First ab Initio and Density Functional Study on the Structure, Bowl-to-Bowl Inversion Barrier, and Vibrational Spectra of the Elusive C_{3v}-Symmetric Buckybowl: Sumanene, $C_{21}H_{12}$

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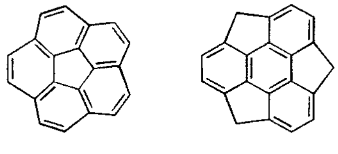
The synthetically elusive C_{3v} symmetric sumanene ($C_{21}H_{12}$), a key structural motif of C_{60}, was subjected to a detailed computational study, exploring the structure, bowl-to-bowl inversion dynamics, vibrational spectra, and some other physicochemical properties. Hartree−Fock (HF), pure (BLYP, BP86, and BPW91), and hybrid density functional (B3LYP, B3P86, and B3PW91) calculations were done with an array of basis sets (STO-3G, 3-21G, 6-31G*, 6-31G**, 6-311G*, 6-311G**, 6-311+G*, 6-311++G*, cc-pVDZ, and cc-pVTZ). The effect of a basis set higher than double-ζ quality and the inclusion of dynamic correlation on the geometry and bowl-to-bowl inversion barrier was insignificant. The B3LYP or HF method with the cc-pVDZ or 6-311G* basis set gave satisfactory results. The previously computed modified neglect of diatomic overlap (MNDO) value of 24.2 kcal/mol for the bowl-to-bowl inversion was found to be too high, and a revised value of 16.9 kcal/mol was obtained by the B3LYP/cc-pVTZ//B3LYP/cc-pVDZ method. Consequently, the computed results indicate that sumanene (**2**) is not locked in the bowl geometry and that a definitive bowl-to-bowl inversion should exist at room temperature. The highest level of theory used in the study (B3LYP/6-311G**) yields values of 1.14 Å, 2.45 D, and 98.8° for the bowl depth, dipole moment, and π-orbital axis vector angle at the hub carbon for sumanene, respectively. Interesting temperature dependency of inversion dynamics is predicted near room temperature.

1. Introduction

Chemistry of buckybowls has received considerable attention in recent years.[1−6] Corannulene (**1**) and sumanene (**2**) are the pristine buckybowl structures, which are readily recognized as fundamental structural motifs of C_{60}, retaining C_5 and C_3 axes, respectively (Scheme 1).[7,8] The synthesis of corannulene (**1**) was reported by Barth and Lawton in their landmark article more than 30 years ago, much before the fullerene era.[9] Recently, more than half a dozen efficient alternative syntheses have been reported on corannulene and it is now available in preparative quantities.[10] On the other hand, it is disheartening to see that the limited number of reported attempts to accomplish the synthesis of sumanene (**2**) have been futile[5,8] and attempts toward the synthesis through transition metal complexes as precursors were also not successful.[11] Still, alternative routes should be actively explored for the synthesis of this key C_3-symmetric buckybowl sumanene (**2**),[12] considering the fact that the syntheses of much more complicated and highly strained analogues have met with success.[13] Although the chief objective in the synthetic attempts toward buckybowl molecules is to ultimately conquer the synthesis of C_{60} by rational means, the syntheses of the intermediate bowl-shaped molecules are challenging and interesting in their own right. Corannulene (**1**) was unambiguously characterized as a flexible molecule exhibiting rapid bowl-to-bowl inversion,[14] whereas higher buckybowls that form a part of C_{60} are found to be rigid bowls.[15−17] To our knowledge, the only available modified neglect of diatomic overlap (MNDO) calculations predict that sumanene (**2**), $C_{21}H_{12}$, is a C_3-symmetric, presumably bowl-shaped molecule, with a calculated inversion barrier of 24.2 kcal/mol and a bowl depth of 1.15 Å, predicting it to be a rigid buckybowl in contrast to corannulene (**1**), whose inversion barrier is 10.2 kcal/mol and the bowl depth is 0.89 Å.[7]

SCHEME 1



1, Corannulene (C_{5v}) **2**, Sumanene (C_{3v})

Previous theoretical studies indicate that adequate basis set functionality and inclusion of dynamic electron correlation are necessary to obtain reliable estimates for equilibrium geometries, inversion barriers, and vibrational spectra.[15−22] However, in some cases, smaller basis sets and Hartree−Fock methods place one in the ballpark for predicting bowl-to-bowl inversion barrier, geometry, and other physicochemical properties, probably because of the fortuitous cancellation of errors.[14−22] Therefore, it is dangerous to arrive at any conclusion that sumanene (**2**) is locked into a single bowl conformation based on semiempirical data.[23−25] For a molecule of this size conventional ab initio post-Hartree−Fock methods with good quality basis sets are prohibitively expensive. Consequently, at present, density functional theory (DFT) becomes the only viable alternative to include the effects of dynamic electron correlation. Thus, the application of density functional methods for electronic structure calculations has reached a peak in the past few years.[26−28]

