



# Tricyclo[2.2.0.0<sup>1,3</sup>]hexane: a new hypothetical molecule which should have only one inverted carbon atom<sup>☆</sup>

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**Abstract**—HF and MP2 calculations with the 6-31G\*\* and 6-311G\*\* basis sets and those at MP2/cc-pVTZ level were carried out for the hypothetical tricyclo[2.2.0.0<sup>1,3</sup>]hexane. The results indicate that the molecule under study should have one carbon atom with highly unusual inverted configuration. The analysis of the vibrational frequencies of this molecule as well as the analysis of its plausible decomposition routes performed at the DFT level indicate that this unique molecule could be a plausible synthetic target.

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## 1. Introduction

The van't Hoff and LeBel hypothesis<sup>1–4</sup> on the tetrahedral arrangements of the substituents around a tetravalent carbon atom has proved its correctness for an enormous number of organic molecules. However, the synthesis of small-ring propellanes **1** by the Wiberg group<sup>5</sup> showed that in very rare cases this hypothesis may not be valid.<sup>1–6</sup> Notably, several properties of the pivotal [1.1.1]propellane **2** (in particular its remarkable stability) had been foreseen before its synthesis on the basis of quantum calculations.<sup>5</sup> This success demonstrated that theoretical calculations are an invaluable tool in studies of hydrocarbons with atypical spatial structure and that they can be applied to propose plausible synthetic targets. Such hydrocarbons not only present a considerable challenge for synthetic chemists but also they have unusual properties, e.g. nonstandard structures or chemical reactivity.<sup>1–6</sup> A long debate questioning the presence of the central bridgehead–bridgehead bond in **2** on the basis of negative values of the deformation density along this bond<sup>7</sup> illustrates the difficulties met by analyses of such peculiar molecules.

In continuation of our studies of new molecules that should

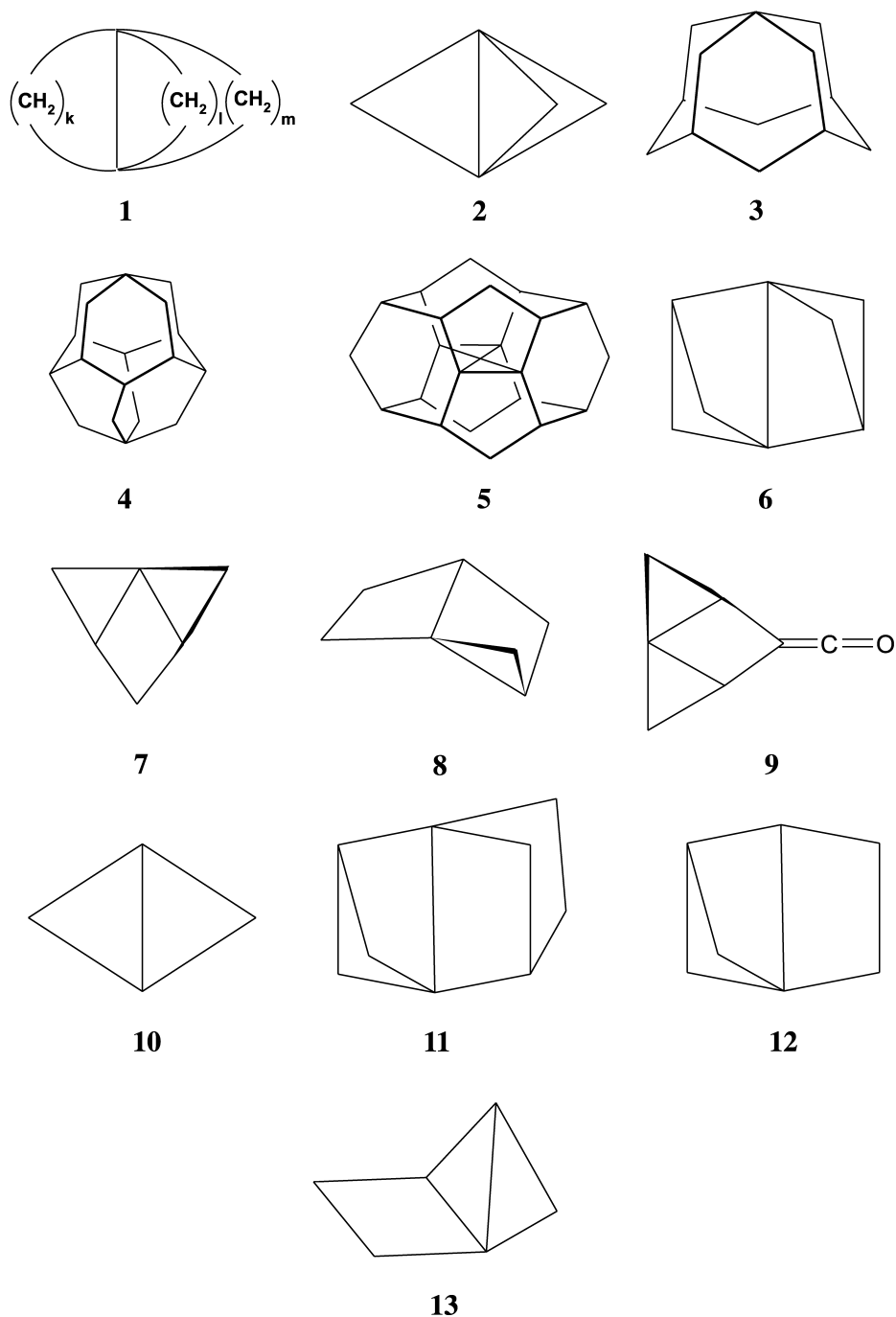
have planar, pyramidal, or inverted carbon atoms, we proposed, among others, bowlane **3**<sup>8</sup> and its higher analogue **4**<sup>9</sup> (that later lead to the polycycle **5** exhibiting the planar arrangement at the central carbon atom,<sup>5</sup>) small-ring geminanes like [1.1.1]geminane **6**,<sup>10</sup> tricyclo[3.1.0.0<sup>1,3</sup>]hexane **7**<sup>11</sup> with a CCC bond angle practically equal to 180° and tricyclo[3.2.0.0<sup>1,3</sup>]heptane **8**.<sup>12</sup> All these molecules have carbon atoms which do not obey the rules of classical stereochemistry but only the synthesis of **7** has been attempted.<sup>13</sup> Compound **9**, which like **7**, should also have one C–C–C angle of 180°, was observed by Wiberg and Snoonian<sup>13</sup> only at a very low temperature. Its synthesis paves the way to the experimental verification of the prediction of the linear arrangement of C–C–C bonds if **9** can be converted to **7**.

