delta(\text{DBOC})$], and special relativity [$\Delta(\text{rel})$]. The final energy difference $\Delta E_0(\text{FPA})$ is boldfaced.

Table 2.14 Focal point analysis of the dissociation energy (kcal mol⁻¹) for C(AIH)₂ $\rightarrow$ C(³P) + 2AIH(¹ Σ^+).^[a]

	$\Delta E_e(\text{RHF})$	$+\delta[\text{CCSD}]$	$+\delta[\text{CCSD(T)}]$	$+\delta[\text{CCSDT(Q)}]$	NET
cc-pV(D+d)Z	+86.89	+42.64	+9.15	+1.06	+139.74
cc-pV(T+d)Z	+90.44	+51.20	+10.99	[+1.06]	[+153.70]
cc-pV(Q+d)Z	+91.31	+55.07	+11.51	[+1.06]	[+158.95]
cc-pV(5+d)Z	+91.47	+56.50	+11.70	[+1.06]	[+160.74]
cc-pV(6+d)Z	+91.53	+57.05	+11.77	[+1.06]	[+161.41]
CBS LIMIT	[+91.55]	[+57.80]	[+11.86]	[+1.06]	[+162.27]
Function	$a+be^{-cX}$	$a+bX^{-3}$	$a+bX^{-3}$	addition	
X (fit points) =	(4,5,6)	(5,6)	(5,6)		

AE-CCSD(T)/cc-pwCVQZ reference geometries.

$\Delta(\text{ZPVE}) = -6.010$; $\Delta(\text{core}) = +0.353$; $\Delta(\text{rel}) = -0.699$; $\Delta(\text{DBOC}) = +0.124$.

$\Delta E_0(\text{FPA}) = +162.27 - 6.010 + 0.353 - 0.699 + 0.124 = \mathbf{+156.04 \text{ kcal mol}^{-1}}$.

^[a] See footnote [a] of Table 2.13 for notation.

The thermodynamic stability of bent $\text{C}(\text{AlH})_2$ with respect to its ground-state fragments was assessed by computing the total dissociation energy (TDE) from the following equation:



The FPA for the homolytic cleavage of the two carbon-aluminum bonds was detailed in Table 2.14. Consistent convergence was observed as expected in the electron correlation treatments, and the TDE given by the final FPA result was $156.04 \text{ kcal mol}^{-1}$, with an accuracy of about 1 kcal mol^{-1} . Hence, the average C–Al bond-dissociation energy (D_0) in $\text{C}(\text{AlH})_2$ is estimated to be 78 kcal mol^{-1} , which is significantly smaller than the corresponding value for a C–B bond ($D_0 = 147 \text{ kcal mol}^{-1}$)⁴⁰ in the sister $\text{C}(\text{BH})_2$ species. Nonetheless, our computed $D_0[\text{C}(\text{AlH})_2]$ is comparable with the dissociation energy of $83.6 \text{ kcal mol}^{-1}$ for the homolytic cleavage of the Al–C single bond in AlCH_2 ($\text{C}_{2v}, {}^2\text{B}_1$).⁸³ Moreover, the bond-dissociation energy for the atomization process $\text{Al}_2\text{C}({}^1\text{A}_1) \rightarrow \text{C}({}^3\text{P}) + 2\text{Al}({}^2\text{P})$ was computed to be $155.64 \text{ kcal mol}^{-1}$ from our precise FPA method, which results in a mean C–Al bond-dissociation value of 78 kcal mol^{-1} .

The CCSD(T) harmonic vibrational frequencies (ω_i) of the parent ${}^{12}\text{C}/{}^{27}\text{Al}/\text{H}$ isotopologue computed with the cc-pV(T,Q,5+d)Z and cc-pwCV(T,Q)Z basis sets for the bent minimum and the linear TS structures of $\text{C}(\text{AlH})_2$ are collected in Table 2.15. Anharmonic vibrational frequencies (ν_i) for the bent minimum obtained with the cc-pV(T+d)Z basis set are also included. In Tables A15 and A16 of Appendix A, the FC-CCSD(T)/cc-pV(T+d)Z harmonic and anharmonic vibrational frequencies are tabulated for a set of 6 isotopologues arising from ${}^{13}\text{C}$ and D substitutions. The choice of this particular level of theory to perform the anharmonic frequency computations for the isotopologues of $\text{C}(\text{AlH})_2$ stems from the success of our previous theoretical work⁸⁴ in which the infrared (IR) spectra⁸⁵ of linear $\text{C}(\text{BH})_2$ and its various isotopologues were accurately predicted. Furthermore, the same level of theory with an open-

shell ROHF reference made excellent predictions for the vibrational spectra of Al_2C and Al_2^{13}C as described later in Section 2.5.3.

Table 2.15 CCSD(T) harmonic (ω_i) and anharmonic (ν_i) vibrational frequencies (cm^{-1}) and IR intensities (km mol^{-1} , in parentheses) of stationary points of $\text{C}(\text{AlH})_2$ computed with several basis sets.^[a]

Mode (sym)	Description ^[b]	cc-pV(T+d)Z ω_i	cc-pV(Q+d)Z ω_i	cc-pV(5+d)Z ω_i	cc-pwCVTZ ω_i	cc-pwCVQZ ω_i	cc-pV(T+d)Z ν_i
Bent $\text{C}(\text{AlH})_2$							
1 (a_1)	sym Al–H stretch	1947 (45)	1958 (44)	1958 (45)	1955 (43)	1965 (44)	1883
2 (a_1)	sym Al–C stretch	767 (4)	774 (5)	775 (5)	773 (4)	781 (4)	755
3 (a_1)	sym H–Al–C ip bend	468 (38)	465 (36)	464 (35)	469 (36)	466 (33)	465
4 (a_1)	Al–C–Al bend	221 (0.03)	219 (0.03)	219 (0.03)	222 (0.03)	220 (0.04)	216
5 (a_2)	asym H–Al–C oop bend	417 (0)	415 (0)	417 (0)	418 (0)	416 (0)	413
6 (b_1)	sym H–Al–C oop bend	386 (58)	383 (59)	385 (60)	386 (57)	383 (58)	381
7 (b_2)	asym Al–H stretch	1940 (384)	1950 (374)	1950 (374)	1947 (374)	1958 (367)	1875
8 (b_2)	asym Al–C stretch	942 (68)	957 (73)	960 (74)	952 (69)	966 (74)	928
9 (b_2)	asym H–Al–C ip bend	427 (56)	428 (56)	429 (56)	428 (55)	429 (55)	424
Linear TS of $\text{C}(\text{AlH})_2$							
1 (σ_g^+)	sym Al–H stretch	1988	1999	1999	1995	2006	
2 (σ_g^+)	sym Al–C stretch	540	545	546	545	550	
3 (σ_u^+)	asym Al–H stretch	1984	1995	1995	1991	2003	
4 (σ_u^+)	asym Al–C stretch	1259	1267	1270	1270	1277	
5 (π_g)	asym H–Al–C bend	434	433	435	434	434	
6 (π_u)	sym H–Al–C bend	329	333	338	328	334	
7 (π_u)	Al–C–Al bend	130i	129i	128i	130i	129i	

^[a] [FC, AE] CCSD(T) for the [cc-pV(X+d)Z, cc-pwCVXZ] basis sets; IR intensities are double-harmonic values.

^[b] Abbreviations: sym = symmetric; asym = antisymmetric; ip = in-plane; oop = out-of-plane.

Table 2.16 Predicted isotopic shifts ($\Delta\nu$, cm^{-1}) of anharmonic vibrational frequencies for $\text{C}(\text{AlH})_2$ at the FC-CCSD(T)/cc-pV(T+d)Z level.

	$\text{HAl}^{12}\text{CAIH}$	$\text{HAl}^{13}\text{CAIH}$	$\text{DAI}^{12}\text{CAID}$	$\text{DAI}^{13}\text{CAID}$	$\text{HAl}^{12}\text{CAID}$	$\text{HAl}^{13}\text{CAID}$
$\nu_1 (a_1)$	0.0	−0.1	−508.2	−508.5	−4.0	−4.0
$\nu_3 (a_1)$	0.0	−0.2	−108.9	−109.3	−17.6	−17.6
$\nu_6 (b_1)$	0.0	−0.7	−93.9	−94.9	−83.6	−84.2
$\nu_7 (b_2)$	0.0	0.0	−506.1	−506.4	−503.2	−503.5
$\nu_8 (b_2)$	0.0	−26.0	−7.9	−33.6	−3.8	−29.7
$\nu_9 (b_2)$	0.0	−0.1	−104.1	−104.3	−88.4	−88.6

The theoretical IR spectrum for $\text{C}(\text{AlH})_2$ is expected to contain six fundamental frequencies with substantial intensity ($> 30\text{ km mol}^{-1}$); ν_7 (asymmetric Al–H stretch)=1875 cm^{-1} , ν_8 (asymmetric Al–C stretch)=928 cm^{-1} , ν_6 (symmetric H–Al–C out-of-plane bend)=381 cm^{-1} , ν_9 (asymmetric H–Al–C in-plane bend)=424 cm^{-1} , ν_1 (symmetric Al–H stretch)=1883 cm^{-1} , and ν_3 (symmetric H–Al–C in-plane bend)=465 cm^{-1} [FC-CCSD(T)/cc-pV(T+d)Z, Table 2.15],

arranged in order of their AE-CCSD(T)/cc-pwCVQZ harmonic intensities. Table 2.16 outlines the predicted FC-CCSD(T)/cc-pV(T+d)Z isotopic shifts in the ν_1 , ν_3 , ν_6 , ν_7 , ν_8 and ν_9 fundamental frequencies.

Both boron and aluminum yield similar products in the reactions with small atoms or molecules like C, H₂, O₂, C₂H₂, CH₄, to name a few.⁸⁶ Laser ablation of boron atoms in a methane/argon mixture⁸⁵ produced linear C(BH)₂ as one of the products observed in the resulting IR spectra. An analogous laser ablation of Al in a CH₄/Ar environment has not yet been performed. However, Parnis and Ozin⁸⁷ conducted a photochemical reaction of matrix-isolated Al atoms co-condensed in solid CH₄ to produce the insertion product CH₃AlH. Aluminum forms a relatively weak bond with hydrogen as demonstrated by Andrews et. al.⁸⁸ in two separate Al + C₂H₂/Ar experiments in which the insertion product HAlCCH decomposed into AlCCH upon subsequent ultraviolet (UV) photolysis or from exposure to high laser power. On the other hand, a similar B + C₂H₂/Ar laser-ablation experiment⁸⁹ generated HBCCH which was photodissociated into BCCH as well as HBCC, the latter being thermodynamically more stable due to the strong B–H bond. Based on the aforementioned observations, employing a low-power laser for the ablation of Al atoms in a CH₄/Ar mixture for a short duration (1 to 2 hours) may allow detection of the insertion product HAlCAIH, or C(AlH)₂, at cryogenic temperatures.

2.5.3 Al₂C as benchmark

Since no experimental data exists for the vibrational spectra of C(AlH)₂, it is advantageous to benchmark our computational techniques on a similar molecular species for which experimental results are available. Al₂C was the obvious choice due to its similarity with C(AlH)₂, as well as its available infrared spectra from the laser ablation process of aluminium in carbon vapor.^{88b} The CASSCF/cc-pV(Q+d)Z wavefunction for the ¹A₁ state of Al₂C in Table

2.17 reveals the dominance of two different closed-shell electronic configurations: $[(\text{core})6a_1^2 5b_1^2 7a_1^2 2b_2^2 8a_1^2]$ and $[(\text{core})6a_1^2 5b_1^2 7a_1^2 2b_2^2 6b_1^2]$, while for the $^3B_1$ state, the corresponding wavefunction exhibits the dominance of only one: $[(\text{core})6a_1^2 5b_1^2 7a_1^2 2b_2^2 8a_1^\alpha 6b_1^\alpha]$. Hence, routine single reference methods would be sufficient in accurately describing the $^3B_1$ state, but they would be inadequate for $^1A_1$. Consequently, several multiconfiguration methods accompanied by a set of correlation-consistent basis sets were employed in an attempt to pinpoint the ground electronic state of Al_2C , as shown in Table 2.18. CASSCF/cc-pV(Q+d)Z computations suggested $^1A_1$ to be lower in energy than $^3B_1$ by 0.30 kcal mol $^{-1}$. However, CASPT2/cc-pV(Q+d)Z, MRCI/cc-pV(Q+d)Z, and internally contracted MRCI with Davidson correction⁹⁰ [MRCI+Q/cc-pV(Q+d)Z] results favored $^3B_1$ by 0.08, 0.18 and 0.47 kcal mol $^{-1}$, respectively. All these computations included ZPVE corrections at the respective optimized geometries.

Table 2.17 Leading determinants in the full-valence (10 electrons/ 12 MOs) CASSCF/cc-pV(Q+d)Z wavefunctions for the triplet ($^3B_1$) and the closed-shell singlet ($^1A_1$) electronic states of Al_2C .^[a]

$\Psi(X^3B_1, M_S = 1) =$	$+0.922 [(\text{core}) 6a_1^2 5b_1^2 7a_1^2 2b_2^2 8a_1^\alpha 6b_1^\alpha]$
	$-0.107 [(\text{core}) 6a_1^2 5b_1^2 2b_2^2 8a_1^\alpha 6b_1^\alpha 9a_1^2]$
	$-0.103 [(\text{core}) 6a_1^2 5b_1^2 7a_1^2 8a_1^\alpha 6b_1^\alpha 3b_2^2]$
	$+0.078 [(\text{core}) 6a_1^2 5b_1^2 7a_1^\alpha 2b_2^2 8a_1^\beta 6b_1^\alpha 9a_1^\alpha]$
$\Psi(a^1A_1, M_S = 0) =$	$+0.817 [(\text{core}) 6a_1^2 5b_1^2 7a_1^2 2b_2^2 8a_1^2]$
	$-0.419 [(\text{core}) 6a_1^2 5b_1^2 7a_1^2 2b_2^2 6b_1^2]$
	$-0.106 [(\text{core}) 6a_1^2 5b_1^2 2b_2^2 8a_1^2 9a_1^2]$
	$-0.089 [(\text{core}) 6a_1^2 5b_1^2 7a_1^2 8a_1^2 3b_2^2]$
	$+0.060 [(\text{core}) 6a_1^2 5b_1^2 2b_2^2 6b_1^2 9a_1^2]$

^[a] All determinants shown are with CI coefficients greater than 0.060 in the natural orbital representation; (core) denotes $1a_1^2 1b_1^2 2a_1^2 3a_1^2 2b_1^2 4a_1^2 1b_2^2 1a_2^2 3b_1^2 5a_1^2 4b_1^2$.

Finally, the FPA treatment was utilized to accurately determine the relative energy difference between the two electronic states, as elaborated in Table 2.19. The anomalous large

negative values for the Mk-MRPT2 increments can be attributed to the use of a small active space [CAS(2,2)] which overestimates the short-range static correlation, similar to the behavior exhibited by CASPT2.⁹¹ Systematic convergence is witnessed at the Mk-MRCCSD(T) level, as demonstrated by the small difference of 0.03 kcal mol⁻¹ between the explicitly computed cc-pV(5+d)Z increment and the extrapolated value. The final FPA result, including the auxiliary corrections, confirmed ³B₁ to be the ground electronic state of Al₂C by placing it 2.29 kcal mol⁻¹ lower in energy than ¹A₁, with an estimated uncertainty of ±0.5 kcal mol⁻¹. As an additional check, the FPA table was reconstructed by replacing Mukherjee multireference energies with the routine single reference ROHF-CCSD and ROHF-CCSD(T) values for ³B₁, and the revised final FPA energy favored the triplet state by 2.19 kcal mol⁻¹, which was within the estimated uncertainty.

Table 2.18 Relative energies (kcal mol⁻¹), $\Delta E_0(^1A_1 - ^3B_1)$, between the singlet and the triplet electronic states of Al₂C with several levels of theory and basis sets.^[a,b]

	CASSCF	CASPT2	MRCI	MRCI+Q
cc-pV(D+d)Z	+0.32	+1.63	+1.53	+1.68
cc-pV(T+d)Z	-0.12	+0.55	+0.63	+0.93
cc-pV(Q+d)Z	-0.30	+0.08	+0.18	+0.47

^[a] Full-valence (10 electrons/12 MOs) CASSCF reference wavefunctions used in computing the absolute energies at the respective optimized geometries.

^[b] All values include zero-point vibrational corrections.

Table 2.19 Focal point analysis of the triplet (³B₁) → singlet (¹A₁) electronic excitation energy (kcal mol⁻¹) for Al₂C.^[a,b]

	$\Delta E_e[\text{TCSCF/ROHF}]$	$+\delta[\text{Mk-MRPT2}]$	$+\delta[\text{Mk-MRCCSD}]$	$+\delta[\text{Mk-MRCCSD(T)}]$	NET
cc-pV(D+d)Z	+6.77	-12.12	+10.68	-2.59	+2.74
cc-pV(T+d)Z	+7.36	-14.36	+11.72	-2.81	+1.92
cc-pV(Q+d)Z	+7.09	-14.80	+11.87	-2.72	+1.43
cc-pV(5+d)Z	+7.05	-15.06	+11.98	-2.70	+1.28
CBS LIMIT	[+7.04]	[-15.33]	[+12.11]	[-2.67]	[+1.15]
Function	$a+be^{-cX}$	$a+bX^{-3}$	$a+bX^{-3}$	$a+bX^{-3}$	
X (fit points) =	(3,4,5)	(4,5)	(4,5)	(4,5)	

FC-MRCI/cc-pV(T+d)Z reference geometries.

$\Delta(\text{ZPVE}) = +0.475$; $\Delta(\text{core}) = +0.396$; $\Delta(\text{rel}) = +0.267$.

$\Delta E_0(\text{FPA}) = +1.15 + 0.475 + 0.396 + 0.267 = \mathbf{+2.29 \text{ kcal mol}^{-1}}$.

^[a] See footnote [a] of Table 2.13 for notation. ^[b] CASSCF(2,2) reference wavefunctions (2 electrons/2 MOs) used for geometry optimizations at the FC-MRCI/cc-pV(T+d)Z level; (TCSCF, ROHF) reference wavefunctions used for (¹A₁, ³B₁) single-point energy computations.

The geometric structure of the ground state, X^3B_1 , of Al_2C was investigated using the routine single reference ROHF-CCSD(T) method with cc-pV(D,T,Q+d)Z and cc-pwCVQZ basis sets, as shown in Table 2.20. The Al–C bond distance converged with the improvement of the basis sets, while the Al–C–Al angle remained somewhat unchanged. The best geometry at AE-CCSD(T)/cc-pwCVQZ is presented in Figure 2.13. Anharmonic vibrational frequencies computed at the FC-CCSD(T)/cc-pV(T+d)Z level using VPT2 analysis yielded $\nu_1(a_1)$ symmetric Al–C stretch, $\nu_2(a_1)$ Al–C–Al bend, and $\nu_3(b_2)$ antisymmetric Al–C stretch values of 641.0, 177.4, and 805.3 cm^{-1} , respectively for the parent Al_2C species. The corresponding (ν_1 , ν_2 , ν_3) values for the $Al_2^{13}C$ isotopologue were computed to be (624.7, 176.4, 783.2), thus revealing ($\Delta\nu_1$, $\Delta\nu_2$, $\Delta\nu_3$) isotopic shifts of (16.3, 1.0, 22.1) cm^{-1} .

Table 2.20 CCSD(T) optimized bond lengths (r_e , Å) and angles ($^\circ$) for the ground electronic state (X^3B_1) of Al_2C .^[a, b]

Basis Set	$r_e(Al-C)$	$\angle(Al-C-Al)$	$r_e(Al-Al)$
cc-pV(D+d)Z	1.8898	97.55	2.8427
cc-pV(T+d)Z	1.8711	97.59	2.8154
cc-pV(Q+d)Z	1.8618	97.41	2.7977
cc-pwCVQZ (AE)	1.8520	97.29	2.7803

^[a] See footnotes [a, b] of Table 2.11

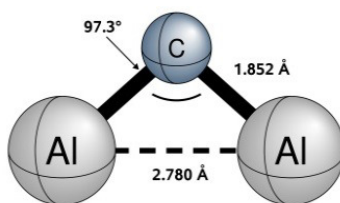


Figure 2.13 AE-CCSD(T)/cc-pwCVQZ optimized geometric structure for the ground-state (X^3B_1) of Al_2C .

The theoretical results were compared with the matrix-isolation experiment^{88b} of pulsed-laser-ablated Al and $^{12}\text{C}/^{13}\text{C}$ atoms in a condensing argon stream that produced $\text{Al}_2\text{C}/\text{Al}_2^{13}\text{C}$ as two of the products. With the aid of harmonic frequency computations at the CASSCF level with a modified VDZ basis set,^{88b,65a,92} the 802.0 and 780.1 cm^{-1} bands in the IR spectra were assigned to the $\nu_3(b_2)$ modes of Al_2C and Al_2^{13}C , respectively, both of which are within 3.3 cm^{-1} of our computed values! Hence, our theoretical $\Delta\nu_3$ prediction of 22.1 cm^{-1} is in excellent agreement with the experimental $\Delta\nu_3$ of 21.9 cm^{-1} originating from the matrix-isolation data.

2.6 CONCLUSIONS

This comprehensive study has produced a number of firm conclusions regarding the $\text{C}(\text{BH})_2$ system. Foremost, the linear (**1a**) and bent (**1b**) isomers are energetically degenerate within an uncertainty of ± 0.10 kcal mol^{-1} and are separated by a barrier of only 1.9 kcal mol^{-1} . Quantum tunneling of the heavy-atom framework engenders interconversion between **1a** and **1b** on a time scale much less than 1 s, even at cryogenic temperatures. The bond distances of the (**1a**, **1b**, TS) structures are $r_e(\text{B}-\text{C}) = (1.355, 1.368, 1.358)$ Å and $r_e(\text{B}-\text{H}) = (1.168, 1.170, 1.169)$ Å, in order, as the AE-CCSD(T)/CBS limit is approached, and the corresponding B–C–B bond angles are (180°, 90.4°, 125.2°). The C–B bond length of **1a** is very short, almost 0.1 Å less than the standard value for a covalent C=B double bond. The B–B interatomic distance of 1.946 Å [AE-CCSD(T)/cc-pCVQZ] in **1b** suggests some degree of attractive interaction but still exceeds the prototypical B–B single bond length by about 0.25 Å. The AIM analysis of **1b** shows that no B–B bond path is present. Careful geometry optimizations do not find an energy minimum for a genuine cyclic form of $\text{C}(\text{BH})_2$.