Buckybowls can potentially mimic some of the properties unique to fullerenes owing to the common feature of curvature both of them share. Defining the structural requirements for locking the bowl structure of buckybowls is an intriguing

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aspect, which has generated a lot of interest. Annulation of a five-membered ring,[29] cyclophane bridge,[30] or a site-specific heteroatom substitution[31] are some of the strategies to arrest the rapid bowl-to-bowl inversion prevailing in corannulene. The question, "How large a size of the surface of a C_{60} fragment is necessary to lock the bowl geometry at room temperature?", is fundamentally important.

We report here the first systematic ab initio and pure and hybrid density functional computational study on the synthetically elusive buckybowl sumanene ($C_{21}H_{12}$, **2**). A detailed analysis including the structure, inversion barrier, suitability of various theoretical procedures, vibrational spectra, population and charge analyses of sumanene (**2**) is presented here. In addition, the strain energy, which chiefly decides the feasibility of strained hydrocarbon synthesis, is estimated through isodesmic equations.

2. Theoretical Methods

The planar and bowl structures of sumanene (**2**) are fully optimized within D_{3h} and C_{3v} symmetry constraints, respectively, using the default gradient techniques implemented in the Gaussian 94 program package.[32] Frequency calculations are performed at several representative levels which unequivocally characterize the C_{3v} bowl structure as a minimum and the corresponding planar D_{3h} structure is characterized as the transition state for bowl-to-bowl inversion.

To scrutinize the sensitivity of the geometries of minima and transition state and the bowl-to-bowl inversion barriers, the calculations are conducted by ab initio (Hartree−Fock), pure and hybrid gradient-corrected density functional methodologies with an array of basis sets, as implemented in the Gaussian 94 package. Becke's gradient-corrected exchange functional[33] and hybrid three-parameter functional[34] were used in conjunction with nonlocal correlation provided by Lee, Yang, and Parr (LYP),[35] Perdew 86 (P86),[36] and Perdew 91 (PW91),[37] which contain both local and nonlocal terms. The quality of basis sets is systematically improved starting from the minimal STO-3G basis set to Pople's double and triple-ζ quality basis sets with added polarization functions, namely, 3-21G, 6-31G*, 6-31G**, 6-311G*, and 6-311G**. In addition, Dunning's correlation consistent basis set, cc-pVDZ, was used for both the Restricted Hartree−Fock (RHF) and DFT calculations.[38] Hybrid DFT methods in conjunction with the cc-pVDZ basis set have been shown to give adequate description of harmonic frequencies for this class of compounds.[22] Optimizations including diffuse functions on carbons met with numerous self-consistent field (SCF) convergence problems and could not be performed. However, single-point calculations are performed using 6-311+G*, 6-311++G*, and cc-pVTZ basis sets; cc-pVTZ, a triple-ζ quality basis set that includes one set of f functions and two sets of d-polarization functions on carbon, gives rise to 798 basis functions for $C_{21}H_{12}$ (**2**). The three popular semiempirical schemes, MNDO,[39] Austin model 1 (AM1),[40] and Parametric Model 3 (PM3),[41] were also performed to ascertain their suitability. Natural population analysis was conducted, in addition to the routine Mulliken analysis, to obtain natural atomic and group charges, that is, the charges on hydrogens are summed up with heavy atoms to which they are linked. Natural bond orbital (NBO) analysis is performed using the subroutine implemented in the Gaussian 94 program package.[42] Unscaled vibrational frequencies are used to obtain zero-point energy and enthalpy corrections in density functional methods, and the scaling factor of 0.89 is adopted for Hartree−Fock-based methods.[43] All the calculations were performed using the Gaussian 94 suite of programs. The best values for optimized geometric parameters are those obtained at the B3LYP/6-311G** level, because it is the largest basis set used, and energetics obtained at the B3LYP/cc-pVTZ level.

