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# The Quest for a Planar and Pyramidal Carbon Atom. 3. Can a Tetrahedrally Coordinated Carbon Form a Nearly Linear C−C−C Bond Angle?[1,2]

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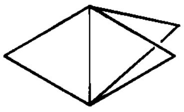
*Ab initio* HF and MP2-level calculations with 6-31G** basis set carried out for known tricyclo[$4.1.0.0^{1,3}$]heptane, hypothetical tricyclo[$3.1.0.0^{1,3}$]hexane, and reaction intermediate tricyclo[$2.1.0.0^{1,3}$]pentane supported by the available experimental data for these molecules indicate that the yet-unknown tricyclohexane should have a C−C−C bond angle close to 180° and should be a plausible synthetic target.

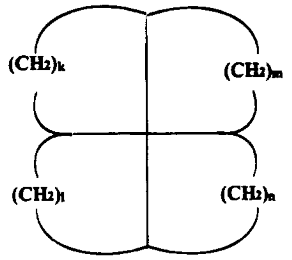
## Introduction

Theoretical calculations play an ever-increasing role in studies of organic molecules with unconventional spatial structure.[3] The investigation of molecules with bonds and angles strongly distorted from the standard geometry seems to be of considerable importance for both synthetic and theoretical chemistry, since it enables a better understanding of the properties of chemical bond. In addition, model calculations of hypothetical molecules with unusual spatial structure play an important role in proposing plausible synthetic targets. Sometimes, as was the case with $C_{60}$,[4] the theoretical predictions were premature,[5] though they could have been of significant help in the interpretation of early experimental data on fullerene. However, when carried out in a timely fashion, the calculations can provide invaluable inspiration for synthetic chemists. The prediction of the existence of an inverted carbon atom and that of the unexpected stability of [1.1.1]propellane (**1**) by Wiberg's group[3c] is probably the best example of a successful interaction between theoretical and synthetic studies.



**1**

Hoffmann's idea of a "planar methane",[6] i.e., the possibility of existence of a carbon atom lying in one plane with its four substituents, has inspired many theoretical and experimental studies. Although the results of early calculations of the energy required to enforce planarity of tetrahedral methane differ significantly,[1,3a] they have triggered numerous synthetic works, especially in the domain of fenestranes **2**[7] and paddlanes **3**.[8] However, in spite of all efforts, no organic molecules with planar configuration on a carbon atom were found. Recent, more reliable *ab initio* calculations on methane have shown that the planar $D_{4h}$ structure does not represent a minimum on the methane energy hypersurface.[9]



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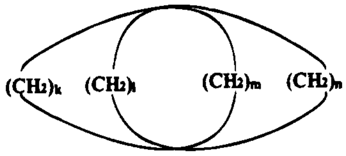

**3**

Other interesting molecules having a pyramidal configuration on a carbon atom that could represent minimum energy structures were proposed on the basis of molecular mechanics[1] and AM1[2] calculations for molecules **4** and **5**. This idea was later verified by *ab initio* studies.[11] In search of a pyramidal or planar configuration on a carbon atom, we have recently studied[1b] a series

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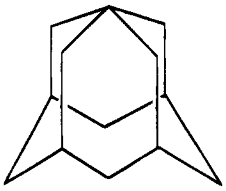
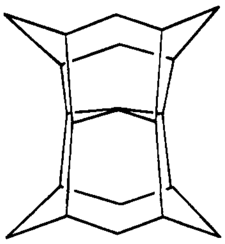
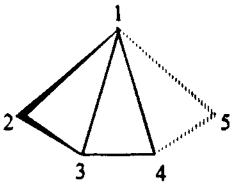


**4**

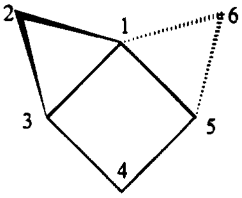


**5**

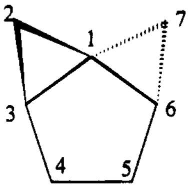
of bridged spiropentanes (encompassing known stable tricycloheptane **8**, hypothetical tricyclohexane **7**, and intermediate tricyclopentane **6** recently detected by Wiberg's group[12] ) using a semiempirical AM1 approach.