Previous matrix isolation IR assignments of the $\nu_3(\sigma_u^+)$ and $\nu_4(\sigma_u^+)$ fundamentals of linear $\text{C}(\text{BH})_2$ are confirmed by precise matching of band origins and isotopic shifts with our anharmonic FC-CCSD(T)/cc-pVTZ and AE-CCSD(T)/cc-pCVQZ vibrational frequencies. The AE-CCSD(T)/cc-pCVQZ infrared spectrum of the heretofore unobserved bent isomer contains only two fundamentals with substantial intensity, $\nu_7 = 2715 \text{ cm}^{-1}$ and $\nu_8 = 1537 \text{ cm}^{-1}$, both of which are occluded and considerably downshifted relative to the corresponding absorptions in the linear form. The ν_7 and ν_8 absorptions of **1b** have only about 40% and 20%, respectively, of the intensity of their **1a** counterparts and thus are inherently more difficult to detect.

Bonding analyses show that **1a** is a classical cumulene $\text{HB}=\text{C}=\text{BH}$ with pairs of three-center two-electron π bonds, whereas **1b** is best characterized as a carbene with little carbene character. Both isomers have a prodigious average C–B bond dissociation energy (D_0) of $147 \text{ kcal mol}^{-1}$. Despite its unusual shape and bonding, **1b** has a predominantly closed-shell electronic structure without substantial diradical character. The Laplacian of the electron density around the carbon atom in **1b** does not have a shape typical for lone-pair electrons. The HOMO in the bent isomer facilitates strong $\text{C} \rightarrow \text{BH}$ π -backdonation that reduces the lone-pair character. The HOMO–1 of **1b** is an in-plane molecular orbital that enhances B–C bonding and yields partial B–B bonding; some σ lone-pair character on carbon is present, but there is significant backside bonding overlap with boron *sp* hybrids. Analysis of local mode adiabatic stretching force constants compared to reference compounds gives C–B bonds orders of 2.25 and 2.03 in **1a** and **1b**, respectively; the same approach assigns a bond order of 0.12 for the B–B interaction in **1b**.

The URVA analysis describes the **1a** $\rightarrow$ **1b** isomerization as a chemical process driven by the reorganization of charge at both C and B atoms leading to a bent carbene structure **1b**, which possesses slightly weaker C–B and B–H bonds but gains some extra stabilization via

favorable 1,3 B–B interactions. Surprisingly, only small changes in the C–B bond lengths (≈ 0.013 Å) occur during the **1a** $\rightarrow$ **1b** isomerization. The curvature of the **1a** $\rightarrow$ **1b** reaction path reveals two phases for the isomerization: a long Phase 1 with smooth curvature decrease over the range $s \in (-3.5, 2.85)$, and a short Phase 2 with sharper curvature increase for $s \in (2.85, 3.8)$. A key point in Phase 1 occurs at $s = -1.62$, where carbon rehybridization changes from resistive to supportive, as signalled by the coupling coefficient for B–C–B bending. The **1a** $\rightarrow$ **1b** isomerization starts with a large negative NBO charge of $-1.18 e$ on carbon; as the transformation proceeds, the C atom loses 0.46 electrons, each B atom gains 0.26 electrons, and the H atom charges hardly change.

Finally, a thorough investigation of the geometric structures, relative energetics, and vibrational spectra of the aluminum analogue, C(AlH)₂, was carried out. The ground-state closed-shell electronic structure was found to be bent, lying 9.60 kcal mol⁻¹ below the linear TS. Anharmonic vibrational frequencies were computed at the FC-CCSD(T)/cc-pV(T+d)Z level for the hitherto unobserved C(AlH)₂ species. Due to the lack of available experimental data for C(AlH)₂, the Al₂C species was chosen as the benchmark for our computational techniques. IR spectra of Al₂C were reproduced to excellent precision, justifying the validity of the theoretical methods pursued for both Al₂C as well as C(AlH)₂.

2.7 ACKNOWLEDGEMENTS

We are grateful to Chia-Hua Wu for assistance with the vibrational anharmonicity computations. The research at the University of Georgia was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Combustion Program, Grant No. DE-FG02-97ER14748.

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CHAPTER 3

QUASILINEARITY IN FULMINIC ACID (HCNO) MOLECULE

3.1 ABSTRACT

The HCNO molecule exhibits a large-amplitude H-C-N bending motion on an extremely flat potential energy surface, and the resulting quasilinear behavior of this species has been the subject of extensive high-resolution rovibrational spectroscopy. Nonetheless, the equilibrium structure of HCNO is in dispute, as myriad levels of theory have been unable to determine whether the true minimum is linear or not. To rigorously investigate this problem, geometry optimizations and vibrational frequency computations were executed using a composite focal point analysis (FPA) approach to converge on the *ab initio* limit. Electron correlation treatments as extensive as CCSD(T) and CCSDT(Q) were performed, the former with cc-pVXZ and cc-pCVXZ correlation-consistent basis sets through $X = 6$, and the latter with cc-pVDZ and cc-pVTZ basis sets. Anharmonic vibrational frequencies were computed with an AE-CCSD(T)/CBS full quartic force field, and harmonic results were obtained at the composite AE-CCSDT(Q)/CBS level. At the AE-CCSD(T)/CBS level, HCNO is a linear molecule with $\omega_5(\text{H-C-N bend}) = 120 \text{ cm}^{-1}$ and $\nu_5 = 280 \text{ cm}^{-1}$. However, the composite AE-CCSDT(Q)/CBS computations give an imaginary frequency ($51i \text{ cm}^{-1}$) at the linear optimized geometry. Finally, geometry optimization at the composite AE-CCSDT(Q)/CBS level predicts a bent minimum

lying only 0.22 cm^{-1} below its linear counterpart with $\angle\text{HCN} = 173.5^\circ$ and $\omega_5 = 75\text{ cm}^{-1}$, justifying the designation of HCNO as a quasilinear molecule.

3.2 INTRODUCTION

Fulminic acid, HCNO, is one of the isomers of the CHNO family. The other well-known members of the group are isofulminic (HONC), cyanic (HOCN), and isocyanic (HNCO) acid. Edward Howard, an English chemist, was the first to prepare and investigate fulminic acid in the form of its mercury and silver salts in 1800.¹ However, it was not until 1824 that German chemists Liebig and Wöhler brought HCNO into widespread attention by explaining the isomerism of organic compounds with fulminic and cyanic acids as examples. Both fulminic acid and its salts have been well known for their unstable and explosive nature. Mercury fulminate was used on a large scale throughout the nineteenth century as an explosive for both warlike and peaceful purposes. Almost two hundred years after the discovery of its established connectivity, the simple four-atom HCNO molecule still attracts continued attention of the spectroscopists²⁻⁴ and theoretical⁵⁻⁹ chemists alike, resulting in large amounts of spectroscopic data and rigorous ab initio calculations.

HCNO is a classic example of a tetra-atomic *quasilinear* molecule with its hydrogen end undergoing “floppy” vibration (Figure 3.1). Bunker et al.¹⁰ described the molecule as a *semi-rigid bender*, and concluded from their experimental study that even though the equilibrium structure of HCNO is linear, the excitation of the two higher stretching modes yields an effective HCN bending potential that has a low barrier to linearity of 11.5 cm^{-1} . Koput et al.¹¹ later predicted a very low barrier to linearity of 7 cm^{-1} for the HCN bending motion of the HCNO structure while carrying out large scale ab-initio calculations using the CCSD(T) coupled-cluster

method with the correlation consistent cc-pVXZ ($X = D, T, Q$) basis sets. In a recent theoretical analysis of this intriguing structure, Mladenović and Lewerenz⁹ have claimed that the molecule has a linear electronic minimum accompanied by a large flat potential energy surface for HCN bending motion. However, the relative energy difference obtained from their calculations using the CCSD(T) method with cc-pV6Z basis set was a mere 0.33 cm^{-1} .⁹ Although energetics and/or harmonic vibrational frequencies for the members of the CHNO family have been reported so far through ab initio studies,⁵⁻⁸ there is only one study that provided variational results for the rovibrational states of HCNO. In that study, Pinnavaia et al.⁷ used the variational method to develop a six-dimensional MP2/DZP potential energy surface of the rovibrational states of HCNO, and computed the optimized bent configuration to be 330 cm^{-1} more stable than the optimized linear structure.

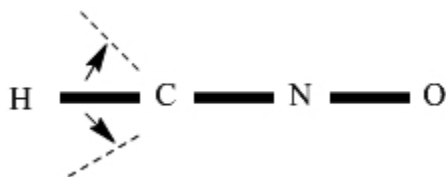


Figure 3.1 Predicted floppy HCN bending mode in the fulminic acid molecule.

In our current research work, a high-level electron-correlation method, accompanied by large basis sets, has been employed in accurately pinpointing the ground-state equilibrium structure and relative energetics of the fulminic acid molecule. A thorough investigation into the vibrational frequencies of both bent and linear HCNO was also performed in an effort to match the available spectroscopic infrared data. The floppy nature of the HCN bending mode was elucidated through computations at various levels of theory in concert with a large number of basis sets. Additionally, the widely known and well-established linear HCN molecule was used

as the benchmark to demonstrate the validity of our employed computational techniques for HCNO.

3.3 THEORETICAL METHODS

High-accuracy electron-correlation methods in the form of coupled cluster theory¹²⁻¹⁵ including full single and double excitations and a perturbative treatment of connected triple excitations [CCSD(T)],¹⁶⁻¹⁸ as well as full single, double, and triple excitations with perturbative accounting of quadruple excitations [CCSDT(Q)]¹⁹⁻²¹ were used in determining the equilibrium geometries and harmonic vibrational frequencies of HCN and HCNO. Restricted Hartree-Fock²²⁻²⁴ (RHF) reference wave functions were always employed. The computations were executed using the systematically convergent family of correlation-consistent polarized valence basis sets of the form cc-pVXZ ($X = D$ to 6) and the associated core-valence cc-pCVXZ ($X = D$ to 6) sets developed by Dunning and co-workers.²⁵⁻²⁷ In order to conduct a thorough investigation into the floppy nature of the HCN bending mode, geometry optimization and harmonic vibrational frequency computations were also carried out utilizing Hartree Fock theory,²²⁻²⁴ second-order Møller-Plesset perturbation (MP2) theory,²⁸ and the coupled cluster singles and doubles (CCSD)²⁹⁻³¹ method, in concert with cc-pVXZ ($X = D$ to 6) and the Pople basis sets 4-31G,³² 6-31G,³³ 6-311G,³⁴ and 6-311G(d).³⁴

The CCSD(T) results were further extended to the complete basis set (CBS) limit by extrapolating cc-pV(Q,5,6)Z Hartree-Fock energies (E_{RHF}) and cc-pV(5,6)Z electron correlation energies (E_{corr}) by means of the functional forms³⁵⁻³⁶ in Equations (3.1) and (3.2):

$$E_{\text{RHF}}(X) = E_{\text{RHF}}^{\text{CBS}} + ae^{-bX} \quad (3.1)$$

$$E_{\text{corr}}(X) = E_{\text{corr}}^{\text{CBS}} + bX^{-3}. \quad (3.2)$$

Total energies at the CBS limit were obtained by adding separate $E_{\text{RHF}}^{\text{CBS}}$ and $E_{\text{corr}}^{\text{CBS}}$ results from Equations (3.1) and (3.2). Finally, a focal point analysis approach developed by Allen and co-workers^{5,8,37-39} was employed to compute the CCSDT(Q) energies at the CBS limit using the following composite (c~) approximation:⁴⁰

$$E_{\text{c-CCSDT(Q)}}^{\text{CBS}} = E_{\text{CCSD(T)}}^{\text{CBS}} + E_{\text{CCSDT(Q)}}^{\text{cc-pVDZ}} - E_{\text{CCSD(T)}}^{\text{cc-pVDZ}}. \quad (3.3)$$

The CCSD(T) geometry optimizations and harmonic vibrational frequency computations were carried out using analytic gradient methods within the Mainz–Austin–Budapest (MAB) version of the ACESII program⁴¹ and/or the successor CFOUR package.⁴² For highly expensive geometry optimizations (e.g. AE-CCSD(T)/cc-pCV6Z level and beyond), numerical five-point central-difference-formula technique, accompanied by the Newton-Raphson⁴³ method, was employed. The absolute energies at each optimized structure were tightly converged to $10^{-12} E_h$ using the MOLPRO program⁴⁴⁻⁴⁵ to ensure accuracy and consistency. The CCSDT(Q) results were obtained with the string-based MRCC code of Kállay using integrals generated from MAB ACESII;^{20,46} MRCC is a stand-alone program capable of carrying out arbitrary-order coupled cluster and configuration interaction energy computations.

The computationally expensive vibrational frequency computations were carried out numerically using the MATHEMATICA⁴⁷ program INTDIF2009.⁴⁸ Energies converged to at least $10^{-10} E_h$ at the displaced geometries were used to determine the (quadratic, full quartic) force fields in terms of internal coordinates for (harmonic, anharmonic) vibrational frequency computations. The energies of the displacements were computed using MAB ACESII and/or CFOUR as well as MOLPRO. A significant portion of the energy computations that required the use of MOLPRO were run at NERSC.⁴⁹ For anharmonic frequency computations, INTDER2005⁵⁰ was used to execute the non-linear transformation of the force-constants in

internal coordinates to the Cartesian space. The ANHARM⁵¹ program was then employed to transform the Cartesian space into normal coordinates, and to perform a second-order vibrational perturbation (VPT2) theory^{5,52-54} analysis in order to obtain the final vibrational anharmonicities and other spectroscopic constants. A Fermi resonance threshold of 25 cm⁻¹ was employed for the VPT2 treatment.

3.4 RESULTS AND DISCUSSION

3.4.1 HCN as benchmark

In an effort to verify the effectiveness of the computationally demanding high-level electron correlation treatment pursued for the enigmatic HCNO molecule, an exhaustive investigation of the equilibrium geometries and vibrational frequencies for the structurally similar HCN was carried out, as summarized in Tables 3.1 and 3.2. Systematic convergence was achieved for both $r_e(\text{H-C})$ and $r_e(\text{C-N})$ at the CCSD(T) level with the improvement in the basis set from cc-pCVQZ to the CBS limit, with relatively faster convergence in the H-C bond length. Very good agreement with the microwave (MW) data⁵⁵ was observed as the CCSD(T)/CBS values for the H-C and C-N bonds lie within 0.0004 Å and 0.0009 Å of the experimental results, respectively. The CCSDT(Q)/CBS bonds show slight elongation with respect to their CCSD(T)/CBS counterparts due to the increased antibonding arising from the full triples and perturbative quadruples terms, and the effect is more prominent in the case of C-N than H-C, as expected. Nevertheless, an excellent agreement with the MW data was found, as the CCSDT(Q)/CBS values for $[r_e(\text{H-C}), r_e(\text{C-N})]$ were within [0.0003, 0.0001] Å of the spectroscopic values, justifying the application of the higher-level treatment.

Table 3.1 Optimized bond distances (r_e , Å) and absolute energies (E_e , E_h) of HCN^[a]

	CCSD(T) cc-pCVQZ	CCSD(T) cc-pCV5Z	CCSD(T) cc-pCV6Z ^[b]	CCSD(T) CBS ^[b]	c~CCSDT(Q) CBS ^[b]	MW ⁵⁵
$r_e(\text{H-C})$	1.0655	1.0652	1.0652	1.0651	1.0652	1.06549
$r_e(\text{C-N})$	1.1538	1.1530	1.1527	1.1523	1.1531	1.15321
E_e	-93.414082	-93.424144	-93.427803	-93.432665	-93.434294	—

^[a] All-electron (AE) CCSD(T) level of theory and analytic gradients in CFOUR were employed for optimization, unless otherwise mentioned. ^[b] Bond distances optimized using the numerical five-point central difference formula technique and the Newton-Raphson method.

Table 3.2 Harmonic (ω_i) and anharmonic (ν_i) vibrational frequencies (cm^{-1}) of HCN^[a]

Mode (sym)	Description	CCSD(T) cc-pCV6Z ω_i	CCSD(T) CBS ω_i	c~CCSDT(Q) CBS ω_i	CCSD(T) cc-pCV6Z ν_i	CCSD(T) CBS ν_i	c~CCSDT(Q) CBS ν_i	IR ⁵⁶
$\nu_1(\sigma^+)$	C-H stretch	3445	3446	3443	3313	3312	3305	3311
$\nu_2(\pi)$	H-C-N bend	730	733	729	718	717	709	712
$\nu_3(\sigma^+)$	C-N stretch	2136	2137	2129	2106	2108	2097	2097

^[a] All results include core-correlation; numerical gradients employed.

Table 3.2 presents the harmonic and anharmonic vibrational frequencies for HCN computed at the CCSD(T) and CCSDT(Q) levels of theory. The $\nu_1(\sigma^+)$ frequency (C-H stretch) obtained at the CCSD(T)/CBS level lies within 1 cm^{-1} of the observed spectroscopic value,⁵⁶ as compared to the 6 cm^{-1} difference arising from the CCSDT(Q)/CBS level. Nonetheless, the CCSDT(Q)/CBS values for the $\nu_2(\pi)$ and $\nu_3(\sigma^+)$ modes were found to be within 3 cm^{-1} of the corresponding infrared values. The maximum deviations demonstrated in the CCSD(T) and CCSDT(Q) anharmonic frequencies with respect to the IR results were 11 cm^{-1} and 6 cm^{-1} , respectively, indicating the better performance of the latter level of electron correlation method.

3.4.2 Structures, Energies, and Vibrational Spectra of HCNO

The optimized geometric parameters and energetics for bent and linear HCNO for a hierarchical series of correlation-consistent basis sets at the CCSD(T) level of theory are detailed in Tables 3.3 and 3.4. The H-C, C-N, and N-O bonds systematically shrink with the enlargement of the basis sets. $\angle\text{HCN}$ and $\angle\text{CNO}$ both converge towards linearity (180°) with the

increase in the basis set size, but the convergence in the former is erratic compared to the latter, indicating the floppiness of the HCN bending mode. For the cc-pVXZ basis sets, the bent structure remains energetically favorable over its linear counterpart for small values of X , but a rapid convergence to linearity is exhibited with the improvement of the basis sets. Consequently, at the CCSD(T)/cc-pV6Z level, bent HCNO lies a miniscule 0.09 cm^{-1} below the linear structure. The convergence to linearity is faster in the case of cc-pCVXZ basis sets, and linear HCNO is predicted to be the minimum at the AE-CCSD(T)/cc-pCV(5,6)Z levels [cf. Table 3.4]. Extrapolating to the complete basis set limit, the AE-CCSD(T)/CBS equilibrium structure is predicted be linear with $[r_e(\text{H-C}), r_e(\text{C-N}), r_e(\text{N-O})]$ values of $[1.0592, 1.1580, 1.2018]\text{\AA}$. However, when the ground-state structure of HCNO is further explored at the AE-CCSDT(Q)/CBS level, the equilibrium geometry is predicted to be bent lying only $0.22 (\pm 0.10) \text{ cm}^{-1}$ below the corresponding linear structure, and having an HCN bending angle of 173.5° .

Table 3.3 Bent HCNO: Optimized CCSD(T) bond distances (r_e , $\text{\AA}$) and angles, and absolute energies (E_e , E_h)^[a]

Bent HCNO	$r_e(\text{H-C})$	$r_e(\text{C-N})$	$r_e(\text{N-O})$	$\angle(\text{H-C-N})$	$\angle(\text{C-N-O})$	$E_e(\text{bent})$
cc-pVDZ	1.0813	1.1960	1.2038	146.24°	171.95°	-168.158163
cc-pVTZ	1.0629	1.1722	1.2024	157.59°	174.82°	-168.321390
cc-pVQZ	1.0615	1.1648	1.2025	165.13°	176.58°	-168.372212
cc-pV5Z	1.0609	1.1621	1.2037	170.72°	177.85°	-168.388547
cc-pV6Z	1.0606	1.1611	1.2040	174.85°	178.80°	-168.394265
cc-pCVDZ (AE)	1.0794	1.1932	1.2028	146.99°	172.21°	-168.278027
cc-pCVTZ (AE)	1.0620	1.1683	1.2003	159.98°	175.42°	-168.484504
cc-pCVQZ (AE)	1.0599	1.1612	1.2009	169.06°	177.52°	-168.546525
CCSDT(Q)/CBS (AE) ^[b]	1.0594	1.1600	1.2033	173.52°	178.51°	-168.584650

^[a] CCSD(T) level of theory and analytic gradients in CFOUR were employed for optimization, unless otherwise mentioned. All-electron, core-correlated results denoted by (AE); frozen-core otherwise.

^[b] Bond distances and angles optimized using the numerical five-point central difference formula technique and the Newton-Raphson method.

Table 3.4 Linear HCNO: Optimized CCSD(T) bond distances (r_e , Å), absolute energies (E_e , E_h), and relative energies (ΔE_e , cm^{-1})^[a]

Linear HCNO	$r_e(\text{H-C})$	$r_e(\text{C-N})$	$r_e(\text{N-O})$	$E_e(\text{linear})$	$\Delta E_e(\text{bent} - \text{linear})$
cc-pVDZ	1.0752	1.1814	1.2094	-168.156973	-261.35
cc-pVTZ	1.0606	1.1660	1.2053	-168.321197	-42.37
cc-pVQZ	1.0605	1.1620	1.2039	-168.372179	-7.44
cc-pV5Z	1.0605	1.1610	1.2042	-168.388542	-1.08
cc-pV6Z	1.0605	1.1607	1.2042	-168.394264	-0.09
cc-pCVDZ (AE)	1.0735	1.1793	1.2082	-168.276957	-234.93
cc-pCVTZ (AE)	1.0603	1.1633	1.2026	-168.484389	-25.13
cc-pCVQZ (AE)	1.0594	1.1597	1.2016	-168.546515	-2.17
cc-pCV5Z (AE)	1.0592	1.1587	1.2019	-168.565763	
cc-pCV6Z (AE) ^[b]	1.0592	1.1584	1.2019	-168.572633	
CBS (AE) ^[b]	1.0592	1.1580	1.2018	-168.581663	
CCSDT(Q)/CBS (AE) ^[b]	1.0592	1.1595	1.2036	-168.584649	-0.22

^[a,b] See footnotes [a,b] of Table 3.3

Harmonic vibrational frequencies associated with the normal modes of bent and linear HCNO were computed at the CCSD(T) level with a series of correlation-consistent basis sets, and the best results are given in Table 3.5. For bent HCNO, cc-pV(Q,5,6)Z and cc-pCV(T,Q)Z harmonic frequencies are reported at the CCSD(T) level, while the corresponding frequency values for the linear structure are reported for cc-pCV5Z basis and beyond. Normal modes ω_1 to ω_4 , and ω_6 for bent HCNO show consistent changes with the enlargement of the basis sets, whereas ω_5 (HCN bend) exhibits some dramatic changes in its values. A similar pattern is observed for the normal modes associated with linear HCNO. At the CCSDT(Q)/CBS level, the bent structure yields a ω_5 value of 75 cm^{-1} , while the linear geometry produces an imaginary frequency of $51i \text{ cm}^{-1}$. Highly-expensive anharmonic frequency computations were performed at the CCSD(T)/CBS level for linear HCNO, and the results were compared with the corresponding IR data.²⁻⁴ The floppy HCN bending motion is known to contribute large anharmonicities to the normal modes associated with $\angle\text{HCN}$, and the HC, CN bonds. Consequently, ν_1 (CH stretch) deviates by 28 cm^{-1} , ν_2 (asymmetric CNO stretch) deviates by 18 cm^{-1} , and ν_3 (symmetric CNO stretch) deviates by 15 cm^{-1} from the corresponding IR values. As expected, an even larger

deviation of 56 cm^{-1} was calculated for the problematic ν_5 mode, which indicates the difficulties of the VPT2 theory in recovering anharmonicities associated with floppy modes.