TABLE 1: Selected Geometric Parameters of Sumanene (2) at Various Levels of Theory[a]

level	r1a	r1b	r2	r3a	r3b	r4	Δ1[b]	Δ2[c]
HF/6-311G**	1.368	1.431	1.385	1.385	1.553	1.424	0.063	0.056
HF/cc-pVDZ	1.371	1.433	1.389	1.389	1.553	1.427	0.062	0.056
B3LYP/6-311G**	1.385	1.432	1.397	1.397	1.553	1.429	0.047	0.044
B3LYP/cc-pVDZ	1.389	1.435	1.402	1.402	1.554	1.433	0.046	0.044
BLYP/cc-pVDZ	1.401	1.444	1.413	1.412	1.565	1.443	0.043	0.042
BP86/cc-pVDZ	1.399	1.440	1.410	1.410	1.555	1.439	0.041	0.040
B3P86/cc-pVDZ	1.386	1.431	1.398	1.399	1.544	1.428	0.045	0.042
BPW91/cc-pVDZ	1.397	1.438	1.409	1.409	1.553	1.438	0.041	0.041
B3PW91/cc-pVDZ	1.387	1.432	1.399	1.400	1.545	1.429	0.045	0.042

[a] Bond lengths and the bond alternations (Δ1 and Δ2) are given in Å. [b] Δ1 = r1b − r1a, is the bond alternation in the hub benzene ring in **2**. [c] Δ2 = r4 − r1a, is the bond alternation in the flank benzene ring in **2**.

SCHEME 2

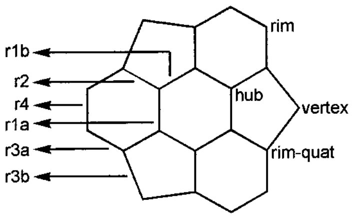


TABLE 2: Selected Geometric Parameters of the Planar Transition State Structure of Sumanene (2a) at Various Levels of Theory[a]

level	r1a	r1b	r2	r3a	r3b	r4	Δ1[b]	Δ2[c]
HF/6-311G**	1.350	1.398	1.362	1.405	1.594	1.444	0.048	0.094
HF/cc-pVDZ	1.354	1.401	1.366	1.409	1.595	1.446	0.047	0.092
B3LYP/6-311G**	1.364	1.398	1.374	1.415	1.596	1.452	0.034	0.088
B3LYP/cc-pVDZ	1.369	1.401	1.379	1.420	1.596	1.456	0.032	0.087
BLYP/cc-pVDZ	1.380	1.409	1.389	1.431	1.610	1.467	0.029	0.087
BP86/cc-pVDZ	1.377	1.406	1.387	1.429	1.598	1.464	0.029	0.087
B3P86/cc-pVDZ	1.365	1.397	1.375	1.417	1.585	1.451	0.032	0.086
BPW91/cc-pVDZ	1.375	1.404	1.386	1.427	1.595	1.462	0.029	0.087
B3PW91/cc-pVDZ	1.366	1.398	1.376	1.418	1.587	1.453	0.032	0.087

[a] All the values are given in Å. [b] Δ1 = r1b − r1a, is the bond alternation in the hub benzene ring in bowl-to-bowl inversion transition state structure of sumanene (**2a**). [c] Δ2 = r4 − r1a, is the bond alternation in the flank benzene ring in bowl-to-bowl inversion transition state structure of sumanene (**2a**).

3 Results and Discussion

3.1. Equilibrium Geometries. Table 1 gives the principal geometric parameters for the minimum energy bowl structure obtained at various levels of theory, based on the labeling given in Scheme 2. Similarly, the principal geometric parameters for the bowl-to-bowl inversion transition state (**2a**) are given in Table 2. As expected, HF consistently underestimates all bond lengths. The geometries are virtually identical at all DFT levels. The bond alternation is overestimated at semiempirical and HF levels, especially with inadequate basis sets. The bond alternation in sumanene (**2**) is higher in the hub six-membered ring when compared with its flank six-membered ring. Thus, surprisingly, r2 and r3a have bond lengths very similar to that of r1a, which is in turn closer to the aromatic C−C bond length. Improving the basis set quality further to 6-31G* does not bring in any significant changes in the geometries and bond alternations. The central six-membered ring witnesses significant bond alternation in **2**, which is only slightly lower than that present

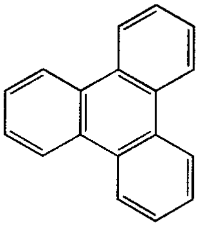
TABLE 3: POAV Angles Obtained for the Hub, Rim-quat, and Rim Positions Obtained Using POAV3 Program for the Optimized Geometries of Sumanene at Various Levels of Theory[a]

level	hub	rim-quat	rim	BD[b]	μ
HF/6-311G**	98.6	94.6	92.3	1.105	2.666
HF/cc-pVDZ	98.6	94.7	92.1	1.111	2.507
B3LYP/6-311G**	98.8	94.9	92.3	1.140	2.454
B3LYP/cc-pVDZ	98.8	94.9	92.3	1.143	2.099
BLYP/cc-pVDZ	98.8	94.9	92.3	1.151	1.932
BP86/cc-pVDZ	99.0	94.9	92.1	1.159	2.238
B3P86/cc-pVDZ	98.9	94.9	92.1	1.147	2.344
BPW91/cc-pVDZ	99.0	94.9	92.1	1.156	2.243
B3PW91/cc-pVDZ	98.9	94.7	92.3	1.144	2.336

[a] Bowl depth (BD) (Å) and dipole moment (μ) (Debyes) are also given. [b] Bowl depth is interplanar distances between the two best planes formed by the hub and rim atoms.

in C_{60}: 1.398 and 1.455 Å.[44] In contrast, five of the flank six-membered ring bond lengths are essentially identical, with a slightly elongated rim bond (r4).