**6**



**7**



**8**

In addition to low-temperature NMR evidence in favor of the latter structure, *ab initio* calculations carried out by Wiberg et al. yielded a pyramidal configuration on the central carbon.[12] On the other hand, its heavier tricycloheptane analog **8** has been known for a long time,[13] but its unusual geometry has not received due recognition. The results of electron diffraction, ED,[13] and X-ray[14] determinations of its bonds and angles differ in some details. However, both techniques evinced a quite nonstandard value of ca. 160° for the C2C1C7 bond angle reproduced by *ab initio* calculations of Wiberg et al.[15] The same result was found by our AM1 study[2] of the series **6**–**8**, in which a highly unusual collinear arrangement of the C1–C2 and C1–C6 bonds on the spiro carbon in hypothetical molecule **7** was found. Since semiempirical AM1 calculations are of limited reliability for highly strained systems, such a finding has to be confirmed by the more reliable *ab initio* calculations, involving a larger basis set and electron correlation effects. The results of these studies are presented in this report.

## Methods

The *ab initio* LCAO-MO method[16] was used for the study of the title species. The calculations were carried out using the GAUSSIAN92 series of programs.[17] All geometries were optimized by the gradient procedure[18] at $C_1$ symmetry (all molecular parameters optimized) at the closed-shell restricted Hartree–Fock, HF, level. Standard 6-31G** Pople's valence double-ζ basis set[19] augmented by d- and p-polarization functions was used. At the same level, all optimized structures were checked by analysis of harmonic vibrational frequencies obtained from diagonalization of force constant matrices to find the order of the stationary points.

**Table 1. Calculated Geometrical Parameters of Tricyclo[2.1.0.0$^{1,4}$]pentane (6)**

| molecular params | HF/ 6-31G** | MP2/ 6-31G** | HF/ 6-31G*$^{12a}$ | MP2/ 6-31G*$^{12b}$ |
|---|---|---|---|---|
| | | Bond Distances, Å | | |
| C1–C2; C1–C5 | 1.475 | 1.483 | 1.477 | 1.492, 1.486 |
| C1–C3; C1–C4 | 1.452 | 1.486 | 1.453 | 1.446, 1.577 |
| C2–C3; C4–C5 | 1.522 | 1.526 | 1.519 | 1.534, 1.505 |
| C3–C4 | 1.492 | 1.493 | 1.489 | 1.497 |
| | | Bond Angles, deg | | |
| 1–2–3 | 57.9 | 57.2 | 57.98 | |
| 1–3–4 | 59.1 | 59.9 | 59.17 | |
| 2–1–3 | 62.6 | 61.8 | 62.45 | |
| 2–1–5 | 193.3 | 195.7 | 193.9 | |
| 3–1–4 | 61.8 | 60.3 | 61.67 | |
| | | Torsional Angle, deg | | |
| 2–3–4–5 | 88.0 | 87.1 | 88.48 | |

**Table 2. Calculated Geometrical Parameters of Tricyclo[3.1.0.0$^{1,5}$]hexane (7)**

| molecular params | HF/6-31G** | MP2/6-31G** |
|---|---|---|
| | Bond Distances, Å | |
| C1–C2 | 1.464 | 1.465 |
| C1–C3 | 1.497 | 1.516 |
| C2–C3 | 1.527 | 1.534 |
| C3–C4 | 1.536 | 1.531 |
| | Bond Angles, deg | |
| 1–2–3 | 60.0 | 60.7 |
| 1–3–4 | 90.1 | 90.0 |
| 2–1–3 | 62.1 | 61.9 |
| 2–1–6 | 176.6 | 177.6 |
| 3–1–5 | 91.4 | 90.6 |
| 3–4–5 | 88.4 | 89.4 |
| | Torsional Angle, deg | |
| 2–3–5–6 | 89.1 | 88.5 |

To improve the predicted geometries, all three molecules were further optimized using second-order Møller–Plesset perturbation theory, MP2,[20] with the 6-31G** basis set. These calculations were carried out using the frozen-core approximation.