Table 3.5 Harmonic (ω_i) and anharmonic (ν_i) vibrational frequencies (cm^{-1}) of the stationary points of HCNO computed with several basis sets and levels of theory^[a]

Mode (sym)	Description ^[b]	CCSD(T) cc-pVQZ ω_i	CCSD(T) cc-pV5Z ω_i	CCSD(T) cc-pV6Z ^[c] ω_i	CCSD(T) cc-pCVTZ ω_i	CCSD(T) cc-pCVQZ ω_i	c~CCSDT(Q) CBS ^[c] ω_i
Bent HCNO							
1 (a')	C–H stretch	3479	3486	3490	3472	3491	3493
2 (a')	asym C–N–O stretch	2268	2273	2276	2262	2282	2273
3 (a')	sym C–N–O stretch	1273	1268	1267	1279	1278	1261
4 (a')	C–N–O ip bend	553	551	550	555	556	545
5 (a')	H–C–N bend	187	115	62	257	138	75
6 (a'')	C–N–O oop bend	553	551	550	556	556	548
		CCSD(T) cc-pCV5Z ω_i	CCSD(T) cc-pCV6Z ^[c] ω_i	CCSD(T) CBS ^[c] ω_i	c~CCSDT(Q) CBS ^[c] ω_i	CCSD(T) CBS ^[c] ν_i	IR ²⁻⁴
Linear HCNO							
1 (σ^+)	C–H stretch	3498	3498	3497	3496	3308	3336
2 (σ^+)	asym C–N–O stretch	2286	2287	2287	2275	2178	2196
3 (σ^+)	sym C–N–O stretch	1272	1272	1272	1261	1269	1254
4 (π)	C–N–O bend	554	554	553	546	540	537
5 (π)	H–C–N bend	54	89	120	51i	280	224

^[a] (FC; AE) CCSD(T) for the (cc-pVXZ; cc-pCVXZ and CBS) basis sets, and analytic gradients in CFOUR used, unless mentioned otherwise. ^[b] Abbreviations: sym = symmetric; asym = antisymmetric; ip = in-plane; oop = out-of-plane.

^[c] Obtained using numerical gradient technique.

Table 3.6 details the angular parameters for bent HCNO optimized at various levels of theories and basis sets to further elucidate the floppy nature of the HCN bending mode. Lack of electron correlation in Hartree-Fock theory results in erroneous predictions, and suggests a linear equilibrium for all the basis sets utilized. MP2 results show a very slow convergence for $\angle\text{HCN}$ with the improvements of the basis sets. CCSD fails to describe the floppy nature and suggests $\angle\text{HCN}$ to be 180° . Finally, the most reliable CCSD(T) theory in concert with cc-pVXZ and cc-pCVXZ basis sets delineates rapid convergence of $\angle\text{HCN}$ towards linearity with the increase in the basis set size. On the other hand, $\angle\text{CNO}$ exhibits a well-behaved pattern, and demonstrates

slower systematic convergence towards linearity. Additionally, harmonic vibrational frequencies associated with the ω_5 mode computed at various levels of theories and basis sets are listed in Table 3.7. Large fluctuations are observed with the improvement of the basis sets, and such an erratic pattern permeates throughout the table for all levels of theories.

Table 3.6 Optimized angular parameters computed with different basis sets and levels of theory for bent HCNO^[a]

	RHF	MP2	CCSD	CCSD(T)	AE-CCSD(T)
$\angle(\text{H-C-N})$					
4-31G	180.00°	152.29°	180.00°	162.51°	—
6-31G	180.00°	150.61°	180.00°	158.38°	—
6-311G	180.00°	149.85°	180.00°	158.57°	—
6-311G(d)	180.00°	149.97°	180.00°	151.95°	—
cc-pVDZ	180.00°	147.50°	163.91°	146.24°	—
cc-pVTZ	180.00°	151.41°	180.00°	157.59°	—
cc-pVQZ	180.00°	153.44°	180.00°	165.13°	—
cc-pV5Z	180.00°	154.35°	180.00°	170.72°	—
cc-pV6Z	180.00°	154.67°	180.00°	174.85°	—
cc-pCVDZ	—	—	—	—	146.99°
cc-pCVTZ	—	—	—	—	159.98°
cc-pCVQZ	—	—	—	—	169.06°
cc-pCV5Z	—	—	—	—	180.00°
$\angle(\text{C-N-O})$					
4-31G	180.00°	171.16°	180.00°	174.51°	—
6-31G	180.00°	170.22°	180.00°	173.16°	—
6-311G	180.00°	170.21°	180.00°	173.61°	—
6-311G(d)	180.00°	172.80°	180.00°	173.64°	—
cc-pVDZ	180.00°	171.43°	176.27°	171.95°	—
cc-pVTZ	180.00°	172.99°	180.00°	174.82°	—
cc-pVQZ	180.00°	173.60°	180.00°	176.58°	—
cc-pV5Z	180.00°	173.81°	180.00°	177.85°	—
cc-pV6Z	180.00°	173.88°	180.00°	178.80°	—
cc-pCVDZ	—	—	—	—	172.21°
cc-pCVTZ	—	—	—	—	175.42°
cc-pCVQZ	—	—	—	—	177.52°
cc-pCV5Z	—	—	—	—	180.00°

^[a] Optimization initiated from an unconstrained bent geometry in each case. Analytic gradients in CFOUR used.

Table 3.7 Harmonic vibrational frequencies for the HCN bending mode, (ω_5 , cm^{-1}), computed with different basis sets and levels of theory for bent HCNO^[a]

	RHF	MP2	CCSD	CCSD(T)	AE-CCSD(T)
4-31G	516	443	243	289	—
6-31G	507	439	152	352	—
6-311G	504	433	188	339	—
6-311G(d)	587	512	169	370	—
cc-pVDZ	567	520	206	462	—
cc-pVTZ	598	489	233	294	—
cc-pVQZ	603	447	284	187	—
cc-pV5Z	604	424	302	115	—
cc-pV6Z	604	415	309	62 ^[b]	—
cc-pCVDZ	—	—	—	—	451
cc-pCVTZ	—	—	—	—	257
cc-pCVQZ	—	—	—	—	138

^[a] Analytic gradients in CFOUR used unless otherwise mentioned.

^[b] Obtained using numerical gradient technique.

3.5 CONCLUSIONS

Our highly expensive electron correlation treatment has produced some key results and assisted us in making some definitive conclusions about the ground-state electronic structure of HCNO. At the AE-CCSD(T)/CBS level, HCNO is found to have a linear minimum, but the addition of the perturbative quadruples corrections at the AE-CCSDT(Q)/CBS level revealed a bent minimum lying only 0.22 cm^{-1} below the corresponding linear geometry, with an HCN bond angle of 173.5° . The difficulty in pinpointing the equilibrium structure with the aid of the two highest levels of electron correlation demonstrates the classic quasilinear character of the enigmatic HCNO molecule. Similarly, harmonic and anharmonic vibrational frequencies computed at high levels of theory exhibit large anharmonicities associated with the problematic HCN floppy bending mode and the connected HC and CN bond stretches, resulting in significant deviations from the experimental results. The erratic pattern in $\angle\text{HCN}$ was further demonstrated utilizing various levels of *ab initio* quantum chemical theory in concert with a series of Pople and correlation-consistent basis sets. In summary, at the highest level of theory

[AE-CCSDT(Q)/CBS] employed in this research, HCNO is predicted to have a “double-well” potential with the bent structure ($\angle\text{HCN}=173.5^\circ$) residing at the two minima, and the corresponding linear geometry lying only $0.22 (\pm 0.1) \text{ cm}^{-1}$ above both of them on an extremely flat potential energy surface.

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CHAPTER 4

POLYTWISTANE[†]

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4.1 ABSTRACT

Twistane, $C_{10}H_{16}$, is a classic D_2 -symmetric chiral hydrocarbon that has been studied for decades due to its fascinating stereochemical and thermodynamic properties. Here we analyze in detail the contiguous linear extension of twistane with ethano (ethane-1,2-diyl) bridges to create a new chiral, C_2 -symmetric hydrocarbon nanotube called polytwistane. Polytwistane, $(CH)_n$, has the same molecular formula as polyacetylene but is composed purely of $C(sp^3)$ -H units, all of which are chemically equivalent. The polytwistane nanotube has the smallest inner diameter (2.6 Å) of hydrocarbons considered to date. A rigorous topological analysis of idealized polytwistane and a $C_{236}H_{242}$ prototype optimized by B3LYP density functional theory reveals that the polymer has a nonrepeating, alternating σ -helix, with an irrational periodicity parameter and an instantaneous rise (or lead) angle near 15° . A theoretical analysis utilizing homodesmotic equations and explicit computations as high as CCSD(T)/cc-pVQZ yields the enthalpies of formation $\Delta_f H_0^\circ(\text{twistane}) = -1.7 \text{ kcal mol}^{-1}$ and $\Delta_f \bar{H}_0^\circ(\text{polytwistane}) = +1.28 \text{ kcal (mol CH)}^{-1}$, demonstrating that the hypothetical formation of polytwistane from acetylene is highly exothermic. Hence, polytwistane is synthetically viable both on thermodynamic grounds and also because no obvious pathways exist for its rearrangement to lower-lying isomers. The present analysis should facilitate the preparation and characterization of this new chiral hydrocarbon nanotube.

4.2 INTRODUCTION

While the parent of all diamondoid hydrocarbons,¹ adamantane² (tricyclo[3.3.1.1^{1,7}]decane), exclusively displays cyclohexane chair skeletons, its isomer twistane (tricyclo[4.4.0.0^{3,8}]decane, **1**, Figure 4.1) is exclusively composed of twist-boat cyclohexane

rings. As a consequence, **1** is strained, which can readily be recognized by the intertwined [2.2.2]bicyclooctane moieties in the cage; strain release is the driving force for the acid-catalyzed rearrangement of **1** to adamantane.³ The inherent chirality of the twist-boat cyclohexane conformer is retained in D_2 -symmetrical twistane, which therefore exists in two enantiomeric forms.⁴ Whitlock first synthesized ($\pm$)-**1** in 1962,⁵ and asymmetric approaches⁶ as well more economical routes to the racemate followed shortly thereafter.⁷ A large variety of substituted twistanes is known.⁸

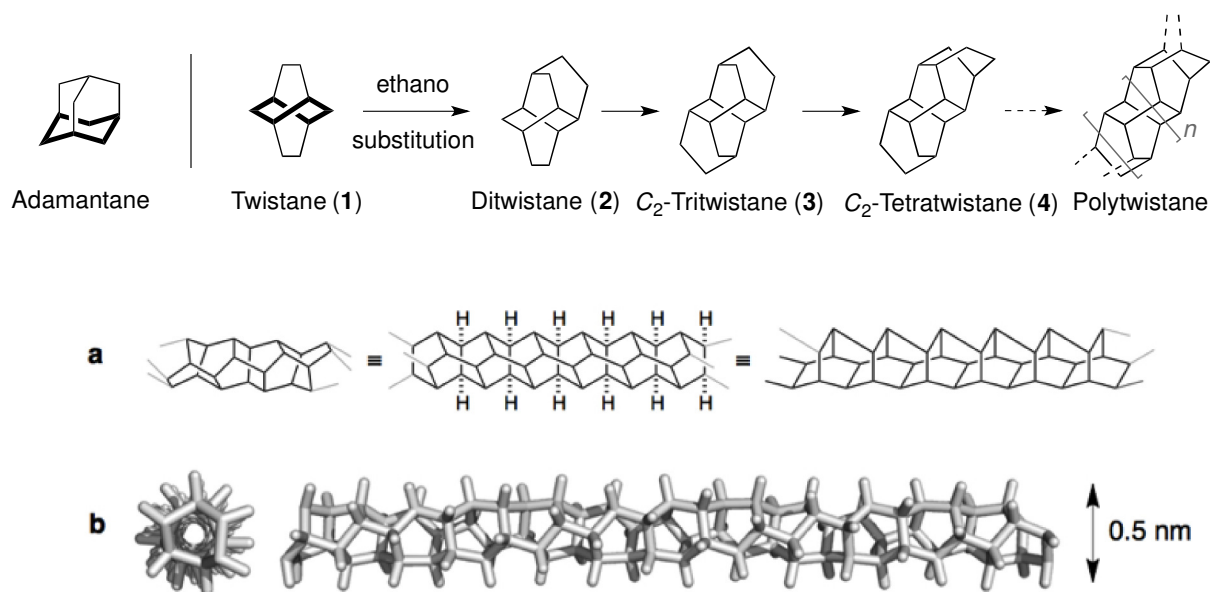


Figure 4.1 Constrained cyclohexane conformations in adamantane and twistane (**1**) and the formal oligomerization of twistane to helical polytwistane. Depictions (a) and (b) show helical polytwistane in its (*M*)-form; the exact outer diameter is 0.468 nm based on H nuclear positions (*vide infra*).

Similar to the higher diamondoids, which can be extended formally through addition of isobutane units,⁹ **1** can be constructed by 1,4-bridging of its six-membered rings with ethano (ethane-1,2-diyl) moieties (Figure 4.1a and 4.1b). The newly formed six-membered rings also display twist-boat skeletons, and continuous addition in the same fashion leads to a homochiral

helical (CH)_n nanotube. The first member of this class of compounds is C₂-symmetric ditwistane (**2**), for which both enantiomers are known.¹⁰ Numerous substituted ditwistanes have been described in the literature, including **5** and **6**¹¹ (Figure 4.2). While the higher unsubstituted linear oligotwistane hydrocarbons are unknown, several derivatives incorporating their carbon skeletons have been described. For instance, **7** is one of three known linear triwistanes.¹² Although not identified as an oligotwistane, the hexatwistane skeleton of **8** is the product of an electrophilic addition of bromine to a laticyclic polyene.¹³ Structure **8** appears to be the largest oligotwistane prepared to date.

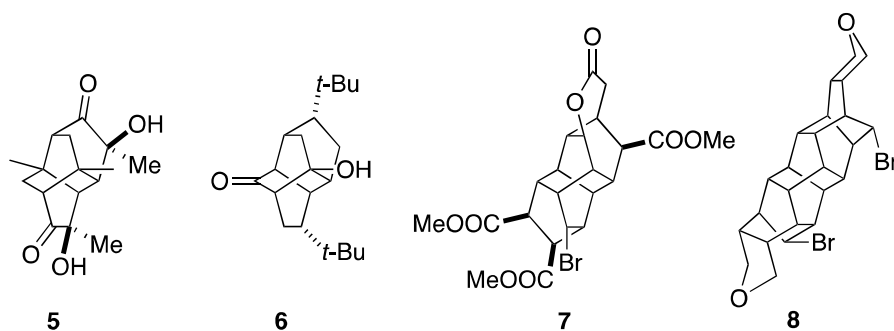


Figure 4.2 A selection of known substituted oligotwistanes.

The sequential linear addition of ethano bridges to **2** produces C₂-symmetric tritwistane (**3**), tetratwistane (**4**), and so forth, eventually resulting in hitherto unknown *polytwistane*.¹⁴ Like the other members of the relatively new family of σ -helicenes, including the triangulanes,¹⁵ spiroannulated four-¹⁶ and five-membered rings,¹⁷ and helical diamondoids such as [1(2)3]-tetramantane,¹⁸ polytwistane is helical and therefore chiral. Apart from their aesthetic appeal, such molecules are well suited for studying fundamental aspects of chemical bonding and helicity. Polytwistane formally is a polyacetylene nanotube that is exclusively composed of

identical CH units with sp^3 -hybridized carbons. To stimulate the synthesis of this intriguing polymer, here we use mathematical analysis and quantum chemical computations to investigate the intricate topology and to predict the thermochemistry of polytwistane.

4.3 TOPOLOGY AND COMPUTATIONAL ANALYSIS

4.3.1 Topology of Polytwistane

An expanded color-coded view of a polytwistane segment is shown in Figure 4.3. The carbon atoms constitute an interlocked helical chain that forms a nanotube of inner radius R . All carbon atoms are equivalent and lie on the inner wall of the tube. Each carbon is bonded to three other carbons and one hydrogen. All hydrogen atoms are also equivalent and project outward from the inner wall. There are three distinct C–C bonds, as depicted in blue, red, and green with lengths r_1 , r_2 , and r_3 , respectively. The C–H bonds of uniform length r_H are shown in black.

The primary helical chain (**I**) involves an alternation of bonds (blue, red), but the structure of polytwistane can also be dissected as a double helix (**II**₁, **II**₂) with bond alternation (red, green), or a triple helix (**III**₁, **III**₂, **III**₃) with a pattern of bonds (blue, green). The (A_{ij} , B_{ij}) labeling of carbon atoms in Figure 4.3 reveals these helices. All chains (**I**, **II**, **III**) involve an (ABAB...) sequence of atoms and bond lengths, while (i, j) designates incorporation in the (**II** _{i} , **III** _{j}) chains. The **II** _{i} ($i = 1, 2$) chains involve the repeating sequences ($A_{i1}B_{i1}A_{i2}B_{i2}A_{i3}B_{i3}$), and the corresponding sequences for **III** _{j} ($j = 1, 2, 3$) are ($A_{1k}B_{1k}A_{2k}B_{2k}$). The primary chain **I** repeats in the twelve-element pattern ($A_{11}B_{13}A_{23}B_{22}A_{12}B_{11}A_{21}B_{23}A_{13}B_{12}A_{22}B_{21}$). None of the chains of consecutively bonded carbon atoms in polytwistane meets the exact mathematical definition of a helix, namely a three-dimensional curve that lies on a cylinder or cone, so that the tangent of the curve has a constant rise (or lead) angle (γ) relative to a plane perpendicular to the axis. In all of

the (**I**, **II**, **III**) polytwistane “helices”, the lead angle formed by the bond vectors actually alternates between two values as the chain is traversed. Nonetheless, polytwistane does exhibit mathematically exact helices in which consecutive atoms are not bonded to each other. An exact double helix (**IV_A**, **IV_B**) comprising (AAAA..., BBBB...) sequences occurs in which each chain involves every second carbon atom in the primary helix **I**. The **IV** helices form the basis for the mathematical description of the structure of polytwistane.

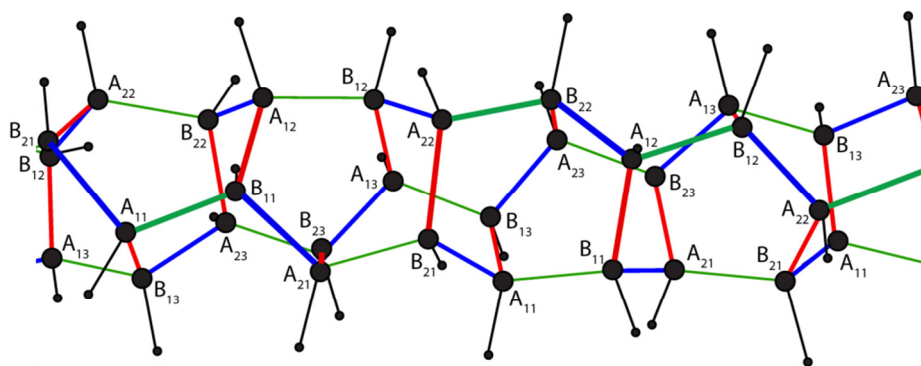


Figure 4.3 Repeating geometric patterns in polytwistane. The C–C bonds are color-coded to identify the three distinct bond distances r_1 (blue), r_2 (red), and r_3 (green) of Table 4.1; C–H bonds are shown in black. The carbon atoms (A, B) belong to the double helix (**IV_A**, **IV_B**).

There are two types of six-membered carbon rings in polytwistane, designated here as **R₁** and **R₂**. These ring types may be distinguished in Figure 4.3 according to whether they contain one green bond (**R₁**) or two (**R₂**). All carbon atoms in polytwistane are members of three **R₁** and three **R₂** rings. The **R₁** rings contain two atoms from each of the type **III** helices, while **R₂** rings contain three atoms from a pair of **III** helices. The torsion angles within **R₁** and **R₂** involving C–C bonds of distances (r_i , r_j , r_k) can be denoted as τ_{ijk} . In this scheme, the two types of rings contain the torsion angle sequences **R₁**(τ_{132} , τ_{123} , τ_{213} , τ_{132} , τ_{123} , τ_{213}) and **R₂**(τ_{123} , τ_{232} , τ_{123} , τ_{212} ,

τ_{121} , τ_{122}). The qualitative description of polytwistane topology must be substantiated by a rigorous mathematical analysis of the atomic positions and geometric degrees of freedom.

To formulate the Cartesian coordinates of the atoms in polytwistane, we arbitrarily assume that the nanotube lies along the z axis. Other orientations can be constructed by applying unitary transformations of the coordinates derived here. First, we define the helical lattice function

$$\mathbf{X}(s; R, \tau, \zeta, \beta, \delta) = R \left\{ \cos \left[\left(\frac{2\pi}{\tau} \right) s + \beta \right], \sin \left[\left(\frac{2\pi}{\tau} \right) s + \beta \right], 4\zeta s + \delta \right\}, \quad (4.1)$$

in which s is the independent variable describing location along the tube axis and all other arguments relate to the internal structure of the helix. The positions of the carbon atoms in the ($\mathbf{IV}_A$, $\mathbf{IV}_B$) helices of polytwistane are given by

$$\begin{aligned} \mathbf{x}_{2j+1}(\mathbf{C}_A) &= \mathbf{X}(j + \tfrac{1}{2}; R, \tau, \zeta, \beta_C, \delta_C) \\ \mathbf{x}_{2j}(\mathbf{C}_B) &= \mathbf{X}(j; R, \tau, \zeta, -\beta_C, -\delta_C), \end{aligned} \quad (4.2)$$

where j runs over all the integers, and R is the inner radius of the tube. Thus, the structure of the carbon framework has five degrees of freedom, represented by the parameters $(R, \tau, \zeta, \beta_C, \delta_C)$.