The bond alternation in central six-membered ring of triphenylene (**3**) is found to be very significant both by experimental[45] and theoretical studies,[46] with the endo and exo bonds measuring 1.41 and 1.47 Å, respectively.



Triphenylene (3)

In going from the minimum energy bowl (**2**) to the flat transition state (**2a**) structure the hub and spoke bond lengths (r1a, r1b, and r2) are shrunk substantially, whereas the flank and rim bond lengths (r3a, r3b, and r4) are elongated at all levels of theory, consistent with the observations in the bowl structures. This is to be expected because the planar form enforces shrinking of the hub six-membered ring and elongation of the rim and flank bonds to accommodate angular strain. Consequently, the bond alternation is much higher in the peripheral six-membered ring than in the hub one, which is in complete contrast with the situation in the bowl.

3.2. Curvature and Polarity. Haddon's π-orbital axis vector (POAV) angle,[47,48] an angle between the normal vector to the pyramidal base and the idealized C_3 symmetric C−C bonds, is the most popular measure of pyramidalization at a given sp^2 carbon center. An angle of 90° corresponds to a flat carbon center; corannulene and C_{60} have POAV angles of 98.2 and 101.6°, respectively.[48a] The POAV angles at the three unique (hub, rim-quat, and rim) sp^2 centers, along with the bowl depth and the dipole moment obtained at various levels of theory, are given in Table 3. Comparison of POAV angles between corannulene (1) and sumanene (**2**) at the hub position clearly indicate that the latter is more pyramidal and the curvature is closer to that of C_{60}. The POAV angle is nearly insensitive to the level of calculation used.

Bowl depth is defined as the distance between the planes formed by the central hub atoms and the rim carbon atoms (Scheme 3). However, bowl depth exhibits greater fluctuations as a function of method, and the best computed value is about 1.14 Å obtained at B3LYP/cc-pVDZ level. Figure 1 gives the plot of variation of bowl depths as a function of levels of theory used. Here, a basis set with the quality equal to or higher than 6-311G* or cc-pVDZ is required to get the correct picture. Buckybowls are polar in contrast to the planar aromatic hydrocarbons because of the anisotropic distribution of π-electrons and the C−H bonds, which trigger separation of charges. Consequently, the base of the hub is charged and the depth of the bowl is proportional to charge separation. Natural charges obtained by NBO analysis at 6-311G* basis set at HF and B3LYP levels of theory are given in Figure 2.[49] The computed dipole moment (μ) of about 2.5 D is substantial for pure hydrocarbons. The dipole moment is very sensitive, and semiempirical or ab initio and DFT methods without the polarization functionality in the basis sets are inadequate. The value of μ is zero for the flat structure because of symmetry, and the value of μ is expected to increase as the curvature or bowl depth increases. Semiempirical levels, which show higher bowl depths, unexpectedly gave lower dipole moments.

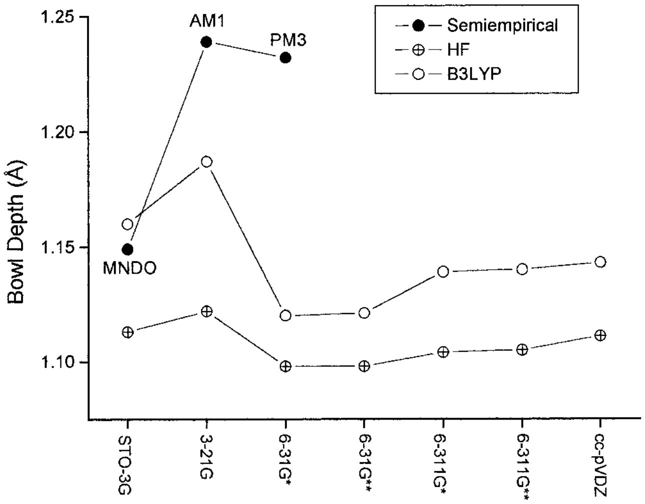


Figure 1. The variations in the bowl depth of sumanene (**2**) at various levels of theory.