Few molecules possessing the inverted carbon atoms and no molecule having a pyramidal atom have been synthesized. Bicyclobutane **10** is the only molecule different from small-ring propellanes which has inverted carbon atoms.<sup>14</sup> In known hydrocarbons with unusual spatial structure **1** and **10**, the inverted atoms are always present in symmetrical pairs. We have proposed nonsymmetrical geminanes like **11** and tricyclo[3.1.1.0<sup>2,5</sup>]heptane **12**<sup>10</sup> as molecules having either nonsymmetrical pairs of inverted carbon atoms (as is in **11**) or possessing a single inverted atom in the molecule (as have been predicted for **12**) and close to the inverted configuration on one carbon atom in **8**.<sup>12</sup> In this paper, on the basis of quantum calculations it is shown that the hypothetical tricyclo[3.2.1.0<sup>1,3</sup>]hexane **13** should possess an isolated inverted carbon atom and be a plausible synthetic target.

<sup>☆</sup> Supplementary data associated with this article can be found at doi: 10.1016/j.tet.2003.10.022

**Keywords:** fused-ring systems; ab initio calculations; strained hydrocarbons; molecular modeling.

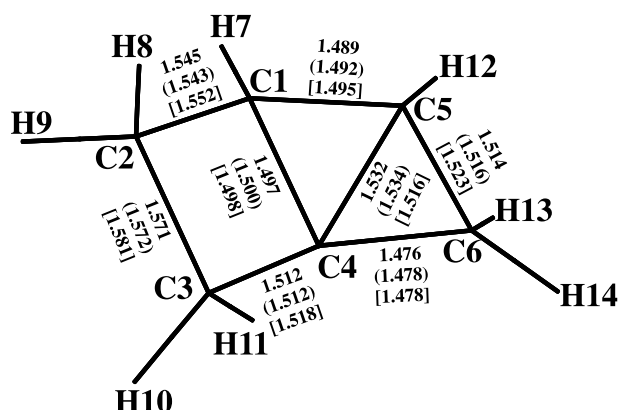
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## 2. Computational methods