The Cartesian coordinates of the hydrogen atoms are

$$\begin{aligned} \mathbf{x}_{2j+1}(\mathbf{H}_A) &= \mathbf{X}(j + \tfrac{1}{2}; \rho_H R, \tau, \zeta \rho_H^{-1}, \beta_H, \delta_H) \\ \mathbf{x}_{2j}(\mathbf{H}_B) &= \mathbf{X}(j; \rho_H R, \tau, \zeta \rho_H^{-1}, -\beta_H, -\delta_H), \end{aligned} \quad (4.3)$$

involving three additional parameters $(\rho_H, \beta_H, \delta_H)$. The (τ, ζ) parameters must be identical in the equations for the C and H coordinates to maintain the correct periodicity.

Equations (4.2) and (4.3) immediately provide formulas for the difference vectors connecting the various atoms, from which internal coordinates can be derived. The index j can be eliminated in the computation of internal coordinates by using the standard trigonometric identities $\cos(A-B) - \cos(A+B) = 2 \sin A \sin B$ and $\sin(A-B) - \sin(A+B) = -2 \cos A \sin B$. The results can be made compact by defining the following generic functions:

$$f(u, \phi) = \sqrt{4u^2 + 2 - 2 \cos \phi}, \quad (4.4)$$

$$g(u, \phi, v, \chi) = 1 + 4uv - \cos \phi - \cos \chi + \cos(\phi - \chi), \quad (4.5)$$

$$f_H(u, v, \phi) = \sqrt{1 + u^2 + v^2 - 2u \cos \phi}, \quad (4.6)$$

$$g_H(u, v, \phi, w, \chi) = 1 + 2vw - u \cos \phi - \cos \chi + u \cos(\phi - \chi), \quad (4.7)$$

as well as the reduced parameters

$$(a_1, a_2, a_3) = (\delta_C + \zeta, \delta_C - \zeta, \delta_C - 5\zeta), \quad (4.8)$$

$$(b_1, b_2, b_3) = \left(2\beta_C + \frac{\pi}{\tau}, 2\beta_C - \frac{\pi}{\tau}, 2\beta_C - \frac{5\pi}{\tau} \right), \quad (4.9)$$

and

$$(a_H, b_H) = (\delta_C - \rho_H \delta_H, \beta_C - \beta_H). \quad (4.10)$$

Accordingly, the C–C and C–H bond distances are

$$r_m = R f(a_m, b_m) \quad \text{for } m = (1, 2, 3), \quad (4.11)$$

and

$$r_H = R f_H(\rho_H, a_H, b_H). \quad (4.12)$$

Similarly, the three C–C–C bond angles (θ_{12} , θ_{13} , θ_{23}) and three H–C–C bond angles ($\theta_1^H, \theta_2^H, \theta_3^H$) are given by

$$\cos \theta_{mn} = \frac{g(a_m, b_m, a_n, b_n)}{f(a_m, b_m) f(a_n, b_n)} \quad (4.13)$$

and

$$\cos \theta_m^H = \frac{g_H(\rho_H, a_H, b_H; a_m, b_m)}{f_H(\rho_H, a_H, b_H) f(a_m, b_m)}. \quad (4.14)$$

Finally, it is useful to define the ratios

$$(\lambda_{mn}, \lambda_m^H, \omega_m, \omega_{mn}^H) = \left(\frac{r_m}{r_n}, \frac{r_H}{r_m}, \frac{\cos \theta_{mn}}{\cos \theta_{mp}}, \frac{\cos \theta_m^H}{\cos \theta_n^H} \right), \quad (4.15)$$

where (m, n, p) are cyclic permutations of $(1, 2, 3)$.

The polytwistane lattice can be determined from internal coordinates by first specifying the parameters $(r_1, r_2, r_3, \omega_1, \omega_2)$ and then numerically solving the following system of nonlinear equations for the reduced parameters (a_1, b_1, a_2, b_2) :

$$\begin{aligned} f(a_1, b_1) &= \lambda_{12} f(a_2, b_2) \\ f(3a_2 - 2a_1, 3b_2 - 2b_1) &= \lambda_{31} f(a_1, b_1) \end{aligned} \quad (4.16)$$

$$\omega_1 f(a_2, b_2) g(a_1, b_1, 3a_2 - 2a_1, 3b_2 - 2b_1) = f(3a_2 - 2a_1, 3b_2 - 2b_1) g(a_1, b_1, a_2, b_2)$$

$$\omega_2 f(3a_2 - 2a_1, 3b_2 - 2b_1) g(a_2, b_2, a_1, b_1) = f(a_1, b_1) g(a_2, b_2, 3a_2 - 2a_1, 3b_2 - 2b_1)$$

Afterwards, the target parameters for the carbon chain can be obtained from

$$(R, \tau, \zeta, \beta_C, \delta_C) = \left[\frac{r_1}{f(a_1, b_1)}, \frac{2\pi}{b_1 - b_2}, \frac{1}{2}(a_1 - a_2), \frac{1}{4}(b_1 + b_2), \frac{1}{2}(a_1 + a_2) \right]. \quad (4.17)$$

To find the positions of the hydrogen atoms, $(r_H, \omega_{12}^H, \omega_{13}^H)$ values are chosen, and then the following system of nonlinear equations is solved for (ρ_H, a_H, b_H) :

$$\begin{aligned} f_H(\rho_H, a_H, b_H) &= \lambda_1^H f(a_1, b_1) \\ g_H(\rho_H, a_H, b_H; a_1, b_1) &= \lambda_{12} \omega_{12}^H g_H(\rho_H, a_H, b_H; a_2, b_2) \\ g_H(\rho_H, a_H, b_H; 3a_2 - 2a_1, 3b_2 - 2b_1) &= \lambda_{31} \omega_{31}^H g_H(\rho_H, a_H, b_H; a_1, b_1) \end{aligned} \quad (4.18)$$

whence

$$(\delta_H, \beta_H) = \left[\frac{a_1 + a_2 - 2a_H}{2\rho_H}, \frac{1}{4}(b_1 + b_2) - b_H \right]. \quad (4.19)$$

Because the mathematical system defined by Equations (4.16) and (4.18) is invariant to both of the transformations $(a_1, a_2, a_H) \rightarrow (-a_1, -a_2, -a_H)$ and $(b_1, b_2, b_H) \rightarrow (-b_1, -b_2, -b_H)$, there is a four-fold degeneracy of solutions for the polytwistane helix for any specified set of bond distances and angles: $\{(\tau, \zeta, \beta_C, \delta_C, \beta_H, \delta_H), (-\tau, -\zeta, -\beta_C, -\delta_C, -\beta_H, -\delta_H), (-\tau, \zeta, -\beta_C, \delta_C, -\beta_H, \delta_H), (\tau, -\zeta, \beta_C, -\delta_C, \beta_H, -\delta_H)\}$, with (helicity, direction of propagation) = $\{(P, +z), (P, -z), (M, +z), (M, -z)\}$, in order. Thus, the first two solutions give right-handed helices, while the second two solutions yield left-handed helices.

Further geometrical analysis of polytwistane is provided in Appendix B. Equations B1–B9 therein formulate three other types of informative parameters, the lead angles $\chi(k)$ measuring inclination of the C–C bonds vis-à-vis the plane perpendicular to the helix axis, the torsion angles τ_{ijk} exhibited by connected C–C bonds, and the azimuthal angles of the C–H bonds.

4.3.2 Computational Analysis of Polytwistane

The three-dimensional structure of polytwistane was investigated computationally by optimizing the geometry of a $C_{236}H_{242}$ prototype utilizing B3LYP/6-31G(d) density functional theory (DFT).^{19,20,21} As apparent in Figure 4.3, excising a $(CH)_{236}$ fragment from a polytwistane strand leaves three severed C–C bonds at each terminus, which are then capped with hydrogen atoms to produce a closed-shell $C_{236}H_{242}$ species. The $C_{236}H_{242}$ segment exhibited C_2 symmetry, and the Cartesian coordinates of the optimized geometry are provided in Appendix B; computational details can be found below. To avoid edge effects uncharacteristic of polytwistane, the $-C_{15}H_{18}$ moieties at the ends of the $C_{236}H_{242}$ molecule were removed from the mathematical analysis of the geometric structure and omitted from the plots given here. The remaining minute random variations in the geometric parameters are primarily a consequence of technical difficulties in exactly converging on the equilibrium geometry of $C_{236}H_{242}$, rather than inherent properties of polytwistane. Table 4.1 presents parameters for an infinite polytwistane helix derived by a precise least-squares fit of Equations (4.2) and (4.3) to the atomic positions of $C_{236}H_{242}$.

The C–C bond distances of $C_{236}H_{242}$ are plotted in Figure 4.4. A remarkable clustering is seen, as each carbon atom displays three distinct bond distances, $r_1 = 1.540 \pm 0.002$ Å, $r_2 = 1.573 \pm 0.002$ Å, and $r_3 = 1.557 \pm 0.002$ Å. The shortest and longest C–C bonds reside in primary chain **I**, while the intermediate bond provides crosslinks that stiffen the helix (Figure 4.3). Although r_1 coincides with the length of a prototypical C–C single bond, the other two distances are elongated by 0.017 – 0.033 Å, evidencing some degree of ring strain. Figure 4.5 shows that the C–C–C bond angles of $C_{236}H_{242}$ also cluster into three narrow ranges: $\theta_{12} = 104.4 \pm 0.1^\circ$, $\theta_{13} = 109.3 \pm 0.1^\circ$, and $\theta_{23} = 109.8 \pm 0.1^\circ$. The first angle repeats within primary chain **I** and is distorted

5° below the ideal tetrahedral angle ($\theta_0 = 109.5^\circ$); the latter two angles involve the crosslinks and lie very near θ_0 .

Table 4.1 Geometric parameters of polytwistane derived from B3LYP/6-31G(d) optimization of a $C_{236}H_{242}$ segment or an idealized structure with equal C–C bond lengths and angles.

	$C_{236}H_{242}$	idealized		$C_{236}H_{242}$	idealized
R	1.2827	1.2851	τ_{132}	−42.75	−35.95
r_1	1.5402	1.5400	τ_{232}	71.20	78.09
r_2	1.5731	1.5400	τ	2.777096	2.731197
r_3	1.5571	1.5400	ζ	0.1587	0.1521
r_H	1.0959	1.0900	β_C	−0.0894	−0.0654
θ_{12}	104.42	106.83	δ_C	0.2289	0.1956
θ_{13}	109.27	106.83	ρ_H	1.8228	1.8086
θ_{23}	109.78	106.83	β_H	0.0274	0.0336
θ_1^H	111.95	112.00	δ_H	0.0335	−0.0129
θ_2^H	110.84	112.00	$\gamma_A=\gamma_B$	19.33	18.43
θ_3^H	110.41	112.00	γ_0	15.68	14.82
τ_{121}	88.96	78.09	γ_1	40.21	35.48
τ_{123}	−28.08	−35.95	γ_2	−6.57	−4.16
τ_{212}	−43.68	−35.95	γ_3	68.52	70.58
τ_{213}	73.71	78.09	γ_H	±11.33	±14.96

R , r_i , r_H in Å; θ_{ij} , θ_i^H , τ_{ijk} , γ_i , in deg; all other parameters are dimensionless. R is the inner diameter of the nanotube. The bond distances (r_i , r_H) are depicted in Figure 4.3; (θ_{12} , θ_{13} , θ_{23}) denote angles between [(blue, red), (blue, green), (red, green)] C–C bonds therein.

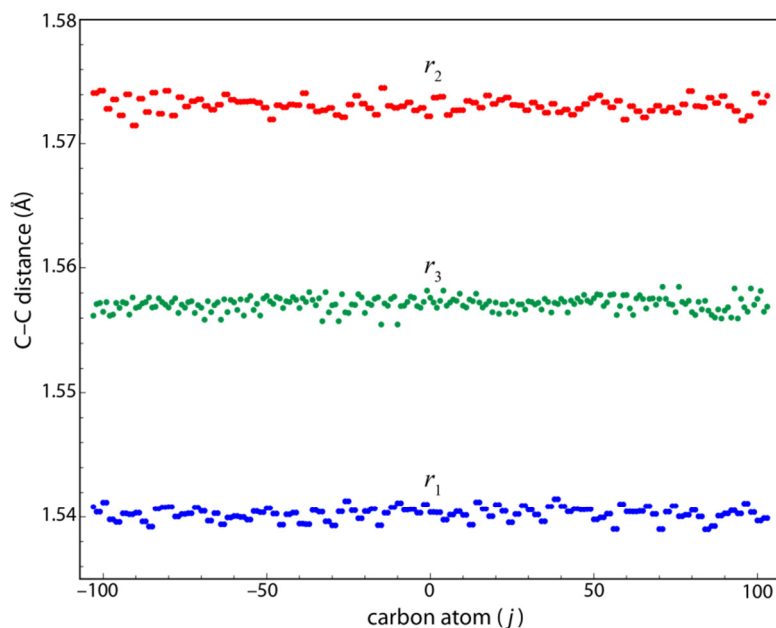


Figure 4.4 Evidence of three distinct C–C bond distances in polytwistane: a plot of the lengths of the C–C bonds made by carbon atom j along the primary chain **I** of the $C_{236}H_{242}$ fragment. The color code is the same as in Figure 4.3.

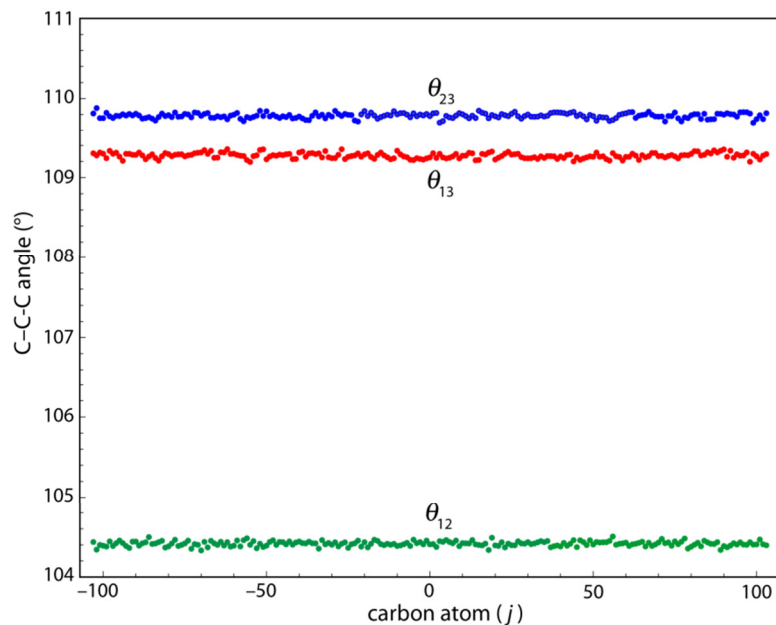


Figure 4.5 Evidence of three distinct C–C–C bond angles in polytwistane: a plot of the angles formed by carbon atom j along the primary chain **I** of the $C_{236}H_{242}$ fragment. Each angle is shown with the color complementary to those of the two included bonds, using the coloring scheme of Figure 4.3.

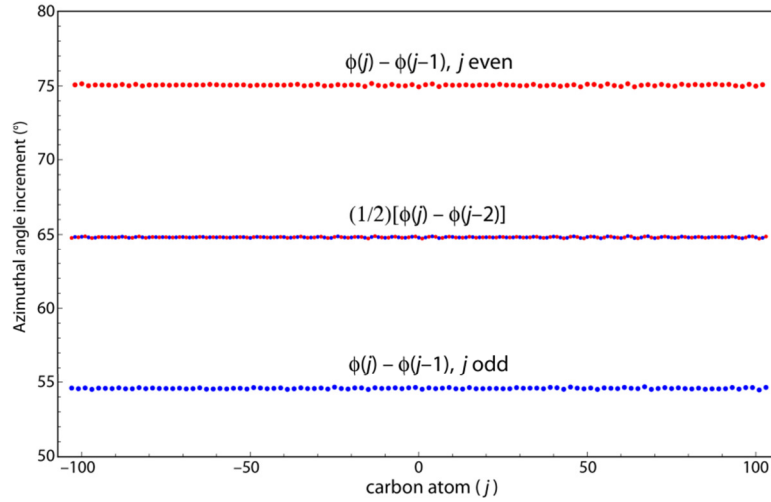


Figure 4.6 Evidence of distinct IV_A and IV_B helices in polytwistane: increments in the azimuthal angle (ϕ) of carbon atoms j along the primary chain **I** of the $\text{C}_{236}\text{H}_{242}$ fragment. Each increment between adjacent atoms is assigned the same color as the corresponding C–C bond in Figure 4.3.

A vivid signature of the distinct IV_A and IV_B helices in polytwistane appears in Figure 4.6. The azimuthal angle differences $[\phi(j) - \phi(j-1)]$ between successive carbon atoms in the primary chain of $\text{C}_{236}\text{H}_{242}$ are $75.1 \pm 0.1^\circ$ for $\text{C}_A \rightarrow \text{C}_B$ (j even) but $54.6 \pm 0.1^\circ$ for $\text{C}_B \rightarrow \text{C}_A$ (j odd). In contrast, the mean differences $\frac{1}{2} [\phi(j) - \phi(j-2)]$ between alternate carbon atoms are $64.8 \pm 0.1^\circ$ regardless of whether j is even or odd. These variations are perfectly described by Equation (4.2), which reckons the three $\Delta\phi$ increments of concern as $(\pi\tau^{-1} - 2\beta_C, \pi\tau^{-1} - 2\beta_C, \pi\tau^{-1}) = (75.06^\circ, 54.57^\circ, 64.82^\circ)$. As in Figure 4.6, the $\Delta\phi$ increments between successive hydrogen atoms in $\text{C}_{236}\text{H}_{242}$ also cluster into (j odd, j even) pairs with the values $(\pi\tau^{-1} + 2\beta_H, \pi\tau^{-1} - 2\beta_H) = (67.96^\circ, 61.68^\circ)$.

For the primary chain of $\text{C}_{236}\text{H}_{242}$, Figure 4.7 reveals that the (r_1, r_2, r_3) bond vectors manifest lead angles clustered around $(\gamma_1, \gamma_2, \gamma_3) = (40.2^\circ, -6.6^\circ, 68.5^\circ)$ with respect to the plane perpendicular to the helix axis. In comparison, the instantaneous lead angle [Equation (B2)] of

the ($\mathbf{IV}_A$, $\mathbf{IV}_B$) helices is $\gamma_0 = 15.7^\circ$, and the corresponding discrete value for the (C_A-C_A , C_B-C_B) line segments is $\gamma_A = \gamma_B = 19.3^\circ$. The (γ_1 , γ_2 , γ_3) values can be understood from the depictions of the C–C bonds in Figure 4.3, wherein the (blue, green) bonds take (moderate, large) steps along the axis, whereas the red bonds actually regress to a small extent.

The success of our mathematical description of polytwistane is demonstrated further by graphs of additional $C_{236}H_{242}$ geometric parameters in Figures B1–B4 in Appendix B. Figure B1 confirms a tight clustering of the axial distances and C–H bond lengths about the values $R = 1.283 \text{ \AA}$ and $r_H = 1.096 \text{ \AA}$, respectively. Figure B2 plots all torsion angles τ_{ijk} of C–C–C–C chains of bonded atoms. As expected, nine distinct τ_{ijk} values are observed, six exhibited within the six-membered rings **R1** and **R2** and three that span these rings. Figure B3 reveals only three distinct H–C–C bond angles, $\theta_1^H = 112.0 \pm 0.1^\circ$, $\theta_2^H = 110.8 \pm 0.1^\circ$, and $\theta_3^H = 110.4 \pm 0.1^\circ$. Finally, Figure B4 shows the existence of only two distinct lead angles of the C–H bonds, $\gamma_H(A) = +11.3^\circ$ and $\gamma_H(B) = -11.3^\circ$, meaning that the C–H bonds alternate between tilting forward and backward by this amount along the polytwistane chain.

An idealized reference structure of polytwistane can be envisioned in which the bond lengths all assume prototypical alkane values [$r(C-C) = 1.54 \text{ \AA}$, $r(C-H) = 1.09 \text{ \AA}$], and all bond angles of a given type are equal [$\theta_{12} = \theta_{13} = \theta_{23} = \theta(C-C-C)$; $\theta_1^H = \theta_1^H = \theta_1^H = \theta(H-C-C)$]. Solving Equations (4.16) and (4.18) for the geometric parameters of this idealized polytwistane yields the values listed in Table 4.1 alongside those of the $C_{236}H_{242}$ prototype. Despite significant differences in the bond and torsion angles, the parameters of the helices are remarkably similar in the two models. For example, $R = (1.2851, 1.2827) \text{ \AA}$, $\zeta = (0.1521,$

0.1587), and $\gamma_0 = (14.82^\circ, 15.68^\circ)$ in the (idealized, $C_{236}H_{242}$) cases. Thus, the idealized model is a useful representation of polytwistane.

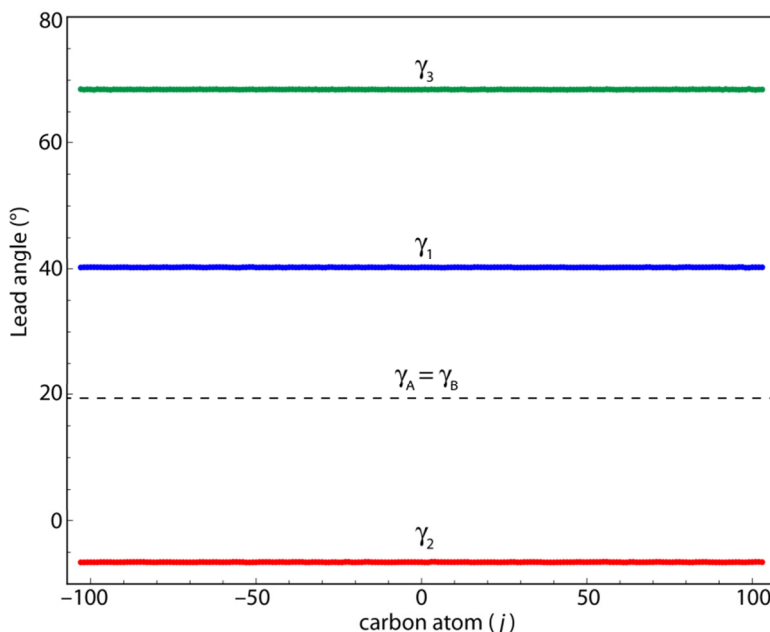


Figure 4.7 Lead angles for the bonds formed by carbon atom j along the primary chain **I** of the $C_{236}H_{242}$ fragment. The color code is the same as in Figure 4.3.