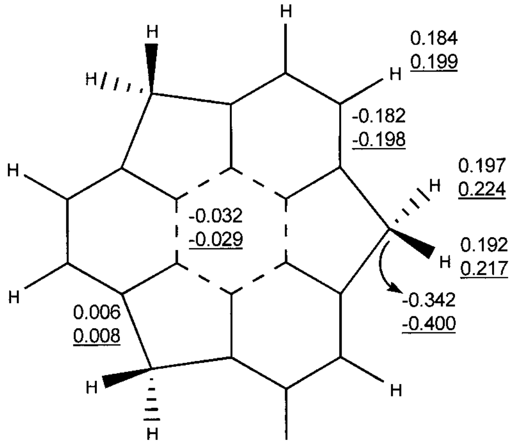
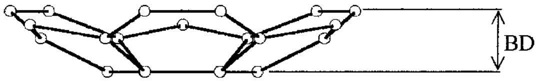


Figure 2. Natural charges obtained at HF and B3LYP (underlined) levels with the 6-311G* basis set.

SCHEME 3



3.3. Bowl-to-Bowl Inversion Barrier. Bowl-to-bowl inversion vividly exhibited by corannulene at room temperature is the most striking feature of buckybowls. The total energies along

TABLE 4: The ab Initio and DFT Total Energies (in hartrees) for the Bowl Structure, the Planar Transition State of Sumanene, and the Bowl-to-bowl Inversion Barriers, $\Delta E^{\ddagger}$, Obtained at Various Levels of Theory

level	bowl (C_{3v})	transition state (D_{3h})	$\Delta E^{\ddagger}$ (kcal/mol)
1. HF/6-311G**	−802.33811	−802.30812	18.8
2. HF/cc-pVDZ	−802.24303	−802.21266	19.1
3. B3LYP/6-311G**	−807.60582	−807.57593	18.8
4. B3LYP/cc-pVDZ	−807.47617	−807.44711	18.2
5. BLYP/6-31G*	−807.07682	−807.05208	15.5
6. BLYP/cc-pVDZ	−807.11874	−807.09146	17.1
7. BP86/6-31G*	−807.42989	−807.40312	16.8
8. BP86/cc-pVDZ	−807.48249	−807.45326	18.3
9. B3P86/6-31G*	−809.93385	−809.90532	17.9
10. B3P86/cc-pVDZ	−809.98602	−809.95531	19.3
11. BPW91/6-31G*	−807.34740	−807.32059	16.8
12. BPW91/cc-pVDZ	−807.39842	−807.36910	18.4
13. B3PW91/6-31G*	−807.13836	−807.11010	17.7
14. B3PW91/cc-pVDZ	−807.19004	−807.15958	19.1
15. B3LYP/6-311+G*[a]	−807.59447	−807.56403	18.4
16. B3LYP/6-311++G*[a]	−807.59463	−807.56421	18.4
17. B3LYP/cc-pVTZ[a]	−807.68393	−807.65583	16.9

[a] Single point calculations on B3LYP/cc-pVDZ optimized geometries. Enthalpy correction at B3LYP/cc-pVDZ level is also included in the $\Delta E\ddagger$ values.

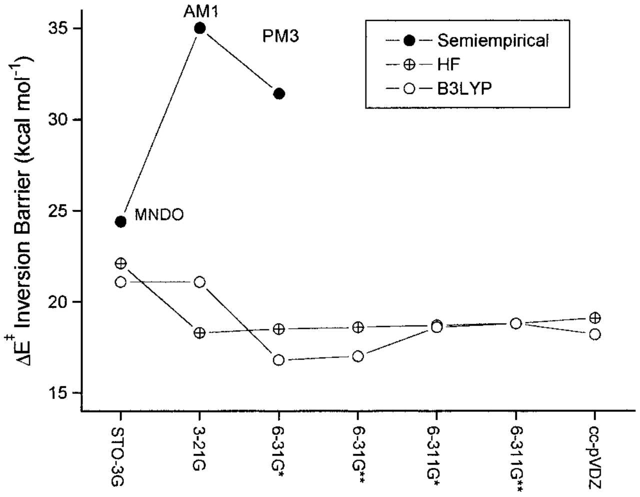


Figure 3. Bowl-to-bowl inversion barrier of sumanene (**2**) versus method of calculation.