## Results and Discussion

The bond length and angle values calculated at the HF/6-31G** and MP2/6-31G** levels for molecules **6**–**8** are collected in Tables 1–3, together with the corresponding experimental data and previous lower-level theoretical results. The calculated HF/6-31G** level harmonic frequencies (along with IR and Raman intensities) are given in Table 4. These values for known **8** cannot be compared with experimental results since, to our knowledge, its vibrational spectra have not been reported. The calculated frequencies for **7** could provide guidance when synthesis of this hypothetical molecule is attempted. Our calculated frequencies were obtained assuming harmonic approximation without inclusion of the electron correla-

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**Table 3. Calculated and Experimental Geometrical Parameters of Tricyclo[4.1.0.0$^{1,6}$]heptane (8)**

| | calculations | | | experiment | |
|---|---|---|---|---|---|
| molecular params | HF/6-31G** | MP2/6-31G** | HF/6-31G*$^{15}$ | ref 13 | ref 14 |
| | | Bond Distances, Å | | | |
| C1−C2; C1−C7 | 1.472 | 1.476 | 1.488 | 1.645(7) | 1.481,$^{a}$ 1.487$^{b}$ |
| C1−C3; C1−C6 | 1.468, 1.472$^{c}$ | 1.481 | 1.487 | 1.519(25) | 1.477,$^{a}$ 1.487$^{b}$ |
| C2−C3; C6−C7 | 1.530, 1.527$^{c}$ | 1.536 | 1.548 | 1.526(10) | 1.537,$^{a}$ 1.546$^{b}$ |
| C3−C4; C5−C6 | 1.528, 1.535$^{c}$ | 1.531 | 1.542 | 1.521(30) | 1.526,$^{a}$ 1.536$^{b}$ |
| C4−C5 | 1.555 | 1.551 | 1.576 | 1.572(14) | 1.550,$^{a}$ 1.555$^{b}$ |
| | | Bond Angles, deg | | | |
| 1−2−3 | 58.5 | 58.9 | 58.6 | | |
| 1−3−4 | 106.5 | 105.5 | 105.3 | 107.5(13) | 105.7 |
| 2−1−3 | 62.7, 62.5$^{c}$ | 62.6 | 62.7 | 61.5(5) | 62.6 |
| 2−1−7 | 158.2 | 158.1 | 158.1 | 162.4(18) | 158.2 |
| 3−1−6 | 110.3 | 110.1 | 110.8 | 105.7(26) | 110.1 |
| 3−4−5 | 103.4, 103.6$^{c}$ | 103.3 | 103.0 | 102.3(30) | 103.4 |
| | | Torsional Angle, deg | | | |
| 2−3−6−7 | 90.2 | 90.6 | | | |

[a] No libration corrections included. [b] Libration corrected values. [c] Slightly asymmetric values have been obtained for this molecule at the 6-31G** level.

**Table 4. Calculated HF/6-31G** Level Harmonic Vibrational Frequencies (cm$^{-1}$) (IR and Raman Intensities Given in Parentheses)**