The periodicity parameters $\alpha(C_{236}H_{242}) = 2.777096\dots$ and $\alpha(\text{idealized}) = 2.731197\dots$ are irrational numbers, demonstrating that polytwistane is a nonrepeating σ -helicene. In particular, the azimuthal angles of the carbon and hydrogen atoms never exactly repeat as the polytwistane chain is traversed. Nonetheless, the periodicity parameters can provide the span of carbon atoms (n_ϵ) in the primary chain necessary to achieve an azimuthal coincidence within a specified threshold (ϵ). For the $C_{236}H_{242}$ prototype, $(\epsilon, n_\epsilon) = (0.8^\circ, 50)$ and $(0.03^\circ, 2716)$, while in the idealized model $(\epsilon, n_\epsilon) = (1.5^\circ, 142)$ and $(0.03^\circ, 3922)$.

4.3.3 Polytwistane as a carbon nanotube

Polytwistane is a chiral carbon nanotube of extraordinary high rigidity. Its relationship to regular carbon nanotubes is similar to the relationship between graphane and graphene,²² with the important difference that all the hydrogens reside on one surface, *viz.* the convex surface of the tube. As such, polytwistane can be considered a completely hydrogenated ultra-small carbon nanotube.²³ The approximate inner and outer diameters of polytwistane are 2.6 and 4.7 Å, respectively. The former is substantially smaller than the 3 Å diameter of the smallest single-walled carbon nanotube known to date, the innermost (2,2) carbon nanotube inside a multiwalled carbon nanotube.²⁴

4.3.4 Computational Methods

Geometric structures were optimized in highest symmetry by means of B3LYP^{19,20} density functional theory conjoined with the 6-31G(d) basis set,²¹ as implemented by the Gaussian09 program suite.²⁵ The “ultrafinegrid” option for the density and “very tight” convergence criterion (SCF convergence = 10^{-8} a.u.) were employed. The final single-point energy computations were executed with the frozen-core CCSD(T) wave function method³⁸ and the correlation-consistent cc-pVXZ ($X = D, T, Q$) basis sets,³⁰ as carried out by the MOLPRO program.²⁶

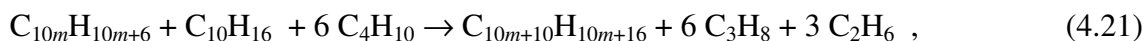
4.4 POLYTWISTANE THERMOCHEMISTRY

Polytwistane has the same $(CH)_n$ molecular formula as polyacetylene. The formation of polytwistane through polymerization of acetylene, if it can be achieved, should be strongly exothermic. Once prepared, there is no obvious pathway for polytwistane to rearrange to a more stable isomer.

To analyze the thermochemistry of polytwistane, we have utilized the systematic error-canceling properties of homodesmotic²⁷ equations that intricately balance the number of bonds of each type on both sides of the equation. Proper homodesmotic equations allow the use of moderate levels of theory to achieve high accuracy. Consider the following homodesmotic reaction for extending polytwistane by one monomer unit,



In explicit form this aggregation can be represented as



whose enthalpy change at 0 K is

$$\Delta H_{\text{agg}}(m) = \Delta_f H_0^\circ(\text{C}_{10m+10}\text{H}_{10m+16}) - \Delta_f H_0^\circ(\text{C}_{10m}\text{H}_{10m+6}) - \Delta_f H_0^\circ(\text{twistane}) + q_{\text{agg}} , \quad (4.22)$$

where

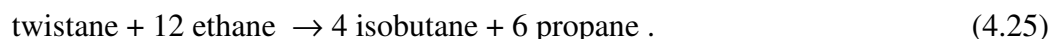
$$q_{\text{agg}} = 6 [\Delta_f H_0^\circ(\text{C}_3\text{H}_8)] + 3 [\Delta_f H_0^\circ(\text{C}_2\text{H}_6)] - 6 [\Delta_f H_0^\circ(\text{C}_4\text{H}_{10})] . \quad (4.23)$$

Taking the limit $m \rightarrow \infty$, Equation (4.22) yields a formula suitable for quantum chemical computations,

$$\Delta_f \bar{H}_0^\circ(\text{polytwistane}) = \frac{1}{10} \left[\Delta H_{\text{agg}}(\infty) + \Delta_f H_0^\circ(\text{twistane}) - q_{\text{agg}} \right] , \quad (4.24)$$

giving the enthalpy of formation of polytwistane *per mol of CH units*.

High levels of theory can be used to compute $\Delta_f H_0^\circ(\text{twistane})$ via the homodesmotic fragmentation equation



Specifically,

$$\Delta_f H_0^\circ(\text{twistane}) = q_{\text{frag}} - \Delta H_{\text{frag}}(\text{twistane}), \quad (4.26)$$

in which $\Delta H_{\text{frag}}(\text{twistane})$ is the computed enthalpy change of Equation (4.25) and

$$q_{\text{frag}} = 4[\Delta_f H_0^\circ(\text{C}_4\text{H}_{10})] + 6[\Delta_f H_0^\circ(\text{C}_3\text{H}_8)] - 12\Delta_f H_0^\circ(\text{C}_2\text{H}_6). \quad (4.27)$$

The quantities q_{agg} and q_{frag} involve enthalpies of the thermochemical building blocks identified in Ref. 25. Adopting the established values $\Delta_f H_0^\circ(\text{C}_2\text{H}_6) = -16.28 \text{ kcal mol}^{-1}$,²⁸ $\Delta_f H_0^\circ(\text{C}_3\text{H}_8) = -19.63 \text{ kcal mol}^{-1}$,²⁸ and $\Delta_f H_0^\circ(\text{C}_4\text{H}_{10}) = -24.70 \text{ kcal mol}^{-1}$,²⁹ we obtain $q_{\text{agg}} = -18.4 \text{ kcal mol}^{-1}$, $q_{\text{frag}} = -21.2 \text{ kcal mol}^{-1}$, and $q_{\text{net}} = q_{\text{frag}} - q_{\text{agg}} = -2.8 \text{ kcal mol}^{-1}$. Insertion of Equation (4.26) into (4.24) provides

$$\Delta_f \bar{H}_0^\circ(\text{polytwistane}) = \frac{1}{10} \left[\Delta H_{\text{agg}}(\infty) - \Delta H_{\text{frag}}(\text{twistane}) + q_{\text{net}} \right]. \quad (4.28)$$

The merits of Equations (4.24), (4.26), and (4.28) are that $\Delta H_{\text{agg}}(\infty)$ can be computed reliably from modest levels of theory, $\Delta H_{\text{frag}}(\text{twistane})$ can be converged with high levels of theory, and the q quantities are pinpointed by precisely known enthalpies of formation.

To ascertain $\Delta H_{\text{agg}}(\infty)$, the B3LYP/6-31G(d) level of theory was employed to compute the enthalpy change $\Delta H_{\text{agg}}(m)$ of Equation (4.21) for the extended series $m = 2, 3, \dots, 24$. Highlighting the balanced nature of the aggregation, the computed $\Delta H_{\text{agg}}(m)$ values were virtually independent of m , displaying a standard deviation of only $0.04 \text{ kcal mol}^{-1}$; extrapolation²⁷ to infinite m was thus unnecessary. Given this conclusion, our final ΔH_{agg} value was taken from a higher-level single-point computation for the $m = 2$ reaction, with adoption of the B3LYP/6-31G(d) geometries and zero-point vibrational energies (ZPVEs). Specifically, the

cc-pVTZ basis set³⁰ was employed with MP2 theory, which can properly account for long-range electron correlation. By this procedure we arrive at $\Delta H_{\text{agg}}(\infty) = -3.88 \text{ kcal mol}^{-1}$. In comparison, the pure B3LYP/6-31G(d) result is $-1.73 \text{ kcal mol}^{-1}$, but after appending both dispersion (+D3)³¹ and geometrical counterpoise corrections (gCP),³² one obtains $-4.60 \text{ kcal mol}^{-1}$, in good agreement with the MP2/cc-pVTZ prediction. From $\Delta H_{\text{agg}}(\infty) = -3.88 \text{ kcal mol}^{-1}$, Equation (4.24) produces the revealing relationship

$$\Delta_f \bar{H}_0^\circ(\text{polytwistane}) = \frac{1}{10} \Delta_f H_0^\circ(\text{twistane}) + 1.45 \text{ kcal mol}^{-1}. \quad (4.29)$$

The Cartesian coordinates and electronic energies of all species involved in the computation of ΔH_{agg} are tabulated in Appendix B.

As detailed in Table B1, a focal point analysis (FPA)^{33,34,35,36,37} employing explicit computations as high as CCSD(T)/cc-pVQZ^{30,38} with extrapolation to the complete basis set limit yields the enthalpy changes $\Delta H_{\text{frag}}(\text{twistane}) = -19.49 \text{ kcal mol}^{-1}$ and hence $\Delta_f H_0^\circ(\text{twistane}) = -1.71 \text{ kcal mol}^{-1}$. These values yield the key thermochemical conclusion $\Delta_f \bar{H}_0^\circ(\text{polytwistane}) = +1.28 \text{ kcal (mol CH)}^{-1}$, from which synthetic possibilities can be assessed. For example, because $\Delta_f \bar{H}_0^\circ(\text{acetylene}) = 27.35 \text{ kcal (mol CH)}^{-1}$,²⁸ the formation of polytwistane by a hypothetical polymerization of acetylene would be accompanied by a large exothermicity of $-26 \text{ kcal mol}^{-1}$ per CH subunit. Finally, the strain energy of polytwistane $(\text{CH})_n$ can be evaluated as the enthalpy change of the homodesmotic equation



Employing our predicted $\Delta_f \bar{H}_0^\circ$ (polytwistane) and the aforementioned $\Delta_f H_0^\circ$ values for isobutane and ethane, we determine $\bar{E}_{\text{strain}}$ (polytwistane) = 1.6 kcal (mol CH)⁻¹. This very modest strain energy bodes well for the eventual synthesis of polytwistane.

4.5 CONCLUSIONS

We have provided a thorough topological and computational analysis of a new helical (C_2 symmetric) hydrocarbon (2,2) nanotube, *polytwistane*, which displays fascinating geometrical properties. Its approximate inner diameter is 2.6 Å, making it the smallest single-walled carbon nanotube considered to date. Both an idealized model and a $C_{236}H_{242}$ prototype optimized by B3LYP/6-31G(d) theory reveal that polytwistane has a nonrepeating, alternating pattern of carbon atoms in its primary helical chain. A mathematically exact double helix is also exhibited, with each strand involving every second carbon atom in the primary chain. Although azimuthal coincidence never occurs exactly in polytwistane, repetition within 0.03° is found every 3922 and 2716 carbon atoms in the primary chain of the idealized and $C_{236}H_{242}$ structures, respectively.

Our thermochemical analysis utilizing homodesmotic equations to derive the enthalpy of formation of polytwistane ($\Delta_f \bar{H}_0^\circ = +1.28$ kcal per mol of CH units) reveals that its hypothetical formation from acetylene is highly exothermic, since triple bonds are transformed into highly favorable single bonds. Polytwistane is synthetically viable on this basis and also because there are no obvious pathways for its rearrangements to lower-lying isomers such as diamondoids. Our work on polytwistane should facilitate the preparation and characterization of this fascinating new hydrocarbon nanotube, which is being actively pursued in our laboratories.¹⁴

4.6 ACKNOWLEDGEMENTS

The research at the University of Georgia was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Combustion Program, Grant No. DE-FG02-97ER1474A.

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CHAPTER 5

SUMMARY AND CONCLUSIONS

High-accuracy computations involving coupled-cluster methods in concert with series of correlation-consistent basis sets were utilized to explore the geometric structures, relative energetics, and vibrational spectra of $\text{C}(\text{BH})_2$, $\text{C}(\text{AlH})_2$ and HCNO . In Chapter 2, reliable focal point analyses (FPA) were carried out targeting the $\text{CCSDT}(\text{Q})/\text{CBS}$ limit for the ground electronic state of $\text{C}(\text{BH})_2$. Highly accurate anharmonic vibrational frequency computations precisely reproduced the experimental IR spectra for linear $\text{C}(\text{BH})_2$, and made excellent predictions for the hitherto unobserved bent isomer. With the aid of elaborate bonding analyses, linear $\text{C}(\text{BH})_2$ was described as a cumulene, while bent $\text{C}(\text{BH})_2$ was characterized as a carbene with a little carbene character. A similar FPA treatment was performed on the ground electronic state of the aluminum analogue, $\text{C}(\text{AlH})_2$. Confident predictions for the heretofore undetected bent $\text{C}(\text{AlH})_2$ were made through anharmonic frequency computations. In Chapter 3, a highly accurate and computationally demanding $\text{AE-CCSDT}(\text{Q})/\text{CBS}$ treatment was employed to predict a bent ground electronic structure for the classic quasilinear HCNO molecule lying a miniscule 0.22 cm^{-1} below the corresponding linear geometry, thus indicating an intermediate between a cumulene and a carbene model. Exhaustive investigation was carried out on the geometric structures and for the harmonic vibrational frequencies for both linear and bent HCNO , and a similarly elaborate benchmarking was pursued for the HCN molecule. Finally, a

rigorous theoretical analysis of the topology of polytwistane was performed to reveal a non-repeating, helical, carbon nanotube. Utilizing homodesmotic equations and including expensive explicit computations, the FPA treatment of the enthalpy of formation demonstrated the thermodynamic and synthetic viability of this polymer when compared to acetylene.

APPENDIX A

SUPPORTING INFORMATION FOR CHAPTER 2[†]

[†] S. R. Barua, W. D. Allen, E. Kraka, P. Jerabek, R. Sure, G. Frenking, *Chem. Eur. J.* **2013**, *19*, 15941.
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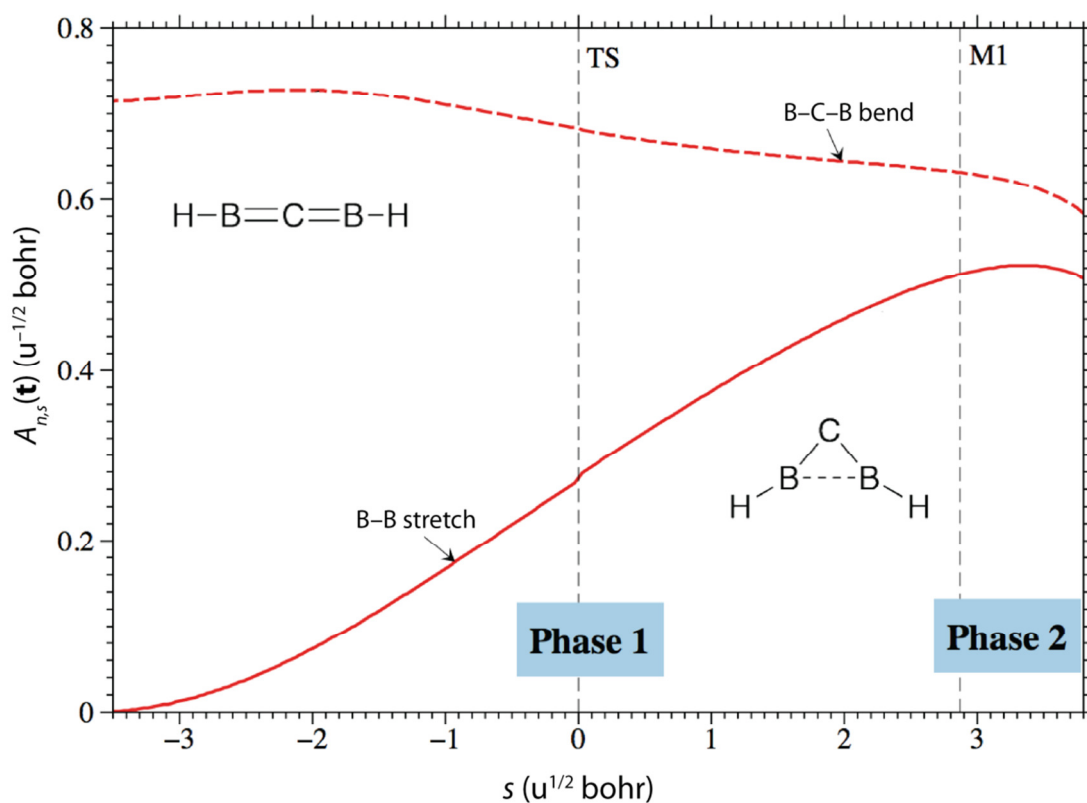


Figure A1 Reaction path direction coupling coefficients $A_{n,s}(\mathbf{t};s)$ for local modes n as a function of arc length s along the $C(BH)_2$ isomerization path. At the beginning of Phase 1, the direction is governed by the B–C–B angle; however, the B–B contribution steadily increases with s . At M1 ($s = 2.85$) both contributions become almost equal in importance. MP2/6-31G(d,p) level of theory.

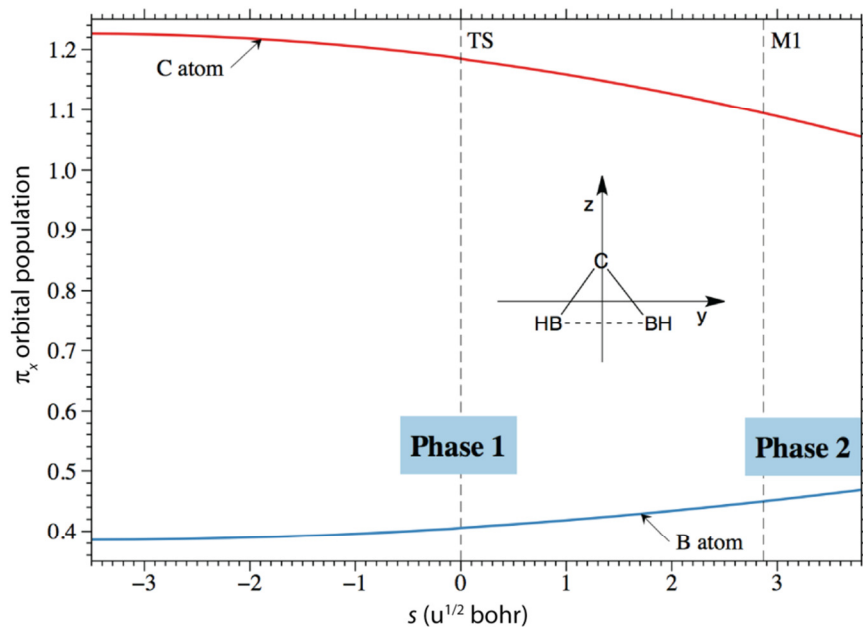


Figure A2 π_x orbital population perpendicular to the plane of bending as a function of arc length s along the $\text{C}(\text{BH})_2$ isomerization path. MP2/6-31G(d,p) level of theory.

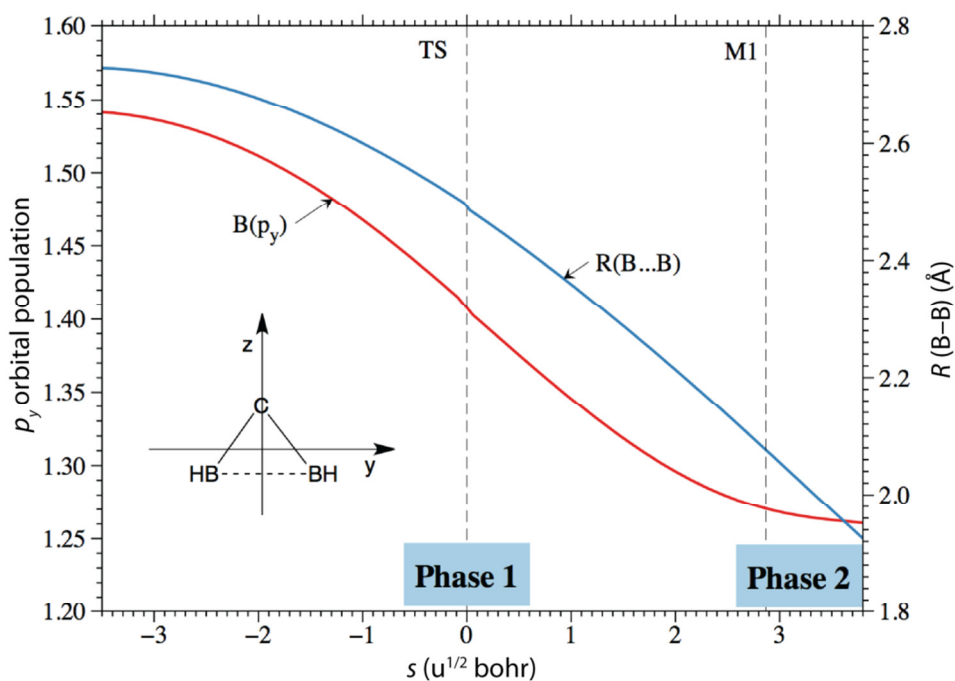


Figure A3 Boron p_y orbital population in the plane of bending as a function of arc length s along the $\text{C}(\text{BH})_2$ isomerization path. MP2/6-31G(d,p) level of theory.