with the bowl-to-bowl inversion barriers at various levels of theory are given in Table 4. HF level shows near insensitivity to the inversion barrier from 3-21G basis set onward and gives satisfactory descriptions. Figure 3 gives the magnitude of bowl-to-bowl inversion barrier at various levels of theory. Although the calculated barrier is essentially similar at HF and DFT levels and less sensitive to the basis set above double-ζ quality, density functional methods seem to require a basis set of cc-pVDZ or triple-ζ quality. The energies reported up to entry 14 are the energetics obtained on the geometries at the same level of theory. Further, single-point energy calculations were conducted at the B3LYP level using cc-pVTZ, 6-311+G*, and 6-311++G* basis sets. All the semiempirical levels were not adequate to quantitatively predict the barrier height, and among them MNDO was better than the rest. Similar observations were made in the bowl-to-bowl inversion barrier of corannulene, where MNDO gave reasonable estimates and AM1 and PM3 proved to be unsatisfactory.[16] After the enthalpy correction, performed at the B3LYP/cc-pVDZ level, the best estimate for the bowl-to-bowl inversion barrier is 16.9 kcal/mol, which is significantly smaller than the earlier MNDO estimate of 24.2 kcal/mol.[7] Considering the same frequency factor for both corannulene (**1**) and sumanene (**2**) inversion dynamics, the rate constant for the later process is about 2.5 s^{-1} indicating that one observes slow real-time inversion near room temperature.[50] The activation barrier for this inversion seems to be the limiting case for locking into a single conformation and will prove to be extremely sensitive to the temperature.

However, the accuracy of the barrier height is hard to prove in the absence of experimental evidence. Yet, based on the track record of DFT methods, and also looking at the near insensitivity of the barrier height to the basis set and the type of exchange correlation functional, it is unlikely that the error in the predicted barrier height will be more than 2 kcal/mol, thus making an upper and lower limit of 19 and 15 kcal/mol, respectively.[51]

3.4. Effect of Temperature on Barrier Height. Figure 4 gives the effect of temperature on the bowl-to-bowl inversion frequency. Assuming that the activation free energy is 16.9 kcal/mol, the bowl structure remains locked in a single conformation at about 250 K. Therefore, the inversion dynamics is expected to exhibit interesting features near room temperature. The inversion dynamics of sumanene (**2**) reminiscent of the situation in cyclohexane and a simple variable temperature ^{1}H NMR experiment will be suffice to follow the dynamics, whereas a proper substituent that distinguishes the protons in its two different bowl forms is essential for following the inversion dynamics of corannulene.[14a]

3.5. Frontier Orbitals. The ordering of the frontier orbital energies is essentially the same at all the levels of theory; both highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are doubly degenerate. Figure 5 depicts the one-electron energy ordering in the frontier range and shapes of the doubly degenerate HOMO and LUMO at HF level. The nature of the frontier orbitals at various levels of theory was examined using the MOPLOT program.[52] The ordering of one-electron energy levels in the frontier region was similar at all levels of theory. The vertical ionization potential value of 7.45 eV for **2** at HF/cc-pVDZ level, and the orbital energies are virtually insensitive to the basis set. The HOMO and LUMO energies at all the theoretical levels used were incorporated in the Supporting Information (Figure S1). The relevance and utility of one-electron wave functions in DFT methods were highlighted recently, providing confidence in the vertical ionization potential values.[53]

3.6. Computed Vibrational Spectra. The predicted IR spectrum of **2** is given in Figure 6. A$_1$ and E irreducible representations are IR active, whereas A$_2$ is inactive because of symmetry. Hartree−Fock-based methods tend to overestimate the vibrational frequencies by about 10%.[43] However, B3LYP together with double-ζ and polarization quality basis set was quite satisfactory for reproducing experimental vibrational frequencies of aromatic hydrocarbons.[22] The normal modes of vibration of **2** are given as the following symmetry-adapted linear combinations:

$$\Gamma_{\mathrm{vib}} = 17\mathrm{A}_1 + 14\mathrm{A}_2 + 31\mathrm{E}$$

The computed IR spectrum indicates that there are about three very intense vibrational fundamentals at 3025, 3086, and 3178 cm^{-1} which belong to E, A$_1$, and E irreducible representations, respectively. Of these the doubly degenerate band (E) at 3178 cm^{-1} was computed to be the most intense band, a trend which was reproduced at all levels of theory (see Supporting Information). The other two intense vibrational fundamentals appear in the regions of 800 and 1400 cm^{-1}, which belong to A$_1$ and E irreducible representations, respectively. The broad features