HF and MP2 calculations with the 6-31G\*\* and 6-311G\*\* basis sets and MP2 calculation using the cc-pVTZ basis set were carried out for **13**. First, the calculations were performed at the HF/6-31G\*\* level, and such optimized geometries were used as initial parameters for the geometry optimizations at the HF/6-311G\*\* level, for the MP2 approximation with the 6-311G\*\* basis set and MP2/cc-pVTZ and DFT B3LYP/6-31G\*\*. In addition, DFT/B3LYP level calculations with the 6-31G\*\* basis set were carried out to analyze plausible decomposition routes of the molecule under study. The sum of bond angles  $\Sigma = \text{C1C4C5} + \text{C3C4C5} + \text{C5C4C6}$ , which should be equal to

$270^\circ$  for the intermediate structure between tetrahedral and pyramidal arrangement of bonds around C4 atom was calculated for each structure since it should assume a value of ca.  $327^\circ$  for the former, typical arrangements of bonds and will be less than  $270^\circ$  for the latter one. To examine possible decomposition routes of **13**, all the C–C bond lengths were changed by the increments of 0.05 Å (in separate runs) from their equilibrium distances. After each incremental change all remaining molecular parameters were reoptimized by DFT B3LYP/6-31G\*\* calculations and the best obtained structures were fully optimized. All geometry optimizations were carried out using the GAUSSIAN 98 program package.<sup>15</sup> Only real values of the analytical harmonic vibrational frequencies confirmed



**Figure 1.** The calculated bond lengths of **13** at the MP2/6-311G\*\*, MP2/cc-pVTZ (in parentheses) and B3LYP/6-31G\*\* (in square brackets) levels.

**Table 1.** The calculated bond angles,  $\Sigma = \text{C1C4C5} + \text{C3C4C5} + \text{C5C4C6}$  values, and minimum energies for **13**

| Method/basis set | HF/6-311G** | MP2/cc-pVTZ | DFT<br>(B3LYP/6-31G**) |
|------------------|-------------|-------------|------------------------|
| Angles           |             |             |                        |
| C1C4C5           | 60.2        | 58.9        | 59.5                   |
| C3C4C5           | 116.1       | 112.3       | 115.2                  |
| C5C4C6           | 61.6        | 60.4        | 61.1                   |
| $\Sigma$         | 237.9       | 231.6       | 235.8                  |
| C1C2C3C4         | 2.7         | 0.1         | 1.8                    |
| C2C3C4C5         | 56.3        | 58.0        | 56.5                   |
| C2C3C4C6         | 134.4       | 127.4       | 131.9                  |
| <i>E</i> (a.u.)  | -231.739    | -232.799    | -233.334               |

that **13** corresponds to the minimum-energy structure. NMR isotropic magnetic shieldings were calculated by the GIAO method.<sup>16,17</sup>

### 3. Results and discussion

The calculated bond lengths at the MP2/6-311G\*\*, MP2/cc-pVTZ and B3LYP/6-31G\*\* levels for the titled molecule are shown in Figure 1. The total energies and the most important values of bond angles are given in Table 1 while the calculated <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are shown in Table 2. Cartesian coordinates of the optimized MP2/cc-pVTZ structure of **13**, harmonic frequencies, IR intensities, reduced masses, force constants, normal coordinates and the structures of the most plausible decompositions products **15** and **16** calculated at DFT level are given in Supplementary Material.

The bond lengths calculated at different levels of theory (Fig. 1) reveal the same trends. In the bicyclobutane fragment, the bridgehead–bridgehead C4C5 bond is slightly

extended in **13** as compared to the corresponding value in bicyclobutane **10** (153.2 vs 151.4 pm at the MP2/6-311G\* level, respectively) while C1C5 and C4C6 are slightly shortened (148.9 and 147.6 pm, respectively, at the MP2/6-311G\* level) in comparison to the value of 149.9 pm in **10**. Understandably, the C1C4 bond in the cyclobutane ring of **13** is considerably shortened in comparison to the standard cyclobutane value of 155.1 pm. The C1C2 and C3C4 bonds are shortened to a smaller extent while the C2C3 bond is somewhat extended (all in comparison to the standard cyclobutane value).