Table A1 Cartesian coordinates (bohr) and total energies (E_e , hartree) of optimized structuresLinear C(BH)₂: FC-CCSD(T)/cc-pVDZ $E_e = -88.630891 E_h$

	X	Y	Z
B ₁	0.000000	0.000000	-2.608035
H ₂	0.000000	0.000000	-4.851167
C ₃	0.000000	0.000000	0.000000
B ₄	0.000000	0.000000	2.608035
H ₅	0.000000	0.000000	4.851167

Linear C(BH)₂: FC-CCSD(T)/cc-pVTZ $E_e = -88.708907 E_h$

	X	Y	Z
B ₁	0.000000	0.000000	-2.579087
H ₂	0.000000	0.000000	-4.794981
C ₃	0.000000	0.000000	0.000000
B ₄	0.000000	0.000000	2.579087
H ₅	0.000000	0.000000	4.794981

Linear C(BH)₂: FC-CCSD(T)/cc-pVQZ $E_e = -88.731962 E_h$

	X	Y	Z
B ₁	0.000000	0.000000	-2.573045
H ₂	0.000000	0.000000	-4.786745
C ₃	0.000000	0.000000	0.000000
B ₄	0.000000	0.000000	2.573045
H ₅	0.000000	0.000000	4.786745

Linear C(BH)₂: AE-CCSD(T)/cc-pCVTZ $E_e = -88.855729 E_h$

	X	Y	Z
B ₁	0.000000	0.000000	-2.572447
H ₂	0.000000	0.000000	-4.785746
C ₃	0.000000	0.000000	0.000000
B ₄	0.000000	0.000000	2.572447
H ₅	0.000000	0.000000	4.785746

Linear C(BH)₂: AE-CCSD(T)/cc-pCVQZ

$E_e = -88.889750 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	0.000000	-2.565893
H ₂	0.000000	0.000000	-4.775448
C ₃	0.000000	0.000000	0.000000
B ₄	0.000000	0.000000	2.565893
H ₅	0.000000	0.000000	4.775448

Linear C(BH)₂: Composite AE-CCSDT(Q)/cc-pCVQZ

$E_e = -88.892145 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	0.000000	-2.567650
H ₂	0.000000	0.000000	-4.777257
C ₃	0.000000	0.000000	0.000000
B ₄	0.000000	0.000000	2.567650
H ₅	0.000000	0.000000	4.777257

Bent C(BH)₂: FC-CCSD(T)/cc-pVDZ

$E_e = -88.630958 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	1.885064	-0.535504
H ₂	0.000000	3.601134	-1.991919
C ₃	0.000000	0.000000	1.317172
B ₄	0.000000	-1.885064	-0.535504
H ₅	0.000000	-3.601134	-1.991919

Bent C(BH)₂: FC-CCSD(T)/cc-pVTZ

$E_e = -88.708715 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	1.854655	-0.529800
H ₂	0.000000	3.537643	-1.977927
C ₃	0.000000	0.000000	1.304356
B ₄	0.000000	-1.854655	-0.529800
H ₅	0.000000	-3.537643	-1.977927

Bent C(BH)₂: FC-CCSD(T)/cc-pVQZ

$E_e = -88.732126 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	1.847128	-0.527794
H ₂	0.000000	3.522439	-1.982030
C ₃	0.000000	0.000000	1.301364
B ₄	0.000000	-1.847128	-0.527794
H ₅	0.000000	-3.522439	-1.982030

Bent C(BH)₂: AE-CCSD(T)/cc-pCVTZ

$E_e = -88.855627 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	1.847791	-0.528149
H ₂	0.000000	3.525118	-1.978887
C ₃	0.000000	0.000000	1.301488
B ₄	0.000000	-1.847791	-0.528149
H ₅	0.000000	-3.525118	-1.978887

Bent C(BH)₂: AE-CCSD(T)/cc-pCVQZ

$E_e = -88.889961 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	1.839050	-0.526434
H ₂	0.000000	3.506462	-1.983177
C ₃	0.000000	0.000000	1.299062
B ₄	0.000000	-1.839050	-0.526434
H ₅	0.000000	-3.506462	-1.983177

Bent C(BH)₂: Composite AE-CCSDT(Q)/cc-pCVQZ

$E_e = -88.891846 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	1.839327	-0.527154
H ₂	0.000000	3.507007	-1.983908
C ₃	0.000000	0.000000	1.300506
B ₄	0.000000	-1.839327	-0.527154
H ₅	0.000000	-3.507007	-1.983908

Isomerization transition state of C(BH)₂: FC-CCSD(T)/cc-pVDZ
 $E_e = -88.627137 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	2.330765	-0.342649
H ₂	0.000000	4.357648	-1.312079
C ₃	0.000000	0.000000	0.849113
B ₄	0.000000	-2.330765	-0.342649
H ₅	0.000000	-4.357648	-1.312079

Isomerization transition state of C(BH)₂: FC-CCSD(T)/cc-pVTZ
 $E_e = -88.705161 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	2.292760	-0.344374
H ₂	0.000000	4.284735	-1.319126
C ₃	0.000000	0.000000	0.853461
B ₄	0.000000	-2.292760	-0.344374
H ₅	0.000000	-4.284735	-1.319126

Isomerization transition state of C(BH)₂: FC-CCSD(T)/cc-pVQZ
 $E_e = -88.728532 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	2.290135	-0.340661
H ₂	0.000000	4.279930	-1.315513
C ₃	0.000000	0.000000	0.846041
B ₄	0.000000	-2.290135	-0.340661
H ₅	0.000000	-4.279930	-1.315513

Isomerization transition state of C(BH)₂: AE-CCSD(T)/cc-pCVTZ
 $E_e = -88.852057 E_h$

	<i>X</i>	<i>Y</i>	<i>Z</i>
B ₁	0.000000	2.285944	-0.343201
H ₂	0.000000	4.273070	-1.321999
C ₃	0.000000	0.000000	0.851792
B ₄	0.000000	-2.285944	-0.343201
H ₅	0.000000	-4.273070	-1.321999

Isomerization transition state of C(BH)₂: AE-CCSD(T)/cc-pCVQZ

$E_e = -88.886283 E_h$

	X	Y	Z
B ₁	0.000000	2.282781	-0.339631
H ₂	0.000000	4.266442	-1.317494
C ₃	0.000000	0.000000	0.844485
B ₄	0.000000	-2.282781	-0.339631
H ₅	0.000000	-4.266442	-1.317494

Table A2 Single-point energies (in hartree) at FC-CCSD(T)/cc-pVQZ geometriesLinear C(BH)₂

	RHF	MP2	CCSD	CCSD(T)	CCSDT(Q)
cc-pVDZ	-88.3132407	-88.5920823	-88.6126097	-88.6299347	-88.6323430
cc-pVTZ	-88.3352277	-88.6707104	-88.6864072	-88.7088848	-88.7112476
cc-pVQZ	-88.3407336	-88.6970542	-88.7081098	-88.7319618	[-88.7343246]
cc-pV5Z	-88.3417666	-88.7060480	-88.7140881	-88.7383942	[-88.7407570]
cc-pV6Z	-88.3419129	-88.7098672	-88.7162161	-88.7406849	[-88.7430477]
CBS LIMIT	[-88.3419370]	[-88.7149364]	[-88.7189624]	[-88.7436546]	[-88.7460174]

Bent C(BH)₂

	RHF	MP2	CCSD	CCSD(T)	CCSDT(Q)
cc-pVDZ	-88.3078085	-88.5909750	-88.6136713	-88.6296731	-88.6315709
cc-pVTZ	-88.3289059	-88.6699987	-88.6873217	-88.7086727	-88.7105045
cc-pVQZ	-88.3345136	-88.6967309	-88.7093896	-88.7321260	[-88.7339577]
cc-pV5Z	-88.3355593	-88.7059820	-88.7156056	-88.7388122	[-88.7406439]
cc-pV6Z	-88.3357113	-88.7098450	-88.7177779	-88.7411494	[-88.7429812]
CBS LIMIT	[-88.3357371]	[-88.7149684]	[-88.7205789]	[-88.7441770]	[-88.7460088]

Isomerization transition state of C(BH)₂

	RHF	MP2	CCSD	CCSD(T)	CCSDT(Q)
cc-pVDZ	-88.3101997	-88.5875990	-88.6097036	-88.6260622	-88.6281778
cc-pVTZ	-88.3317608	-88.6665052	-88.6835538	-88.7051314	-88.7071757
cc-pVQZ	-88.3373887	-88.6931412	-88.7055958	-88.7285316	[-88.7305760]
cc-pV5Z	-88.3384175	-88.7022853	-88.7117204	-88.7351155	[-88.7371599]
cc-pV6Z	-88.3385653	-88.7061351	-88.7138816	-88.7374385	[-88.7394829]
CBS LIMIT	[-88.3385901]	[-88.7112452]	[-88.7166721]	[-88.7404513]	[-88.7424956]

Dissociated products C(³P) + 2 BH(¹Σ⁺)

	RHF	CCSD	CCSD(T)	CCSDT(Q)
cc-pVDZ	-87.9372124	-88.1860622	-88.1896984	-88.1909577
cc-pVTZ	-87.9514205	-88.2358838	-88.2419883	-88.2434878
cc-pVQZ	-87.9558819	-88.2498771	-88.2566675	[-88.2581670]
cc-pV5Z	-87.9567724	-88.2536379	-88.2606607	[-88.2621602]
cc-pV6Z	-87.9569555	-88.2549135	-88.2620175	[-88.2635170]
CBS LIMIT	[-87.9570028]	[-88.2564618]	[-88.2636773]	[-88.2651767]

Table A3 AE-CCSD(T)/cc-pCVQZ harmonic vibrational frequencies (ω , cm^{-1}) for 12 isotopologues of linear $\text{C}(\text{BH})_2$

	$\omega_3(\sigma_u^+)$	$\omega_1(\sigma_g^+)$	$\omega_4(\sigma_u^+)$	$\omega_2(\sigma_g^+)$	$\omega_5(\pi_g)$	$\omega_6(\pi_u)$	$\omega_7(\pi_u)$
$\text{H}^{11}\text{B}^{12}\text{C}^{11}\text{BH}$	2858.1	2845.5	1913.0	1126.0	755.7	737.5	154.3
$\text{H}^{10}\text{B}^{12}\text{C}^{11}\text{BH}$	2872.6	2849.6	1924.9	1150.1	761.1	740.7	155.0
$\text{H}^{10}\text{B}^{12}\text{C}^{10}\text{BH}$	2877.9	2862.7	1936.2	1174.1	764.7	745.7	155.6
$\text{H}^{11}\text{B}^{13}\text{C}^{11}\text{BH}$	2856.5	2845.6	1864.1	1126.4	755.7	735.0	150.8
$\text{H}^{10}\text{B}^{13}\text{C}^{11}\text{BH}$	2871.1	2849.2	1876.7	1150.0	761.0	738.2	151.5
$\text{H}^{10}\text{B}^{13}\text{C}^{10}\text{BH}$	2875.9	2862.7	1888.5	1174.1	764.7	743.2	152.2
$\text{D}^{11}\text{B}^{12}\text{C}^{11}\text{BD}$	2255.4	2147.5	1762.0	1055.8	595.3	598.9	138.1
$\text{D}^{10}\text{B}^{12}\text{C}^{11}\text{BD}$	2278.9	2159.7	1764.2	1073.9	596.9	608.1	138.4
$\text{D}^{10}\text{B}^{12}\text{C}^{10}\text{BD}$	2296.8	2177.5	1766.2	1091.9	606.7	609.1	138.7
$\text{D}^{11}\text{B}^{13}\text{C}^{11}\text{BD}$	2239.5	2147.5	1727.1	1055.8	595.3	595.6	135.2
$\text{D}^{10}\text{B}^{13}\text{C}^{11}\text{BD}$	2262.9	2159.4	1730.0	1073.8	595.4	606.2	135.5
$\text{D}^{10}\text{B}^{13}\text{C}^{10}\text{BD}$	2280.0	2177.5	1732.8	1091.9	606.7	605.8	135.8

Table A4 AE-CCSD(T)/cc-pCVQZ harmonic vibrational frequencies (ω , cm^{-1}) for 12 isotopologues of bent $\text{C}(\text{BH})_2$

	$\omega_1(a_1)$	$\omega_7(b_2)$	$\omega_8(b_2)$	$\omega_2(a_1)$	$\omega_9(b_2)$	$\omega_3(a_1)$	$\omega_5(a_2)$	$\omega_6(b_1)$	$\omega_4(a_1)$
$\text{H}^{11}\text{B}^{12}\text{C}^{11}\text{BH}$	2823.6	2822.7	1550.7	1432.0	799.3	774.6	786.2	732.2	320.3
$\text{H}^{10}\text{B}^{12}\text{C}^{11}\text{BH}$	2840.7	2823.2	1568.2	1445.5	805.1	778.8	791.4	735.6	324.6
$\text{H}^{10}\text{B}^{12}\text{C}^{10}\text{BH}$	2840.9	2840.5	1581.7	1462.9	809.1	784.7	795.9	739.8	328.8
$\text{H}^{11}\text{B}^{13}\text{C}^{11}\text{BH}$	2823.3	2822.3	1520.4	1405.9	799.0	774.0	786.2	730.0	318.1
$\text{H}^{10}\text{B}^{13}\text{C}^{11}\text{BH}$	2840.2	2822.8	1538.5	1419.6	804.7	778.2	791.4	733.5	322.3
$\text{H}^{10}\text{B}^{13}\text{C}^{10}\text{BH}$	2840.4	2839.9	1552.2	1437.6	808.8	784.0	795.9	737.7	326.4
$\text{D}^{11}\text{B}^{12}\text{C}^{11}\text{BD}$	2145.3	2157.2	1465.6	1359.4	634.0	626.9	621.6	587.5	282.2
$\text{D}^{10}\text{B}^{12}\text{C}^{11}\text{BD}$	2150.0	2185.4	1474.5	1368.0	643.9	630.3	628.5	591.4	284.6
$\text{D}^{10}\text{B}^{12}\text{C}^{10}\text{BD}$	2176.9	2191.4	1482.1	1378.1	646.2	641.4	633.8	597.0	287.0
$\text{D}^{11}\text{B}^{13}\text{C}^{11}\text{BD}$	2143.0	2153.6	1437.9	1334.7	633.6	626.0	621.6	584.8	280.4
$\text{D}^{10}\text{B}^{13}\text{C}^{11}\text{BD}$	2147.3	2181.8	1447.6	1343.7	643.4	629.5	628.5	588.8	282.8
$\text{D}^{10}\text{B}^{13}\text{C}^{10}\text{BD}$	2174.3	2187.3	1455.6	1354.3	645.8	640.4	633.8	594.3	285.2

Table A5 Composite AE-CCSDT(Q)/cc-pCVQZ harmonic vibrational frequencies (ω , cm⁻¹) for 12 isotopologues of linear C(BH)₂

	$\omega_3(\sigma_u^+)$	$\omega_1(\sigma_g^+)$	$\omega_4(\sigma_u^+)$	$\omega_2(\sigma_g^+)$	$\omega_5(\pi_g)$	$\omega_6(\pi_u)$	$\omega_7(\pi_u)$
H ¹¹ B ¹² C ¹¹ BH	2856.7	2844.3	1904.8	1122.5	752.0	733.1	157.5
H ¹⁰ B ¹² C ¹¹ BH	2871.1	2848.3	1916.7	1146.0	757.4	736.2	158.2
H ¹⁰ B ¹² C ¹⁰ BH	2876.4	2861.3	1928.0	1170.0	761.0	741.1	158.8
H ¹¹ B ¹³ C ¹¹ BH	2855.2	2844.3	1856.1	1122.5	752.0	730.5	153.9
H ¹⁰ B ¹³ C ¹¹ BH	2869.7	2847.9	1868.7	1146.0	757.3	733.8	154.6
H ¹⁰ B ¹³ C ¹⁰ BH	2874.5	2861.3	1880.5	1170.0	761.0	738.6	155.3
D ¹¹ B ¹² C ¹¹ BD	2251.2	2146.0	1756.9	1052.4	592.4	595.3	141.0
D ¹⁰ B ¹² C ¹¹ BD	2274.6	2158.1	1759.1	1070.4	593.8	604.7	141.2
D ¹⁰ B ¹² C ¹⁰ BD	2292.3	2175.8	1761.2	1088.4	603.8	605.4	141.5
D ¹¹ B ¹³ C ¹¹ BD	2235.7	2146.0	1721.7	1052.4	592.4	592.0	138.0
D ¹⁰ B ¹³ C ¹¹ BD	2259.0	2157.7	1724.7	1070.3	603.0	592.2	138.3
D ¹⁰ B ¹³ C ¹⁰ BD	2276.0	2175.8	1727.6	1088.4	603.8	602.1	138.6

Table A6 Composite AE-CCSDT(Q)/cc-pCVQZ harmonic vibrational frequencies (ω , cm⁻¹) for 12 isotopologues of bent C(BH)₂

	$\omega_1(a_1)$	$\omega_7(b_2)$	$\omega_8(b_2)$	$\omega_2(a_1)$	$\omega_9(b_2)$	$\omega_3(a_1)$	$\omega_5(a_2)$	$\omega_6(b_1)$	$\omega_4(a_1)$
H ¹¹ B ¹² C ¹¹ BH	2821.8	2820.9	1544.9	1427.8	797.2	772.4	783.8	729.1	317.8
H ¹⁰ B ¹² C ¹¹ BH	2838.8	2821.4	1562.4	1441.3	802.9	776.6	788.8	732.7	322.1
H ¹⁰ B ¹² C ¹⁰ BH	2839.0	2838.6	1575.8	1458.7	807.0	782.5	793.1	737.0	326.2
H ¹¹ B ¹³ C ¹¹ BH	2821.4	2820.4	1514.8	1401.8	796.9	771.8	783.8	726.7	315.6
H ¹⁰ B ¹³ C ¹¹ BH	2838.3	2820.9	1532.8	1415.5	802.6	776.0	788.8	730.4	319.8
H ¹⁰ B ¹³ C ¹⁰ BH	2838.6	2838.0	1546.4	1433.5	806.6	781.8	793.1	734.6	323.9
D ¹¹ B ¹² C ¹¹ BD	2143.3	2154.9	1460.7	1355.9	632.3	624.7	617.1	588.9	280.1
D ¹⁰ B ¹² C ¹¹ BD	2147.9	2183.0	1469.7	1364.4	642.0	628.2	624.0	592.8	282.6
D ¹⁰ B ¹² C ¹⁰ BD	2174.7	2188.9	1477.3	1374.5	644.5	639.1	628.9	598.6	284.9
D ¹¹ B ¹³ C ¹¹ BD	2141.1	2151.4	1433.1	1331.2	631.9	623.8	617.1	585.9	278.4
D ¹⁰ B ¹³ C ¹¹ BD	2145.2	2179.5	1442.8	1340.1	641.5	627.4	623.9	589.9	280.8
D ¹⁰ B ¹³ C ¹⁰ BD	2172.2	2184.9	1450.8	1350.8	644.0	638.1	628.9	595.7	283.1

Table A7 FC-CCSD(T)/cc-pVTZ anharmonic vibrational frequencies (ν_i , cm^{-1}) for 12 isotopologues of linear $\text{C}(\text{BH})_2$

	$\nu_3(\sigma_u^+)$	$\nu_1(\sigma_g^+)$	$\nu_4(\sigma_u^+)$	$\nu_2(\sigma_g^+)$	$\nu_5(\pi_g)$	$\nu_6(\pi_u)$	$\nu_7(\pi_u)$
$\text{H}^{11}\text{B}^{12}\text{C}^{11}\text{BH}$	2744.0	2733.9	1874.0	1113.2	746.0	723.2	150.8
$\text{H}^{10}\text{B}^{12}\text{C}^{11}\text{BH}$	2757.8	2737.5	1885.9	1135.4	750.7	726.0	151.3
$\text{H}^{10}\text{B}^{12}\text{C}^{10}\text{BH}$	2762.9	2749.9	1897.2	1158.1	754.8	731.0	151.7
$\text{H}^{11}\text{B}^{13}\text{C}^{11}\text{BH}$	2741.5	2733.9	1827.4	1112.0	746.1	720.8	147.5
$\text{H}^{10}\text{B}^{13}\text{C}^{11}\text{BH}$	2755.9	2737.1	1839.9	1134.3	750.7	723.8	148.0
$\text{H}^{10}\text{B}^{13}\text{C}^{10}\text{BH}$	2760.5	2749.9	1851.7	1157.0	754.8	728.7	148.6
$\text{D}^{11}\text{B}^{12}\text{C}^{11}\text{BD}$	2187.9	2084.4	1727.1	1033.7	588.2	586.4	136.6
$\text{D}^{10}\text{B}^{12}\text{C}^{11}\text{BD}$	2210.3	2093.7	1729.5	1048.7	595.4	584.7	136.8
$\text{D}^{10}\text{B}^{12}\text{C}^{10}\text{BD}$	2227.6	2110.4	1731.8	1063.5	599.4	596.3	136.9
$\text{D}^{11}\text{B}^{13}\text{C}^{11}\text{BD}$	2172.1	2084.4	1694.2	1032.7	588.2	583.3	133.8
$\text{D}^{10}\text{B}^{13}\text{C}^{11}\text{BD}$	2194.4	2093.4	1697.4	1047.7	594.9	583.1	134.0
$\text{D}^{10}\text{B}^{13}\text{C}^{10}\text{BD}$	2210.9	2110.4	1700.4	1062.5	599.4	593.2	134.2

Resonance threshold: 25 cm^{-1}

Table A8 FC-CCSD(T)/cc-pVTZ anharmonic vibrational frequencies (ν_i , cm^{-1}) for 12 isotopologues of bent $\text{C}(\text{BH})_2$

	$\nu_1(a_1)$	$\nu_7(b_2)$	$\nu_8(b_2)$	$\nu_2(a_1)$	$\nu_9(b_2)$	$\nu_3(a_1)$	$\nu_5(a_2)$	$\nu_6(b_1)$	$\nu_4(a_1)$
$\text{H}^{11}\text{B}^{12}\text{C}^{11}\text{BH}$	2708.0	2704.0	1525.2	1386.3	784.8	765.8	769.5	715.9	287.0
$\text{H}^{10}\text{B}^{12}\text{C}^{11}\text{BH}$	2720.0	2703.4	1539.4	1399.1	790.5	769.9	774.3	719.4	290.4
$\text{H}^{10}\text{B}^{12}\text{C}^{10}\text{BH}$	2720.9	2720.8	1554.6	1414.9	794.2	776.0	778.4	723.5	293.7
$\text{H}^{11}\text{B}^{13}\text{C}^{11}\text{BH}$	2712.1	2701.7	1477.8	1359.4	784.5	765.0	769.5	713.6	284.9
$\text{H}^{10}\text{B}^{13}\text{C}^{11}\text{BH}$	2720.8	2705.4	1492.2	1371.4	790.2	769.1	774.2	717.1	288.3
$\text{H}^{10}\text{B}^{13}\text{C}^{10}\text{BH}$	2723.6	2719.3	1503.8	1392.0	793.9	775.1	778.4	721.2	291.6
$\text{D}^{11}\text{B}^{12}\text{C}^{11}\text{BD}$	2076.5	2089.1	1440.3	1333.1	623.0	623.9	606.2	578.0	257.4
$\text{D}^{10}\text{B}^{12}\text{C}^{11}\text{BD}$	2081.5	2115.4	1450.2	1343.2	634.5	625.3	612.8	581.9	259.4
$\text{D}^{10}\text{B}^{12}\text{C}^{10}\text{BD}$	2106.3	2121.8	1458.5	1354.9	634.8	637.8	617.6	587.5	261.4
$\text{D}^{11}\text{B}^{13}\text{C}^{11}\text{BD}$	2074.3	2085.2	1414.6	1312.8	622.6	622.5	606.2	575.2	255.7
$\text{D}^{10}\text{B}^{13}\text{C}^{11}\text{BD}$	2078.7	2111.6	1425.4	1323.9	633.8	624.2	612.7	579.1	257.7
$\text{D}^{10}\text{B}^{13}\text{C}^{10}\text{BD}$	2103.8	2117.4	1434.2	1336.5	634.4	636.4	617.6	584.7	259.7