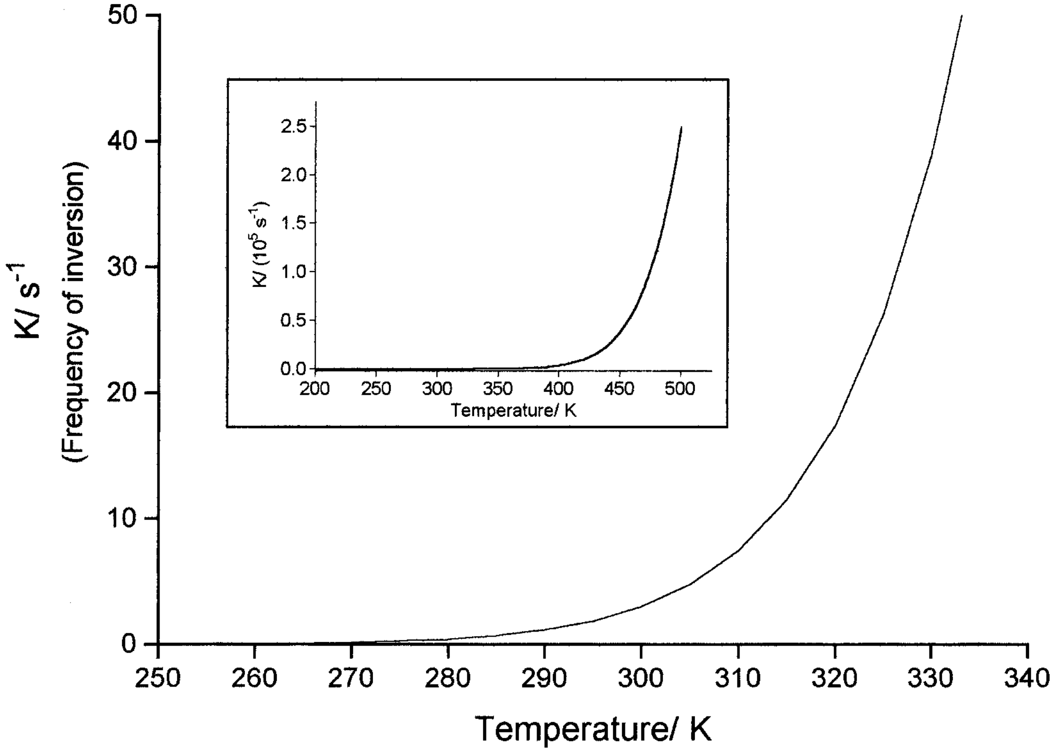


Figure 4. The plot of bowl-to-bowl inversion frequency, the first-order rate constant, versus temperature. The inset includes a broader range of temperatures, and the inversion frequency is in the order of 10^5 s^{-1} units.

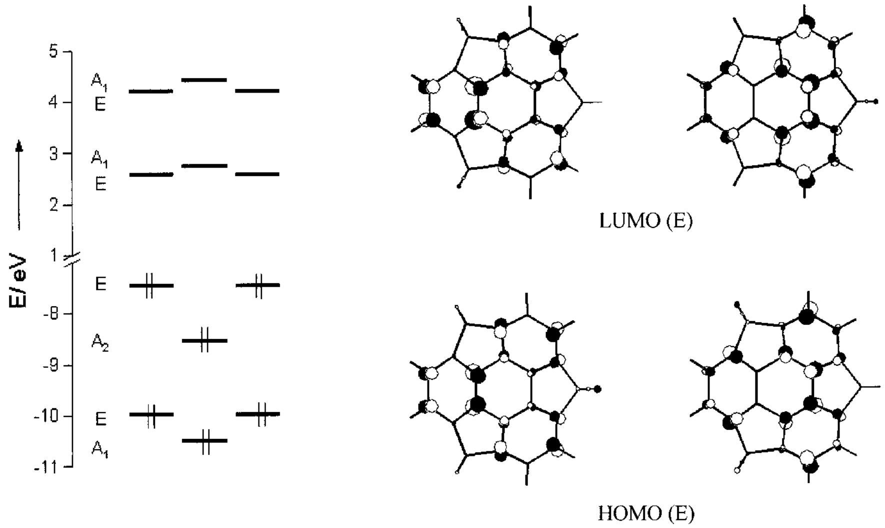


Figure 5. The frontier orbitals of sumanene (**2**) and the shapes of the doubly degenerate HOMO and LUMO.

obtained at this level are essentially similar to the other levels of theory used here. The computed harmonic frequencies along with the IR intensities at various levels of theory are provided in the Supporting Information.

3.7. Strain Energy. The strain energy is evaluated using the isodesmic equation, presented in Scheme 4, obtained at the B3LYP/cc-PVDZ level.