As mentioned in the Section 2, a value of the  $\Sigma$  parameter (equal to the sum of the C1C4C5, C3C4C5 and C5C4C6 bond angles) indicates whether the configuration at the quaternary C4 atom is close to the tetrahedral or pyramidal configuration. The intermediate case is characterized by  $\Sigma = 270^\circ$ . The  $\Sigma$  values given in Table 1 are significantly smaller than this value and they slightly decrease when the larger basis sets and higher level of theory are applied. Therefore, **13** is expected to have an inverted configuration at the C4 carbon atom.

The calculated values of the harmonic vibrational frequencies and intensities (given in Supplementary Material) revealed that only positive values were calculated for **13**. Thus, the calculated structure represents the minimum on the potential energy surface. It will be interesting to compare the calculated NMR shifts for **13** collected in Table 2 with the experimental values after the synthesis of this molecule to check whether the existing methods of the shifts prediction are sufficiently accurate for hydrocarbons with unusual spatial structures.

To get an insight into the kinetic stability of **13**, the dependence of its minimized energy on the elongation of all CC bonds was studied using B3LYP/6-31G\*\* calculations. The corresponding bond lengths were changed in increments of 0.05 Å from the optimum values given in Figure 1 to 3.5 Å. This was followed by full geometry optimization and vibrational frequency calculations for the best obtained structures. Only the extensions of C1C5, C2C3 and C4C5 bonds yielded structures of lower energy than the starting one with the barriers of ca. 42.8, 49.2 and 64.1 kcal/mol (Figs. 2–4). Out of these structures, the one with the lowest barrier **14** led to an apparently unstable structure of the decomposition product (Fig. 2). Thus, since the barrier is equal to ca. 49.2 kcal/mol for the most admissible stable decomposition product **15** (Fig. 3), the title tricyclo[2.2.0.0<sup>1,3</sup>]hexane **13** is expected to be reasonably stable. Interestingly, the distortion of one of the most strained bonds in the molecule under study, C1C4 one, was accompanied by quite a high the barrier of ca. 91 kcal/mol probably due to an unfavorable orientation of the hydrogen atom at C1 for  $\Delta L$  equal to 1.25 Å. In our previous paper,<sup>12</sup> we proposed that tricyclo[3.2.0.0<sup>1,3</sup>]heptane **8** composed of

**Table 2.** Calculated GIAO/MP2/cc-pVTZ values of chemical shifts for **13** relative to TMS<sup>a</sup> (ppm)

| Atom           | C1    | C2    | C3    | C4    | C5   | C6    | H7   | H8   | H9   | H10  | H11  | H12   | H13  | H14  |
|----------------|-------|-------|-------|-------|------|-------|------|------|------|------|------|-------|------|------|
| $\delta$ (ppm) | 57.50 | 28.10 | 31.10 | 19.15 | 5.20 | 50.17 | 2.68 | 1.84 | 2.06 | 2.64 | 2.00 | -0.79 | 1.94 | 2.82 |

<sup>a</sup> Calculated isotropic shieldings of TMS at MP2/cc-pVTZ level equal to 195.16 ppm (C) and 32.10 ppm (H).