Resonance threshold: 25 cm^{-1}

Table A9 AE-CCSD(T)/cc-pCVQZ anharmonic vibrational frequencies (ν_i , cm^{-1}) for 12 isotopologues of linear $\text{C}(\text{BH})_2$

	$\nu_3(\sigma_u^+)$	$\nu_1(\sigma_g^+)$	$\nu_4(\sigma_u^+)$	$\nu_2(\sigma_g^+)$	$\nu_5(\pi_g)$	$\nu_6(\pi_u)$	$\nu_7(\pi_u)$
$\text{H}^{11}\text{B}^{12}\text{C}^{11}\text{BH}$	2753.8	2744.5	1884.1	1123.0	754.1	735.8	149.0
$\text{H}^{10}\text{B}^{12}\text{C}^{11}\text{BH}$	2767.9	2748.0	1896.0	1145.4	758.7	738.2	149.5
$\text{H}^{10}\text{B}^{12}\text{C}^{10}\text{BH}$	2772.8	2760.6	1907.3	1168.2	763.0	743.8	150.0
$\text{H}^{11}\text{B}^{13}\text{C}^{11}\text{BH}$	2751.4	2744.6	1837.2	1121.7	754.1	733.3	145.7
$\text{H}^{10}\text{B}^{13}\text{C}^{11}\text{BH}$	2766.0	2747.5	1849.8	1144.1	758.7	735.9	146.2
$\text{H}^{10}\text{B}^{13}\text{C}^{10}\text{BH}$	2770.4	2760.6	1861.6	1167.1	763.0	741.3	146.8
$\text{D}^{11}\text{B}^{12}\text{C}^{11}\text{BD}$	2198.0	2093.4	1735.3	1043.0	594.3	597.4	133.6
$\text{D}^{10}\text{B}^{12}\text{C}^{11}\text{BD}$	2220.5	2102.4	1737.6	1058.3	593.3	604.1	133.8
$\text{D}^{10}\text{B}^{12}\text{C}^{10}\text{BD}$	2237.8	2119.2	1739.8	1073.3	605.7	607.5	134.0
$\text{D}^{11}\text{B}^{13}\text{C}^{11}\text{BD}$	2181.9	2093.4	1702.3	1041.9	594.3	594.1	130.8
$\text{D}^{10}\text{B}^{13}\text{C}^{11}\text{BD}$	2204.4	2102.0	1705.5	1057.2	602.2	591.6	131.0
$\text{D}^{10}\text{B}^{13}\text{C}^{10}\text{BD}$	2221.0	2119.2	1708.5	1072.2	605.7	604.3	131.2

Resonance threshold: 25 cm^{-1}

Table A10 AE-CCSD(T)/cc-pCVQZ anharmonic vibrational frequencies (ν_i , cm^{-1}) for 12 isotopologues of bent $\text{C}(\text{BH})_2$

	$\nu_1(a_1)$	$\nu_7(b_2)$	$\nu_8(b_2)$	$\nu_2(a_1)$	$\nu_9(b_2)$	$\nu_3(a_1)$	$\nu_5(a_2)$	$\nu_6(b_1)$	$\nu_4(a_1)$
$\text{H}^{11}\text{B}^{12}\text{C}^{11}\text{BH}$	2716.6	2717.4	1543.1	1400.0	790.4	770.6	777.3	725.2	292.1
$\text{H}^{10}\text{B}^{12}\text{C}^{11}\text{BH}$	2734.3	2717.5	1556.6	1410.7	796.1	774.9	782.1	728.8	295.6
$\text{H}^{10}\text{B}^{12}\text{C}^{10}\text{BH}$	2734.7	2734.4	1571.6	1433.3	799.9	781.1	786.3	732.9	298.9
$\text{H}^{11}\text{B}^{13}\text{C}^{11}\text{BH}$	2720.4	2715.6	1491.7	1377.6	790.1	769.9	777.3	722.9	290.1
$\text{H}^{10}\text{B}^{13}\text{C}^{11}\text{BH}$	2734.2	2718.8	1506.4	1389.9	795.8	774.1	782.1	726.4	293.5
$\text{H}^{10}\text{B}^{13}\text{C}^{10}\text{BH}$	2731.0	2733.0	1518.1	1405.1	799.5	780.3	786.3	730.6	296.8
$\text{D}^{11}\text{B}^{12}\text{C}^{11}\text{BD}$	2100.3	2087.4	1453.1	1349.7	628.0	630.0	613.2	586.5	261.2
$\text{D}^{10}\text{B}^{12}\text{C}^{11}\text{BD}$	2092.5	2126.9	1463.1	1359.8	640.0	631.2	619.9	590.3	263.3
$\text{D}^{10}\text{B}^{12}\text{C}^{10}\text{BD}$	2117.5	2133.4	1471.4	1371.5	640.0	644.1	624.7	596.1	265.3
$\text{D}^{11}\text{B}^{13}\text{C}^{11}\text{BD}$	2085.1	2096.2	1427.4	1329.0	627.6	628.5	613.2	583.5	259.6
$\text{D}^{10}\text{B}^{13}\text{C}^{11}\text{BD}$	2089.6	2123.0	1438.2	1340.0	639.2	630.0	619.8	587.5	261.6
$\text{D}^{10}\text{B}^{13}\text{C}^{10}\text{BD}$	2114.9	2128.8	1447.0	1352.7	639.5	642.6	624.7	593.2	263.6

Resonance threshold: 25 cm^{-1}

Table A11 Composite AE-CCSDT(Q)/cc-pCVQZ anharmonic vibrational frequencies (ν_i , cm^{-1}) for 12 isotopologues of linear $\text{C}(\text{BH})_2$

	$\nu_3(\sigma_u^+)$	$\nu_1(\sigma_g^+)$	$\nu_4(\sigma_u^+)$	$\nu_2(\sigma_g^+)$	$\nu_5(\pi_g)$	$\nu_6(\pi_u)$	$\nu_7(\pi_u)$
$\text{H}^{11}\text{B}^{12}\text{C}^{11}\text{BH}$	2751.9	2743.1	1875.3	1119.0	750.6	731.6	152.5
$\text{H}^{10}\text{B}^{12}\text{C}^{11}\text{BH}$	2766.0	2746.4	1887.2	1141.3	755.2	734.1	153.0
$\text{H}^{10}\text{B}^{12}\text{C}^{10}\text{BH}$	2770.8	2759.1	1898.5	1164.1	759.5	739.6	153.5
$\text{H}^{11}\text{B}^{13}\text{C}^{11}\text{BH}$	2749.4	2743.1	1828.6	1117.7	750.6	729.1	149.1
$\text{H}^{10}\text{B}^{13}\text{C}^{11}\text{BH}$	2764.1	2746.0	1841.2	1140.1	755.2	731.8	149.6
$\text{H}^{10}\text{B}^{13}\text{C}^{10}\text{BH}$	2768.4	2759.1	1853.0	1162.9	759.5	737.1	150.2
$\text{D}^{11}\text{B}^{12}\text{C}^{11}\text{BD}$	2193.4	2091.6	1729.8	1039.4	591.5	594.0	136.7
$\text{D}^{10}\text{B}^{12}\text{C}^{11}\text{BD}$	2215.8	2100.7	1732.3	1054.6	590.1	600.8	136.9
$\text{D}^{10}\text{B}^{12}\text{C}^{10}\text{BD}$	2232.9	2117.5	1734.6	1069.6	602.8	604.1	137.1
$\text{D}^{11}\text{B}^{13}\text{C}^{11}\text{BD}$	2177.8	2091.6	1696.7	1038.3	591.5	590.7	133.8
$\text{D}^{10}\text{B}^{13}\text{C}^{11}\text{BD}$	2200.1	2100.4	1699.9	1053.5	599.1	588.5	134.0
$\text{D}^{10}\text{B}^{13}\text{C}^{10}\text{BD}$	2216.5	2117.5	17023.0	1068.5	602.8	600.8	134.2

Resonance threshold: 25 cm^{-1}

Table A12 Composite AE-CCSDT(Q)/cc-pCVQZ anharmonic vibrational frequencies (ν_i , cm^{-1}) for 12 isotopologues of bent $\text{C}(\text{BH})_2$

	$\nu_1(a_1)$	$\nu_7(b_2)$	$\nu_8(b_2)$	$\nu_2(a_1)$	$\nu_9(b_2)$	$\nu_3(a_1)$	$\nu_5(a_2)$	$\nu_6(b_1)$	$\nu_4(a_1)$
$\text{H}^{11}\text{B}^{12}\text{C}^{11}\text{BH}$	2713.6	2715.1	1537.0	1395.4	788.3	768.4	775.0	722.4	288.6
$\text{H}^{10}\text{B}^{12}\text{C}^{11}\text{BH}$	2731.8	2715.1	1550.6	1412.8	794.0	772.6	779.9	726.0	292.0
$\text{H}^{10}\text{B}^{12}\text{C}^{10}\text{BH}$	2732.3	2732.0	1565.5	1428.8	797.8	778.8	784.0	730.1	295.3
$\text{H}^{11}\text{B}^{13}\text{C}^{11}\text{BH}$	2718.2	2713.1	1486.1	1373.3	788.0	767.6	775.0	720.1	286.6
$\text{H}^{10}\text{B}^{13}\text{C}^{11}\text{BH}$	2731.8	2716.6	1501.0	1385.5	793.7	771.8	779.8	723.6	289.9
$\text{H}^{10}\text{B}^{13}\text{C}^{10}\text{BH}$	2727.4	2730.6	1512.7	1400.5	797.4	777.9	784.0	727.8	293.2
$\text{D}^{11}\text{B}^{12}\text{C}^{11}\text{BD}$	2085.2	2097.7	1448.0	1345.6	626.3	627.5	611.4	584.2	258.4
$\text{D}^{10}\text{B}^{12}\text{C}^{11}\text{BD}$	2090.2	2124.2	1458.0	1355.7	637.9	629.0	618.0	588.0	260.5
$\text{D}^{10}\text{B}^{12}\text{C}^{10}\text{BD}$	2115.2	2130.6	1466.3	1367.3	638.2	641.6	622.8	593.7	262.4
$\text{D}^{11}\text{B}^{13}\text{C}^{11}\text{BD}$	2082.9	2093.7	1422.3	1324.8	625.9	626.1	611.4	581.2	256.8
$\text{D}^{10}\text{B}^{13}\text{C}^{11}\text{BD}$	2087.3	2120.4	1433.2	1335.8	637.1	627.9	617.9	585.2	258.8
$\text{D}^{10}\text{B}^{13}\text{C}^{10}\text{BD}$	2112.6	2126.1	1442.0	1348.5	637.8	640.1	622.8	590.8	260.7

Resonance threshold: 25 cm^{-1}

Table A13 AE-CCSD(T)/cc-pCVQZ harmonic IR intensities (I_i , km mol⁻¹) for 12 isotopologues of linear C(BH)₂

	$I_3(\sigma_u^+)$	$I_1(\sigma_g^+)$	$I_4(\sigma_u^+)$	$I_2(\sigma_g^+)$	$I_5(\pi_g)$	$I_6(\pi_u)$	$I_7(\pi_u)$
H ¹¹ B ¹² C ¹¹ BH	139.7	0	439.9	0	0	29.3	37.1
H ¹⁰ B ¹² C ¹¹ BH	123.1	26.2	441.3	0.09	1.6	28.7	37.3
H ¹⁰ B ¹² C ¹⁰ BH	158.9	0	442.9	0	0	31.3	37.6
H ¹¹ B ¹³ C ¹¹ B H	133.0	0	420.5	0	0	27.9	35.5
H ¹⁰ B ¹³ C ¹¹ BH	113.7	28.3	422.5	0.1	1.3	27.6	35.7
H ¹⁰ B ¹³ C ¹⁰ BH	151.0	0	424.6	0	0	29.9	36.0
D ¹¹ B ¹² C ¹¹ BD	368.8	0	201.3	0	0	36.6	28.8
D ¹⁰ B ¹² C ¹¹ BD	378.4	6.5	196.2	0.04	13.3	24.5	28.9
D ¹⁰ B ¹² C ¹⁰ BD	400.8	0	191.4	0	0	39.0	28.9
D ¹¹ B ¹³ C ¹¹ BD	331.5	0	212.4	0	0	34.8	27.7
D ¹⁰ B ¹³ C ¹¹ BD	340.1	7.7	207.1	0.05	17.9	18.0	27.7
D ¹⁰ B ¹³ C ¹⁰ BD	363.9	0	202.1	0	0	37.1	27.8

Table A14 AE-CCSD(T)/cc-pCVQZ harmonic IR intensities (I_i , km mol⁻¹) for 12 isotopologues of bent C(BH)₂

	$I_1(a_1)$	$I_7(b_2)$	$I_8(b_2)$	$I_2(a_1)$	$I_9(b_2)$	$I_3(a_1)$	$I_5(a_2)$	$I_6(b_1)$	$I_4(a_1)$
H ¹¹ B ¹² C ¹¹ BH	12.0	52.3	85.1	11.9	11.0	3.2	0	2.6	0.03
H ¹⁰ B ¹² C ¹¹ BH	34.1	33.0	84.4	13.3	11.2	3.4	0.03	2.7	0.03
H ¹⁰ B ¹² C ¹⁰ BH	13.0	56.9	85.8	12.4	11.9	3.3	0	2.9	0.02
H ¹¹ B ¹³ C ¹¹ B H	11.9	51.5	80.9	11.7	11.1	3.1	0	2.4	0.03
H ¹⁰ B ¹³ C ¹¹ BH	33.5	32.7	80.1	13.1	11.3	3.4	0.03	2.5	0.02
H ¹⁰ B ¹³ C ¹⁰ BH	12.9	56.0	81.6	12.2	12.0	3.2	0	2.7	0.02
D ¹¹ B ¹² C ¹¹ BD	13.6	69.7	58.0	8.0	9.8	2.2	0	5.0	0.00
D ¹⁰ B ¹² C ¹¹ BD	30.8	57.1	56.3	8.3	8.2	4.3	0.1	5.1	0.00
D ¹⁰ B ¹² C ¹⁰ BD	15.1	77.5	55.5	7.9	10.7	2.3	0	5.4	0.00
D ¹¹ B ¹³ C ¹¹ BD	13.3	66.6	56.0	7.9	9.8	2.2	0	4.6	0.00
D ¹⁰ B ¹³ C ¹¹ BD	30.5	53.9	54.5	8.3	8.3	4.2	0.1	4.7	0.00
D ¹⁰ B ¹³ C ¹⁰ BD	14.8	74.1	53.8	7.8	10.7	2.3	0	5.1	0.00

Table A15 FC-CCSD(T)/cc-pV(T+d)Z harmonic vibrational frequencies (ω_i , cm^{-1}) for 6 isotopologues of bent $\text{C}(\text{AlH})_2$

	$\omega_1(a_1)$	$\omega_7(b_2)$	$\omega_8(b_2)$	$\omega_2(a_1)$	$\omega_9(b_2)$	$\omega_3(a_1)$	$\omega_5(a_2)$	$\omega_6(b_1)$	$\omega_4(a_1)$
$\text{HAl}^{12}\text{CAIH}$	1947.2	1939.5	942.4	767.1	427.0	467.8	416.8	385.5	221.3
$\text{HAl}^{13}\text{CAIH}$	1947.2	1939.5	915.6	748.1	426.9	467.7	416.8	384.8	219.7
$\text{DAI}^{12}\text{CAID}$	1408.4	1402.8	934.0	759.0	321.5	358.3	314.0	289.6	205.0
$\text{DAI}^{13}\text{CAID}$	1408.3	1402.4	907.4	740.0	321.4	358.0	314.0	288.7	203.6
$\text{HAl}^{12}\text{CAID}$	1943.4	1405.6	938.3	763.0	337.6	450.3	403.1	299.9	212.7
$\text{HAl}^{13}\text{CAID}$	1943.4	1405.3	911.6	743.9	337.3	450.2	402.9	299.3	211.2

Table A16 FC-CCSD(T)/cc-pV(T+d)Z anharmonic vibrational frequencies (ν_i , cm^{-1}) for 6 isotopologues of bent $\text{C}(\text{AlH})_2$

	$\nu_1(a_1)$	$\nu_7(b_2)$	$\nu_8(b_2)$	$\nu_2(a_1)$	$\nu_9(b_2)$	$\nu_3(a_1)$	$\nu_5(a_2)$	$\nu_6(b_1)$	$\nu_4(a_1)$
$\text{HAl}^{12}\text{CAIH}$	1883.0	1875.1	927.8	755.2	423.8	464.9	413.1	381.1	215.9
$\text{HAl}^{13}\text{CAIH}$	1882.9	1875.1	901.8	736.7	423.7	464.7	413.1	380.3	214.3
$\text{DAI}^{12}\text{CAID}$	1374.8	1369.0	920.0	749.7	319.6	355.9	311.9	287.2	200.5
$\text{DAI}^{13}\text{CAID}$	1374.5	1368.7	894.3	729.8	319.5	355.6	311.9	286.2	199.2
$\text{HAl}^{12}\text{CAID}$	1879.0	1371.9	924.0	751.9	335.4	447.2	399.2	297.5	207.8
$\text{HAl}^{13}\text{CAID}$	1877.0	1371.6	898.1	733.3	335.1	447.3	399.0	296.8	206.4

Resonance threshold: 25 cm^{-1}

APPENDIX B

SUPPORTING INFORMATION FOR CHAPTER 4[†]

[†] S. R. Barua, H. Quanz, M. Olbrich, P. R. Schreiner, D. Trauner, W. D. Allen, **2014**, 20, 1638.
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Further Geometrical Analysis of Polytwistane

The lead angle $\chi(k)$ of the vector $\mathbf{x}_{2j+k}(\mathbf{C}) - \mathbf{x}_{2j}(\mathbf{C})$, representing inclination relative to the plane perpendicular to the axis of the helix, is given by

$$\sin[\chi(k)] = \frac{(k\zeta + \delta_c \varepsilon_k) \operatorname{sgn}(k)}{\sqrt{\sin^2\left(\frac{\pi k}{2\tau} + \beta_c \varepsilon_k\right) + (k\zeta + \delta_c \varepsilon_k)^2}}, \quad (\text{B1})$$

in which $\varepsilon_k = (0, 1)$ for $k = (\text{even}, \text{odd})$. The (blue, red, green) bonds of polytwistane (Figure 4.3) have the lead angles $(\chi_1, \chi_2, \chi_3) = [\chi(1), \chi(-1), \chi(-5)]$, which are obtained by setting $k = (1, -1, -5)$ in Equation B1. The instantaneous lead angle of the curves connecting the carbon atoms in the (**IV**_A, **IV**_B) helices is

$$\gamma_0 = \arcsin\left(\frac{2\zeta\tau}{\sqrt{\pi^2 + 4\zeta^2\tau^2}}\right), \quad (\text{B2})$$

while the corresponding discrete value for the inclination of the C_A–C_A and C_B–C_B line segments is $\gamma_A = \gamma_B = \gamma(2)$. The lead angle (γ_H) of the (C_A–H_A, C_B–H_B) bond vectors is obtained from

$$\sin \gamma_H = \pm \frac{(\rho_H \delta_H - \delta_c)}{\sqrt{1 + \rho_H^2 + (\rho_H \delta_H - \delta_c)^2 - 2\rho_H \cos(\beta_c - \beta_H)}}, \quad (\text{B3})$$

with the (+, –) sign applying to the (A, B) cases, respectively.

Extended algebraic derivations reveal that the torsion angles involving connected C–C bonds of distances (r_i, r_j, r_k) satisfy the following equations:

$$\sin \tau_{ijk} = \frac{a_k s_{ij} \sin\left[\frac{1}{2}(b_j - b_i)\right] + a_j s_{ik} \sin\left[\frac{1}{2}(b_i + b_k - 2b_j)\right] + a_i s_{jk} \sin\left[\frac{1}{2}(b_j - b_k)\right]}{f(a_i, b_i) f(a_j, b_j) f(a_k, b_k) \sin \theta_{ij} \sin \theta_{jk}} \quad (\text{B4})$$

and

$$\cos \tau_{ijk} = \cot \theta_{ij} \cot \theta_{jk} - \frac{s_{ik} \cos\left[\frac{1}{2}(b_i + b_k - 2b_j)\right] + 8a_i a_k}{2f(a_i, b_i) f(a_k, b_k) \sin \theta_{ij} \sin \theta_{jk}}, \quad (\text{B5})$$

which involve the reduced parameters (a_i, b_i) from Equations (4.8) and (4.9) as well as

$$s_{ij} = 8 \sin\left(\frac{1}{2}b_i\right) \sin\left(\frac{1}{2}b_j\right). \quad (\text{B6})$$

Finally, the azimuthal angles (ϕ_A, ϕ_B) of the (C_A–H_A, C_B–H_B) bonds indexed by integer j are given by

$$\tan \phi_{\text{A}} = \left\{ \eta_1 \tan \left[\frac{(2j+1)\pi}{\tau} \right] + \eta_2 \right\} \left\{ \eta_1 - \eta_2 \tan \left[\frac{(2j+1)\pi}{\tau} \right] \right\}^{-1} \quad (\text{B7})$$

and

$$\tan \phi_{\text{B}} = \left[\eta_1 \tan \left(\frac{2\pi j}{\tau} \right) - \eta_2 \right] \left[\eta_1 + \eta_2 \tan \left(\frac{2\pi j}{\tau} \right) \right]^{-1}, \quad (\text{B8})$$

where

$$\begin{aligned} \eta_1 &= \cos \beta_{\text{C}} - \rho_{\text{H}} \cos \beta_{\text{H}} \\ \eta_2 &= \sin \beta_{\text{C}} - \rho_{\text{H}} \sin \beta_{\text{H}} . \end{aligned} \quad (\text{B9})$$

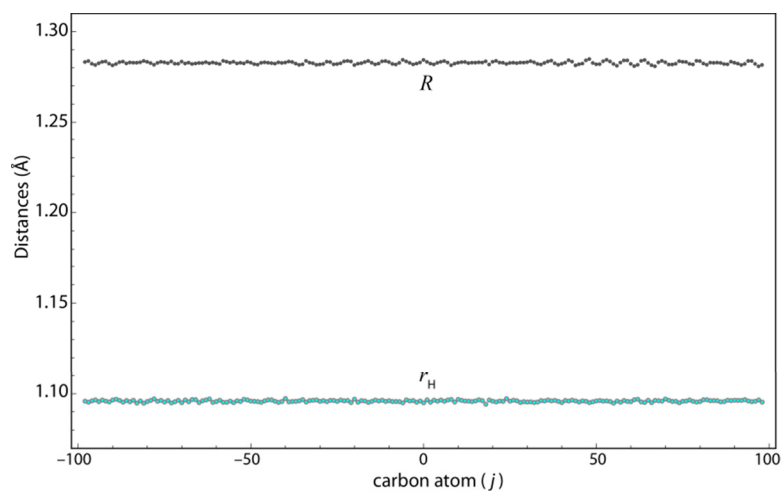


Figure B1 Axial distance (R) and C–H bond distance (r_H) for carbon atom j along the primary chain **I** of the $C_{236}H_{242}$ segment.