The computed strain is 63.3 kcal/mol using the isodesmic equation. Obviously, this is not a unique way of measuring the strain. A simple molecular mechanics (using MM2 force field of Allinger)[54] calculation gives the strain energy of 125.8 kcal/mol. However, this strain definitely does not seem to be a stumbling block for the synthesis of sumanene (**2**), because many hydrocarbon analogues with comparable or higher strain energies, such as prismane (252.9 kcal/mol), cubane (169.8 kcal/mol), corannulene (109.9 kcal/mol), and circumtrindene (284.2 kcal/mol) could be synthesized successfully.[54,55] Therefore, we think that serious attempts by experimentalists should accomplish the synthesis of this elusive compound. Exploring alternative synthetic strategies probably has greater chances for success than the pathways conceived previously.[8,11] Triphenylene[1,12-*bcd*:4,5-*b*′*c*′*d*′:8,9-*b*″*c*″*d*″]trithiophene, which can be viewed as trithiasumanene, where the three vertex methylene groups are replaced by isovalent S, was synthesized by a different strategy.[56]

4. Conclusions

The structure, curvature, bowl rigidity, vibrational spectra, charge analysis, etc., of the elusive key structural motif of buckminsterfullerene, sumanene (**2**), are discussed using ab initio and density functional methods with a wide range of basis

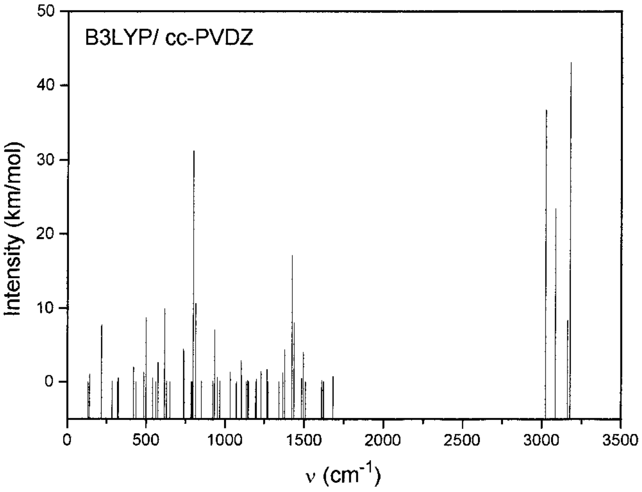
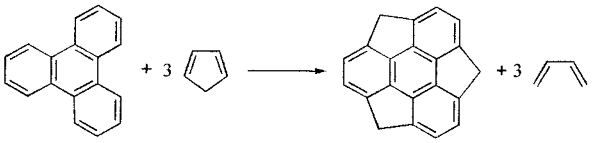


Figure 6. The B3LYP/cc-PVDZ computed vibrational spectrum of sumanene (**2**).

SCHEME 4



sets for the first time. The bowl-to-bowl inversion barrier is predicted to be 16.9 kcal/mol at the B3LYP/cc-pVTZ//B3LYP/cc-pVDZ level including the enthalpy correction, which is about 7 kcal/mol lower than the earlier semiempirical-MNDO result. The revised estimate predicts slow bowl-to-bowl inversion near room temperature. This is because the barrier is clearly higher than that of corannulene (**1**)[14a] and many other familiar dynamic processes, all of which exhibit rapid inversion at room temperature, such as: (a) between two tub conformers of cyclootatetraene,[57] (b) between the two chair forms of cyclohexane,[58] (c) pyramidal inversion of ammonia,[59] and (d) automerization of cyclobutadiene.[60] Thus the bowl-to-bowl inversion barrier of sumanene (**2**) is "in the ballpark" to provide interesting perturbation in the dynamics near room temperature, as a function of many factors, namely, temperature, solvent, counterion, etc. The computed results show interesting temperature dependence of inversion dynamics near room temperature. The bowl depth, curvature (POAV angle), and polarity (μ) of sumanene are found to be higher than those of corannulene. The vibrational spectra of sumanene have been calculated by the hybrid density functional B3LYP method with a basis set of split valence plus polarization quality. The computed strain energies indicate that the high built-in strain is not a bottleneck and calls for the attention of synthetic organic chemists toward the synthesis of sumanene (**2**). We hope that this computational study, which highlights some very interesting properties of the experimentally elusive sumanene (**2**), draws the attention of our colleagues in research.

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Supporting Information Available: The optimized geometries at HF/6-311G*, HF/6-311G**, B3LYP/6-311G*, B3LYP/6-311G**, and B3LYP/cc-pVDZ levels of theory and the harmonic frequencies along with the IR intensities obtained at the HF/6-31G*, B3LYP/6-31G*, and B3LYP/cc-pVDZ level of theory are given. The total energies, relative energies, and enthalpy corrections at many other levels (not given in the text) are also included. Also given are the energies of the degenerate HOMO and LUMO and the charge densities (both atomic and group) at the four unique skeletal positions computed at various levels of theory. The procedure used for calculating the inversion frequency of sumanene based on free energy of activation is given. This material is available free of charge via the Internet at http://pubs.acs.org.

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