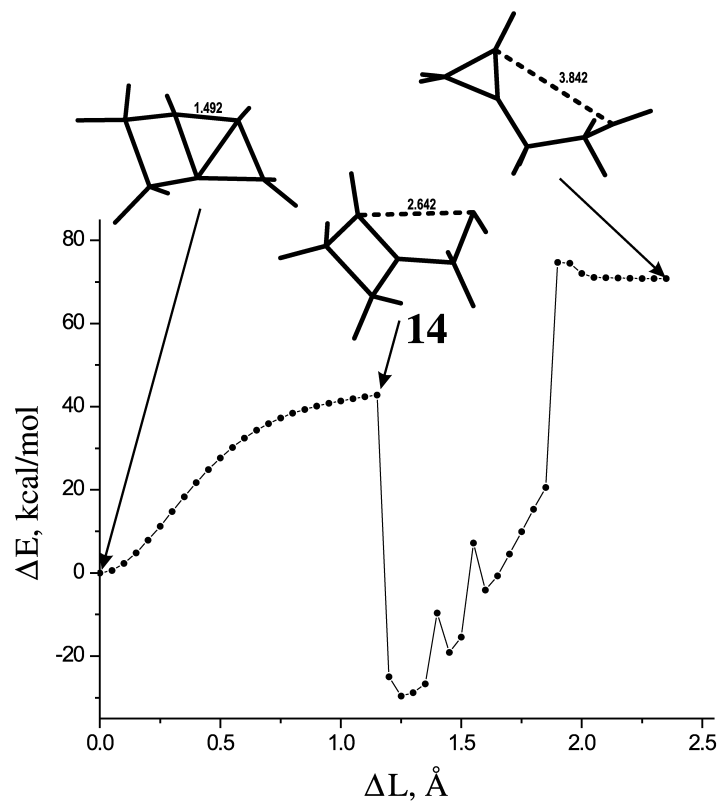


Figure 2. The dependence of the DFT (B3LYP/6-31G\*\*) energy of **13** on the elongation of C1–C5 bond from the starting value of 1.492 Å.

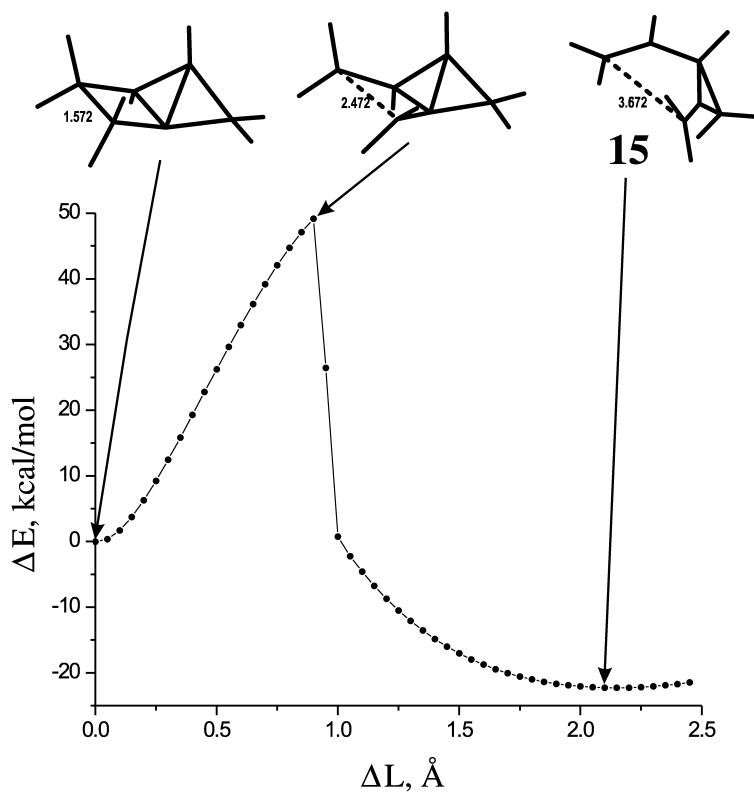


Figure 3. The dependence of the DFT (B3LYP/6-31G\*\*) energy of **13** on the elongation of C2–C3 bond from the starting value of 1.572 Å.