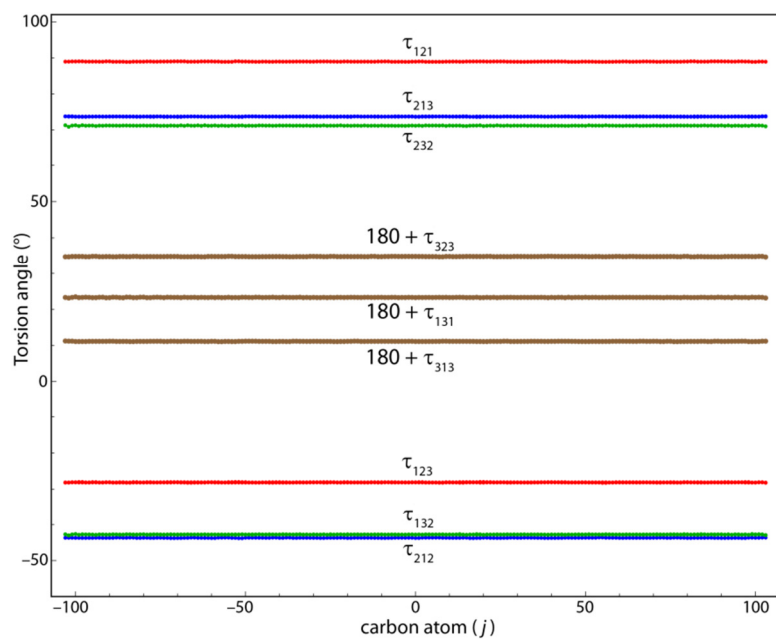


Figure B2 Torsion angles for C–C–C–C chains containing carbon atom j along the primary chain **I** of the $C_{236}H_{242}$ fragment. For torsion angles contained in rings **R1** and **R2**, the color is the same as that of the central bond (Figure 4.4); torsion angles connecting two rings are shown in brown.

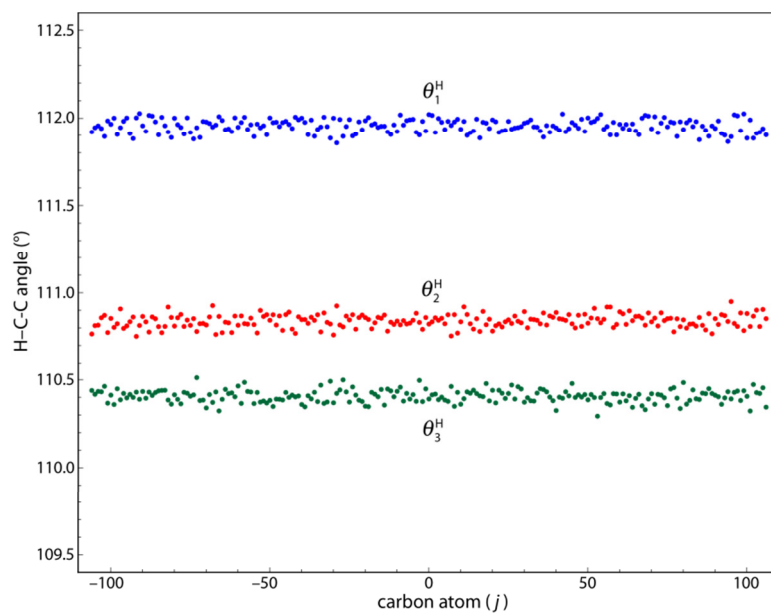


Figure B3 Evidence of three distinct H–C–C bond angles in polytwistane: a plot of the angles formed by the C–H bond of carbon atom j along the primary chain **I** of the $C_{236}H_{242}$ fragment. Each angle is assigned the color in Figure 4.4 of the included C–C bond.

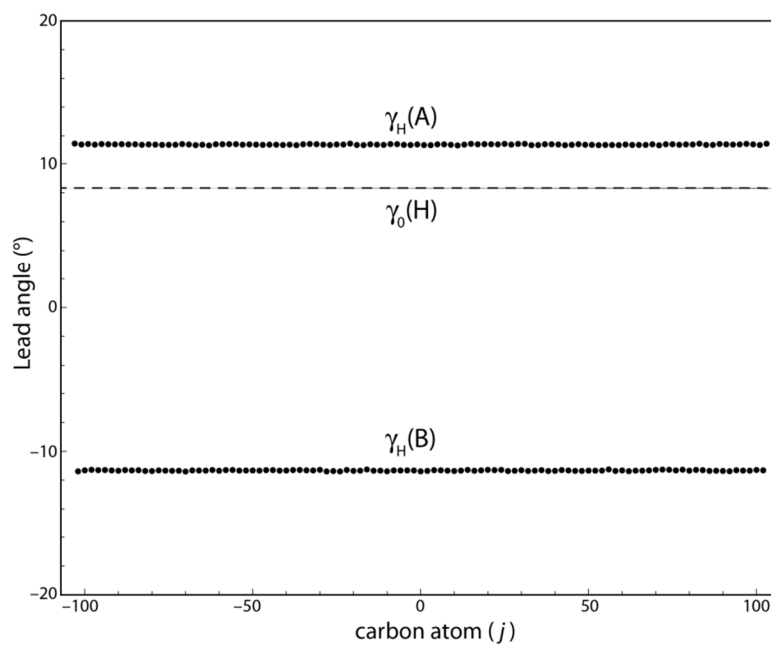


Figure B4 Lead angles for the C–H bond of carbon atom j along the primary chain **I** of the $C_{236}H_{242}$ fragment. For comparison, the instantaneous lead angle of the H_A and H_B helices is given, $\gamma_0(H) = 8.32^\circ$.

Table B1 Focal point analysis of the reaction energy (in kcal mol⁻¹) of
twistane + 12 ethane → 4 isobutane + 6 propane

	$\Delta E_e(\text{RHF})$	$+\delta [\text{MP2}]$	$+\delta [\text{CCSD}]$	$+\delta [\text{CCSD(T)}]$	NET
cc-pVDZ	-21.742	1.230	-2.220	0.297	-22.435
cc-pVTZ	-21.261	1.393	-2.121	0.223	-21.767
cc-pVQZ	-21.287	0.502	-2.030	0.121	-22.694
CBS LIMIT	[-21.291]	[-0.147]	[-1.963]	[0.046]	[-23.355]
FUNCTION	$a + b(X+1)e^{-9\sqrt{X}}$	$a + bX^{-3}$	$a + bX^{-3}$	$a + bX^{-3}$	
X (Fit points) =	(3,4)	(3,4)	(3,4)	(3,4)	

$\Delta(\text{ZPVE}) = +3.940$; $\Delta(\text{core correlation}) = -0.010$; $\Delta(\text{DBOC}) = -0.012$; $\Delta(\text{Relativity}) = -0.051$.

$\Delta E_0 = -23.355 + 3.940 - 0.012 - 0.051 - 0.010 = \mathbf{-19.49 \text{ kcal mol}^{-1}}$

Notation: The symbol δ denotes the *increment* in the energy difference (ΔE_e) with respect to the previous level of theory in the hierarchy RHF → MP2 → CCSD → CCSD(T). Bracketed numbers result from basis set extrapolations using the specified functions and fit points, while unbracketed numbers were explicitly computed. The focal-point table targets $\Delta E_e[\text{CCSD(T)}]$ in the complete basis set limit (NET/CBS LIMIT). The main table involves correlation of valence electrons only. Auxiliary energy terms are appended for zero-point vibrational energy (ZPVE), core electron correlation [$\Delta(\text{core correlation})$], the diagonal Born-Oppenheimer correction [$\Delta(\text{DBOC})$], and special relativity [$\Delta(\text{relativity})$]. The final energy difference ΔE_0 is boldfaced. MP2/cc-pVTZ theory was used for optimum geometries, ZPVE, DBOC, and relativistic corrections, while the core correlation correction was computed with MP2/cc-pCVTZ.

Table B2 MP2/cc-pVTZ optimized Cartesian coordinates (bohr) for twistane thermochemistry

Twistane (D_2)			
C	-1.173070	2.119387	0.880929
C	-2.948863	0.000056	0.000000
C	-1.173150	-2.119343	-0.880929
C	1.173070	-2.119387	0.880929
C	2.948863	-0.000056	0.000000
C	1.173150	2.119343	-0.880929
H	-4.174399	0.585473	-1.551893
H	-4.174421	-0.585316	1.551893
H	-2.100206	3.959969	0.835053
H	-2.100356	-3.959890	-0.835053
H	2.100206	-3.959969	0.835053
H	4.174399	-0.585473	-1.551893
H	4.174421	0.585316	1.551893
H	2.100356	3.959890	-0.835053
C	0.374816	1.413354	-3.575210
C	-0.374816	-1.413354	-3.575210
H	1.928559	1.752342	-4.887208
H	-1.203235	2.591088	-4.188619
H	1.203235	-2.591088	-4.188619
H	-1.928559	-1.752342	-4.887208
C	0.374763	-1.413368	3.575210
C	-0.374763	1.413368	3.575210
H	1.928492	-1.752415	4.887208
H	-1.203333	-2.591042	4.188618
H	1.203333	2.591042	4.188618
H	-1.928492	1.752415	4.887208
Energy: $-389.82750528 E_h$			
ZPVE: $+153.668 \text{ kcal mol}^{-1}$			

Isobutane (C_{3v})

H	0.000000	0.000000	2.794564
C	0.000000	0.000000	0.728822
C	2.733432	0.000000	-0.176907
C	-1.366716	-2.367221	-0.176907
C	-1.366716	2.367221	-0.176907
H	2.798800	0.000000	-2.238606
H	-1.399400	-2.423831	-2.238606
H	-1.399400	2.423831	-2.238606
H	3.743615	-1.667468	0.486570
H	-3.315877	-2.408333	0.486570
H	3.743615	1.667468	0.486570
H	-0.427738	-4.075800	0.486568
H	-3.315877	2.408333	0.486570
H	-0.427738	4.075800	0.486568

Energy: $-158.07672545 E_h$

ZPVE: $+83.363 \text{ kcal mol}^{-1}$

Propane (C_{2v})

C	2.385012	0.000000	-0.449936
C	-2.385012	0.000000	-0.449936
C	0.000000	0.000000	1.160739
H	4.087137	0.000000	0.705846
H	-4.087137	0.000000	0.705846
H	2.444320	1.662066	-1.665066
H	-2.444320	1.662066	-1.665066
H	2.444320	-1.662066	-1.665066
H	-2.444320	-1.662066	-1.665066
H	0.000000	1.650900	2.395327
H	0.000000	-1.650900	2.395327

Energy: $-118.85186069 E_h$

ZPVE: $+65.659 \text{ kcal mol}^{-1}$

Ethane (D_{3d})

C	0.000000	0.000000	-1.439403
C	0.000000	0.000000	1.439403
H	1.917185	0.000000	2.184107
H	-0.958592	-1.660330	2.184108
H	0.958592	-1.660330	-2.184108
H	-1.917185	0.000000	-2.184108
H	0.958592	1.660330	-2.184108
H	-0.958592	1.660330	2.184108

Energy: $-79.62990828 E_h$

ZPVE: $+47.483 \text{ kcal mol}^{-1}$

Table B3 Total energies (in E_h) at MP2/cc-pVTZ optimized geometries for the reaction
twistane + 12 ethane $\rightarrow$ 4 isobutane + 6 propane

	RHF	MP2	CCSD	CCSD(T)
Reactants				
cc-pVDZ	-1338.84018985	-1343.87091890	-1344.41232712	-1344.56446762
cc-pVTZ	-1339.23743566	-1345.38640470	-1345.83173568	-1346.07286616
cc-pVQZ	-1339.32380217	-1345.84308006	-1346.21430328	-1346.47744865
Products				
cc-pVDZ	-1338.87483751	-1343.90360671	-1344.44855289	-1344.60021966
cc-pVTZ	-1339.27131679	-1345.41806593	-1345.86677755	-1346.10755327
cc-pVQZ	-1339.35772586	-1345.87620299	-1346.25066114	-1346.51361446

Table B4 B3LYP/6-31G(d) optimized Cartesian coordinates (bohr) for twistane
thermochemistry

Twistane (D_2)			
C	-1.184726	2.133451	0.894254
C	-2.974107	-0.000008	-0.000001
C	-1.184714	-2.133458	-0.894253
C	1.184726	-2.133451	0.894254
C	2.974107	0.000008	-0.000001
C	1.184714	2.133458	-0.894253
H	-4.213940	0.598812	-1.548702
H	-4.213941	-0.598833	1.548697
H	-2.117029	3.983449	0.852177
H	-2.117009	-3.983461	-0.852174
H	2.117029	-3.983449	0.852177
H	4.213940	-0.598812	-1.548702
H	4.213941	0.598833	1.548697
H	2.117009	3.983461	-0.852174
C	0.394775	1.419132	-3.613559
C	-0.394775	-1.419132	-3.613559
H	1.970995	1.742020	-4.920391
H	-1.166253	2.621292	-4.258987
H	1.166253	-2.621292	-4.258987
H	-1.970995	-1.742020	-4.920391
C	0.394784	-1.419129	3.613560
C	-0.394784	1.419129	3.613560
H	1.971005	-1.742008	4.920392
H	-1.166237	-2.621297	4.258989
H	1.166237	2.621297	4.258989
H	-1.971005	1.742008	4.920392

Energy: $-390.692066727 E_h$

ZPVE: $+153.437 \text{ kcal mol}^{-1}$

Isobutane (C_{3v})

H	0.000000	0.000000	2.785569
C	0.000000	0.000000	0.705860
C	2.763061	0.000000	-0.180983
C	-1.381530	-2.392881	-0.180983
C	-1.381530	2.392881	-0.180983
H	2.873030	0.000000	-2.253293
H	-1.436515	-2.488117	-2.253293
H	-1.436515	2.488117	-2.253293
H	3.775222	-1.674934	0.501277
H	-3.338146	-2.431971	0.501277
H	3.775222	1.674934	0.501277
H	-0.437076	-4.106905	0.501277
H	-3.338146	2.431971	0.501277
H	-0.437076	4.106905	0.501277

Energy: $-158.456044262 E_h$

ZPVE: $+83.083 \text{ kcal mol}^{-1}$

Propane (C_{2v})

C	2.414121	0.000000	-0.451879
C	-2.414121	0.000000	-0.451879
C	0.000000	0.000000	1.147590
H	4.112323	0.000000	0.734490
H	-4.112323	0.000000	0.734490
H	2.499525	1.671826	-1.675465
H	-2.499525	1.671826	-1.675465
H	2.499525	-1.671826	-1.675465
H	-2.499525	-1.671826	-1.675465
H	0.000000	1.658644	2.395999
H	0.000000	-1.658644	2.395999

Energy: $-119.142154225 E_h$

ZPVE: $+65.346 \text{ kcal mol}^{-1}$

Ethane (D_{3d})

C	0.000000	0.000000	1.446455
C	0.000000	0.000000	-1.446455
H	1.929463	0.000000	-2.200502
H	-0.964731	1.670964	-2.200502
H	0.964731	1.670964	2.200502
H	-1.929463	0.000000	2.200502
H	0.964731	-1.670964	2.200502
H	-0.964731	-1.670964	-2.200502

Energy: $-79.829016299 E_h$

ZPVE: $+47.220 \text{ kcal mol}^{-1}$

Table B5 B3LYP/6-31G(d) optimized Cartesian coordinates (Å) for polytwistane thermochemistry

C ₂₀ H ₂₆			
C	-0.104071	3.791431	-0.084975
C	1.058141	3.622111	-1.103268
C	1.806917	2.321387	-0.750619
C	2.043796	2.340467	0.779856
C	0.715097	1.832808	1.379486
C	-0.451054	2.408816	0.499396
C	-0.580448	1.400102	-0.661003
C	0.903598	1.089889	-1.070230
C	1.276801	-0.107188	-0.172540
C	0.715097	0.282618	1.245674
C	-0.715097	-0.282618	1.245674
C	-1.276801	0.107188	-0.172540
C	-0.903598	-1.089889	-1.070230
C	0.580448	-1.400102	-0.661003
C	0.451054	-2.408816	0.499396
C	-0.715097	-1.832808	1.379486
C	-2.043796	-2.340467	0.779856
C	-1.806917	-2.321387	-0.750619
C	-1.058141	-3.622111	-1.103268
C	0.104071	-3.791431	-0.084975
H	-0.988052	4.223163	-0.570457
H	0.673430	3.571342	-2.130067
H	2.750640	2.247624	-1.304659
H	2.875425	1.693637	1.083608
H	0.597868	2.126194	2.429962
H	-1.381785	2.465269	1.077262
H	-1.145011	1.829575	-1.498801
H	0.980369	0.833890	-2.134476
H	2.361537	-0.268502	-0.143627
H	1.322449	-0.154436	2.048614
H	-1.322449	0.154436	2.048614
H	-2.361537	0.268502	-0.143627
H	-0.980369	-0.833890	-2.134476
H	1.145011	-1.829575	-1.498801
H	1.381785	-2.465269	1.077262
H	-0.597868	-2.126194	2.429962
H	-2.875425	-1.693637	1.083608
H	-2.75064	-2.247624	-1.304659
H	-0.67343	-3.571342	-2.130067
H	0.988052	-4.223163	-0.570457

H	0.178226	4.483440	0.718545
H	1.740199	4.480376	-1.064331
H	2.295204	3.353211	1.117770
H	-2.295204	-3.353211	1.117770
H	-1.740199	-4.480376	-1.064331
H	-0.178226	-4.48344	0.718545

Energy: -777.7760249446 E_h
 ZPVE: +267.066 kcal mol⁻¹

C₃₀H₃₆

C	-1.015937	5.588436	-0.849569
C	0.512184	5.815917	-1.021392
C	1.242524	4.834628	-0.083113
C	0.542024	4.926028	1.295255
C	-0.689108	4.005033	1.160233
C	-1.242524	4.166895	-0.300647
C	-0.402184	3.17599	-1.132765
C	1.064219	3.374644	-0.604222
C	1.166365	2.365636	0.558867
C	-0.189994	2.542328	1.339046
C	-1.139477	1.535563	0.665317
C	-0.865063	1.722696	-0.868946
C	0.268327	0.726538	-1.173417
C	1.268490	0.917140	0.020357
C	0.780075	-0.087371	1.081661
C	-0.780075	0.087371	1.081661
C	-1.268490	-0.917140	0.020357
C	-0.268327	-0.726538	-1.173417
C	0.865063	-1.722696	-0.868946
C	1.139477	-1.535563	0.665317
C	0.189994	-2.542328	1.339046
C	-1.166365	-2.365636	0.558867
C	-1.064219	-3.374644	-0.604222
C	0.402184	-3.17599	-1.132765
C	1.242524	-4.166895	-0.300647
C	0.689108	-4.005033	1.160233
C	-0.542024	-4.926028	1.295255
C	-1.242524	-4.834628	-0.083113
C	-0.512184	-5.815917	-1.021392
C	1.015937	-5.588436	-0.849569
H	-1.537685	5.705374	-1.807498
H	0.818070	5.644346	-2.061527
H	2.309401	5.078860	-0.011157

H	1.186302	4.589872	2.116310
H	-1.462288	4.238589	1.902522
H	-2.308381	3.910782	-0.342286
H	-0.473576	3.397998	-2.205461
H	1.803588	3.162566	-1.386758
H	2.029360	2.576826	1.202339
H	-0.065577	2.324663	2.407656
H	-2.188434	1.742602	0.913050
H	-1.760929	1.506543	-1.465182
H	0.747296	0.945935	-2.136329
H	2.301713	0.707118	-0.284758
H	1.207551	0.132344	2.068405
H	-1.207551	-0.132344	2.068405
H	-2.301713	-0.707118	-0.284758
H	-0.747296	-0.945935	-2.136329
H	1.760929	-1.506543	-1.465182
H	2.188434	-1.742602	0.913050
H	0.065577	-2.324663	2.407656
H	-2.029360	-2.576826	1.202339
H	-1.803588	-3.162566	-1.386758
H	0.473576	-3.397998	-2.205461
H	2.308381	-3.910782	-0.342286
H	1.462288	-4.238589	1.902522
H	-1.186302	-4.589872	2.116310
H	-2.309401	-5.078860	-0.011157
H	-0.818070	-5.644346	-2.061527
H	1.537685	-5.705374	-1.807498
H	-1.447472	6.332304	-0.167905
H	0.782883	6.851196	-0.779998
H	0.265724	5.963736	1.518585
H	-0.265724	-5.963736	1.518585
H	-0.782883	-6.851196	-0.779998
H	1.447472	-6.332304	-0.167905

Energy: -1164.8595902931 E_h

ZPVE: +380.530 kcal mol⁻¹

Table B6 Electronic energies (in E_h) at B3LYP/6-31G* optimized geometries for computing the reaction energy of $C_{20}H_{26} + C_{10}H_{16} + 6 C_4H_{10} \rightarrow C_{30}H_{36} + 6 C_3H_8 + 3 C_2H_6$

	B3LYP/6-31G*	MP2/6-31G*(fc)	MP2/cc-pVDZ(fc)	MP2/cc-pVTZ(fc)
Ethane	-79.82901630	-79.49214414	-79.53731458	-79.62963818
Propane	-119.14215422	-118.65638038	-118.71791324	-118.85141724
Isobutane	-158.45604426	-157.82330935	-157.90128427	-158.07607341
Twistane	-390.69206673	-389.29639482	-389.43260425	-389.82586742
$C_{20}H_{26}$	-777.77602494	-775.12143605	-775.35296873	-776.10902556
$C_{30}H_{36}$	-1164.85959029	-1160.94668388	-1161.27321822	-1162.39255931