| $C_4H_6$ (**6**) | $C_6H_8$ (**7**) | $C_7H_{10}$ (**8**) |
|---|---|---|
| 80 (1, 1) | 311 (2, 1) | 192 (0, 0) |
| 441 (30, 2) | 363 (2, 1) | 316 (0, 1) |
| 689 (27, 13) | 403 (4, 3) | 378 (0, 1) |
| 828 (47, 5) | 656 (11, 12) | 439 (0, 4) |
| 913 (3, 13) | 749 (5, 1) | 614 (3, 4) |
| 915 (17, 18) | 790 (14, 21) | 618 (5, 11) |
| 989 (3, 0) | 888 (9, 2) | 744 (0, 5) |
| 1036 (26, 2) | 903 (3, 17) | 847 (14, 1) |
| 1094 (8, 14) | 933 (5, 1) | 899 (2, 7) |
| 1106 (26, 1) | 1036 (2, 13) | 903 (0, 27) |
| 1138 (6, 14) | 1046 (0, 3) | 920 (2, 1) |
| 1170 (1, 15) | 1052 (2, 20) | 976 (0, 11) |
| 1206 (6, 12) | 1105 (11, 12) | 1005 (0, 7) |
| 1253 (16, 1) | 1118 (0, 4) | 1018 (3, 10) |
| 1259 (3, 8) | 1152 (0, 8) | 1022 (0, 12) |
| 1313 (3, 0) | 1194 (6, 3) | 1096 (8, 6) |
| 1359 (0, 8) | 1209 (1, 0) | 1142 (4, 2) |
| 1441 (0, 31) | 1214 (9, 3) | 1158 (0, 4) |
| 1536 (11, 1) | 1245 (2, 7) | 1173 (0, 6) |
| 1652 (23, 8) | 1246 (3, 11) | 1204 (0, 0) |
| 1653 (1, 16) | 1308 (0, 16) | 1215 (3, 1) |
| 3243 (126, 30) | 1396 (1, 0) | 1241 (4, 3) |
| 3244 (10, 226) | 1401 (5, 5) | 1262 (4, 4) |
| 3324 (16, 130) | 1471 (0, 3) | 1276 (5, 7) |
| 3325 (22, 65) | 1570 (0, 4) | 1312 (1, 0) |
| 3338 (64, 24) | 1606 (0, 17) | 1345 (2, 11) |
| 3339 (4, 181) | 1622 (1, 10) | 1408 (1, 4) |
| | 1682 (11, 7) | 1441 (1, 2) |
| | 3192 (74, 124) | 1462 (2, 3) |
| | 3238 (34, 89) | 1484 (0, 1) |
| | 3264 (64, 65) | 1574 (0, 12) |
| | 3265 (20, 170) | 1615 (2, 16) |
| | 3310 (37, 97) | 1617 (0, 6) |
| | 3311 (27, 134) | 1633 (1, 11) |
| | 3349 (8, 132) | 1698 (7, 1) |
| | 3349 (41, 61) | 3185 (53, 33) |
| | | 3188 (41, 133) |
| | | 3228 (47, 84) |
| | | 3240 (48, 89) |
| | | 3267 (57, 51) |
| | | 3268 (20, 179) |
| | | 3305 (60, 0) |
| | | 3307 (0, 223) |
| | | 3349 (16, 118) |
| | | 3349 (34, 54) |

tion effect. Therefore, they should be scaled down by a factor of ca. 0.89[21] before being compared with the experimental anharmonic frequencies.

All our calculations were performed without imposing any symmetry constraints, and the $C_2$ symmetry obtained for **6**−**8** was the result of geometry search. With few exceptions (see Table 2), the differences between symmetry-related parameters lay within the accuracy of the calculations. However, it should be stressed that the more accurate calculations involving electron correlation always yielded more symmetrical structures. Thus, only the data describing structures of $C_2$ symmetry are given for all but one set of results,[12b] in agreement with the experimental evidence. In some cases, significantly different values were obtained for molecular parameters calculated at the HF and MP2 levels. In agreement with expectations, the largest discrepancies have been found for the smallest molecule, **6**, which exhibits the strongest distortions from standard geometry. This observation indicates that correlation energy is of importance in the stabilization of nonstandard structures. An inspection of the data collected in the Tables 1−3 reveals information for the following compounds:

**Tricyclo[2.1.0.0$^{1,3}$]pentane (6).** As noted before, this molecule was claimed by Wiberg et al. to be an intermediate in the reaction of 1,1-dibromo-2,3-bis(chloromethyl)cyclopropane with methyllithium.[12] It corresponds to a minimum energy structure, as revealed by the vibrational frequency calculations carried out by us at the HF/6-31G** level. The results of Wiberg's HF/6-31*[12a] and MP2/6-31G*[12b] calculations for **6** are also given in Table 1. His electron-correlated calculations predicted two minimum energy structures. The lower-energy structure exhibits considerable asymmetry, with the difference between C1C3 and C1C5 bond lengths being larger than 0.1 Å. We believe that there are no obvious reasons for the existence of such an asymmetric structure, nor for a C−C bond in a three-membered ring to be as long as 1.577 Å. The results of our MP2/6-31G**-level calculations do not confirm existence of such an asymmetric structure for **6**.