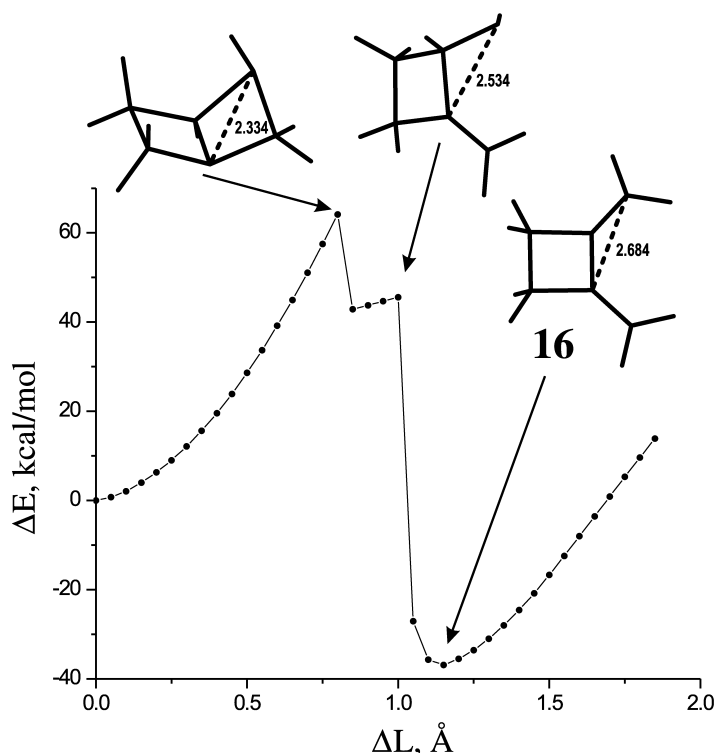


Figure 4. The dependence of the DFT (B3LYP/6-31G\*\*) energy of **13** on the elongation of C4–C5 bond from the starting value of 1.534 Å.

bicyclo[2.1.0]pentane fused with a four-membered ring should have one carbon atom with the configuration close to the intermediate one between the tetrahedral and pyramidal configurations. From this study, one can see that the analogous fusion of the smaller bicyclo[1.1.0]butane with the same four-membered ring forces a flattened pyramidal configuration on the atom common to all three rings.

These results and the analysis of the dependence of the energy of **13** upon distortions of all C–C bonds indicate that **13**, having quite an unusual configuration at the quaternary carbon atom, could be a plausible synthetic target. Recent advances in the stabilization of short-lived species in ‘molecular flasks’<sup>18</sup> might pave the way to the observation of this exciting hydrocarbon, even though it could be not very stable.

#### 4. Conclusion

The results of ab initio calculations at different levels of theory indicate that tricyclo[2.2.0.0<sup>1,3</sup>]heptane **13** should have a very unusual structure. Namely, it should possess an isolated inverted carbon atom. This finding as well as the analysis of the plausible routes of decomposition of the titled molecule indicate that **13** could be a plausible synthetic target. It should be stressed that no organic molecule having an isolated inverted carbon atom is known.

#### Acknowledgements

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#### References

- Liebman, J. F.; Greenberg, A. *Strained Organic Molecules*; Academic: New York, 1978.
- A special issue devoted solely to molecules, mainly hydrocarbons with unusual spatial structure appeared in *Chem. Rev.* **1989**, 89, 5.
- Dodziuk, H. *Top. Stereochem.* **1994**, 21, 351–380.
- Dodziuk, H. *Modern conformational analysis. Elucidating Novel Exciting Molecular Structures*; VCH: New York, 1995.
- Radom, L.; Rasmussen, D. R. *Pure Appl. Chem.* **1998**, 70, 1977–1984.
- Wiberg, K. B. *Chem. Rev.* **1989**, 89, 975–983.
- Chakrabati, P.; Seiler, P.; Dunitz, J. D.; Schlüter, A.-D.; Szeimies, D. *J. Am. Chem. Soc.* **1981**, 103, 7378–7380.
- Dodziuk, H. *J. Mol. Struct.* **1990**, 239, 167–172.
- Dodziuk, H.; Lipkowitz, H. A communication to the 2nd WATOC Congress; Toronto, Canada, 1990.
- (a) Dodziuk, H. *Tetrahedron* **1988**, 44, 2951–2955. (b) Dodziuk, H.; Leszczynski, J.; Jackowski, K. *J. Org. Chem.* **1999**, 64, 6177–6181.
- Dodziuk, H.; Leszczynski, J.; Nowinski, K. S. *J. Org. Chem.* **1995**, 60, 6860–6863.
- Dodziuk, H.; Dolgonos, G.; Leszczynski, J. *Tetrahedron* **2003**, 59, 2561–2565.
- Wiberg, K. B.; Snoonian, J. R. *J. Org. Chem.* **1998**, 63, 1390–1401.
- Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, 94, 767–773.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford,

S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.;

Replogle, E. S.; Pople, J. A. GAUSSIAN; Inc., Pittsburgh, PA, 1998.

16. Schindler, M.; Kutzelnigg, W. *Mol. Phys.* **1983**, *48*, 781–798.
17. Helgaker, T.; Jaszunski, M.; Ruud, K. *Chem. Rev.* **1999**, *99*, 293–352.
18. (a) Dodziuk, H. *Introduction to Supramolecular Chemistry*; Kluwer Academic: Dordrecht, 2002; p 196 and ff. (b) Dodziuk, H. *Int. J. Mol. Sci.* **2002**, *3*, 814–821.