All bond lengths calculated by Wiberg et al. for the symmetrical structure at the HF/6-31G* level[12a] are within 0.003 Å from our HF results. Also, the bond angles calculated at the same level deviate insignificantly (less than 0.2°) from our data. The C2 carbon atom in this structure assumes a pyramidal arrangement of bonds around it, indicated by a C2C1C5 bond angle value

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(21) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Intern. J. Quantum Chem. Symp.* **1981**, *15*, 269. DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333.

larger than 180° (194°) at all levels of the previous calculations[2,12] and the present ones. Understandably, the outer cyclopropane rings point in opposite directions and the C2C3C4C5 torsional angle assumes a value of ca. 88°.

**Tricyclo[3.1.0.0$^{1,3}$]hexane (7).** The hypothetical molecule **7** is the most interesting member of the series under investigation. To our knowledge, it has not yet been studied theoretically. Both HF- and MP2-levels of the calculations revealed that this molecule is a stationary point on the potential energy surface. The vibrational frequency calculations carried out at the HF level concluded that this is a minimum energy structure. The most striking feature of **7** is virtually collinear arrangement of the C1C2 and C1C6 bonds. Therefore, the configuration at the C1 carbon seems to be an intermediate between the tetrahedral and pyramidal ones. According to the calculations presented here, a molecule with such an unusual arrangement of bonds around a carbon atom should represent a stable structure. Similar to the situation in molecule **6**, the cyclopropane rings in **7** point to the opposite directions with the C2C3C5C6 torsional angle assuming the value of ca. 89°.

**Tricyclo[4.1.0.0$^{1,3}$]heptane (8).** As mentioned before, the known molecule **8** exhibits a highly unusual value of the C2C1C7 bond angle. The determinations of its structure by older ED[13] and recent X-ray[14] studies differ significantly, with a largest bond length difference of 0.04 Å and a difference in the C2C1C7 bond angle of ca. 4°. However, to our knowledge the value of ca. 160° of the C2C1C7 angle found in both experimental works[13,14] is the largest reported in the literature, deviating enormously from the standard values for C−C−C bond angle. We believe that this important observation has not received due recognition. Both our calculations at HF and MP2 levels (6-31G** basis set) and Wiberg's calculations at the HF/6-31G* approximation[15] reproduce this value well. The results of the calculations at both HF and MP2 levels seem to better reproduce the recent, more accurate X-ray bond lengths.

## Conclusions

Both the calculations of Wiberg's group[12b,15] and our more accurate results reproduce reasonably the available experimental data for **8**. On the other hand, they differ considerably for **6**. The asymmetrical structure (with C1C3 and C1C5 differing by as much as 0.13 Å and a C−C bond in a three-membered ring as long as 1.577 Å) found for this molecule by Wiberg et al.[12b] does not correspond to the minimum at the higher level calculations reported in this paper. The most interesting results presented in this paper have been those obtained for hypothetical tricyclo[3.1.0.0$^{1,3}$]hexane (**7**), in which the C2C1C6 bond angle is equal to 178°. This bond angle value can be somewhat overestimated by the calculations. However, we expect that this system, when synthesized, will exhibit near-collinear arrangement of the C1C2 and C1C6 bonds, since **7**, having such an unusual bond angle, was found to correspond to a stationary structure at both levels of our calculations. This fact, together with the stability of **8** and the identification of **6** as an intermediate by Wiberg's group,[12] strongly suggests the possibility of the synthesis of this highly unusual molecule. Therefore, we believe that the answer to the title question is yes. A C−C−C bond angle can assume a value close to 180°.

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