

A quantum chemical study of tricyclo[3.2.0.0^{1,3}]heptane: a new hypothetical molecule with unusual spatial structure. Similarities and differences with *syn*- and *anti*-tricyclo[3.2.0.0^{2,4}]heptanes

H. Dodziuk,^{a,*} G. Dolgonos^a and J. Leszczynski^{b,*}

^aInstitute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

^bComputational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, Jackson, MS 39217, USA

Received 9 September 2002; revised 8 January 2003; accepted 13 February 2003

Abstract—HF and MP2 calculations with the 6-31G** and 6-311G** basis sets for the titled molecules and those at MP2/cc-pVTZ level for the hypothetical tricyclo[3.2.0.0^{1,3}]heptane indicate that the latter molecule should have a carbon atom with highly unusual configuration strongly departing from the tetrahedral one. Both analysis of vibrational frequencies of this molecules and comparison of its energy with those of known isomeric *syn*- and *anti*-tricyclo[3.2.0.0^{2,4}]heptanes as well as the DFT analysis of its plausible decomposition routes performed at the DFT level indicate that it could be a plausible synthetic target. © 2003 Published by Elsevier Science Ltd.

1. Introduction

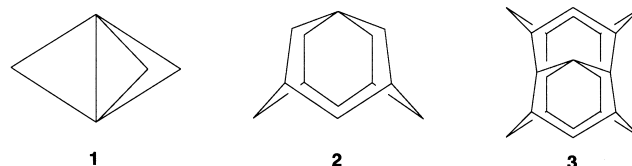
An interest in saturated hydrocarbons having carbon atoms strongly departing from the tetrahedral arrangements of the substituents began to emerge approximately one hundred years after the formulation of the hypothesis of van't Hoff and LeBel.^{1–6} The syntheses of several exciting molecules followed, accompanied by model calculations. A major breakthrough in this development was the synthesis of molecules with inverted carbon atoms like [1.1.1]propellane **1** by the Wiberg group who showed that the properties of such nonstandard hydrocarbons could be predicted on the basis of quantum chemical calculations.⁶ The latter success has proved that theoretical methods can be used to propose plausible synthetic targets. It should be stressed that studies of saturated hydrocarbons having carbon atoms with arrangements of substituents strongly departing from the tetrahedral distribution are of importance both from theoretical and synthetic points of view. First, they usually present considerable challenges for synthetic chemists. Secondly, such molecules exhibit unusual properties, e.g. atypical structures or chemical reactions.² Thirdly, by studying them one could address a fascinating question: to what extent can a bond be distorted without being broken?

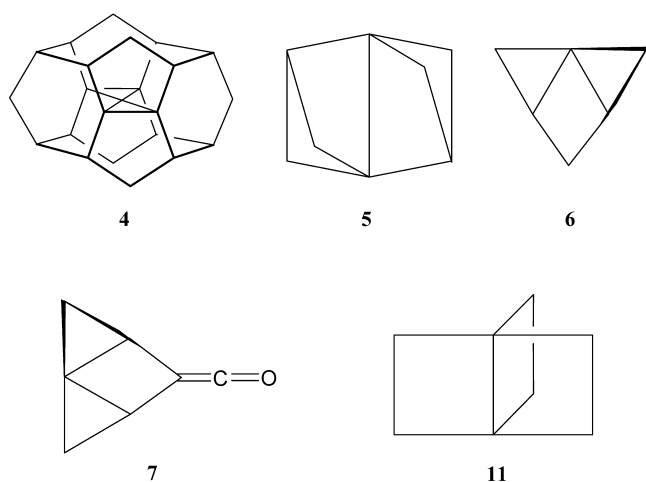
In the quest for new molecules that should have planar, pyramidal, or inverted carbon atoms, we propose, among others, bowlane **2**⁷ and its higher analogue **3**⁸ (that later lead to the polycycle **4** exhibiting the planar arrangement at the central carbon atom⁵), small-ring geminanes like [1.1.1]propellane **5**⁹ and tricyclo[3.1.0.0^{1,3}]hexane **6**¹⁰ that should have a CCC bond angle very close to 180°. The latter value contradicts the foundations of classical stereochemistry. Compound **7**, which should also have such an angle, was observed by Wiberg and Snoonian¹¹ only at very low temperature. Thus, an experimental verification of the linear arrangement of C–C–C bonds will be possible after **7** is converted to **6**.

Of the possible isomers of tricyclo[3.2.0.0]heptanes which we have analyzed by molecular mechanics,¹² **8–10** were characterized by low steric energy. The hypothetical tricyclo[3.2.0.0^{1,3}]heptane **8** exhibited pyramidal quaternary carbon atom while *syn*-**9**¹³ and *anti*-**10**¹⁴ isomers of tricyclo[3.2.0.0^{2,4}]heptane are known although poorly characterized. Therefore, it is of interest to study the molecule **8** by reliable quantum mechanical methods and compare the results obtained with those for **9** and **10**.

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

* Corresponding authors. Address: Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland. Tel.: +48-226323221; fax: +48-39120238; e-mail: dodziuk@ichf.edu.pl; jerzy@ccmsi.jsu.edu.





2. Computational methods

HF and MP2 calculations with the 6-31G** and 6-311G** basis sets were carried out for all titled compounds, while MP2 calculation using the cc-pVTZ basis set was performed only for **8**. 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 and for the MP2 approximation with the 6-311G** basis set and MP2/cc-pVTZ and DFT B3LYP/6-31G** calculations for **8**. In addition, DFT/B3LYP level calculations with the 6-31G** basis set were performed for **8–10**. The sum of bond angles $\Sigma=C2C1C6+C4C1C6+C6C1C7$ which should be equal to 270° for the intermediate structure between tetrahedral and pyramidal arrangement of bonds around C1 atom was calculated for each structure since it should assume the value of ca. 327° for the former, typical arrangements of bonds and will be less than 270° for the latter one. Possible routes of decomposition of **8** were investigated. Each of the C1–C4, C1–C6 and C1–C7 bond lengths was changed by the increments of 0.05 \AA (in separate runs) from their equilibrium distances. After each incremental change all remaining molecular parameters were reoptimized by DFT B3LYP/6-31G** calculations. The best obtained structures were fully optimized. All geometry optimizations were carried out using the GAUSSIAN 98 program package.¹⁵ Only real values of the analytical harmonic vibrational frequencies confirmed that the isomers under study correspond to the minimum-energy structures. NMR isotropic magnetic shieldings were calculated by GIAO method.^{16,17}

3. Results and discussion

The calculated bond lengths at the MP2/6-311G** level for molecules **8–10** are shown in Figure 1 together with the corresponding values for **8** obtained at the MP2/cc-pVTZ (given in parentheses) and B3LYP/6-31G** (given in square brackets) levels. The total energies and the most important values of bond angles are given in Table 1. The calculated vibrational frequencies are collected in Table 2, while the ^1H and ^{13}C NMR chemical shifts are shown in Table 3.

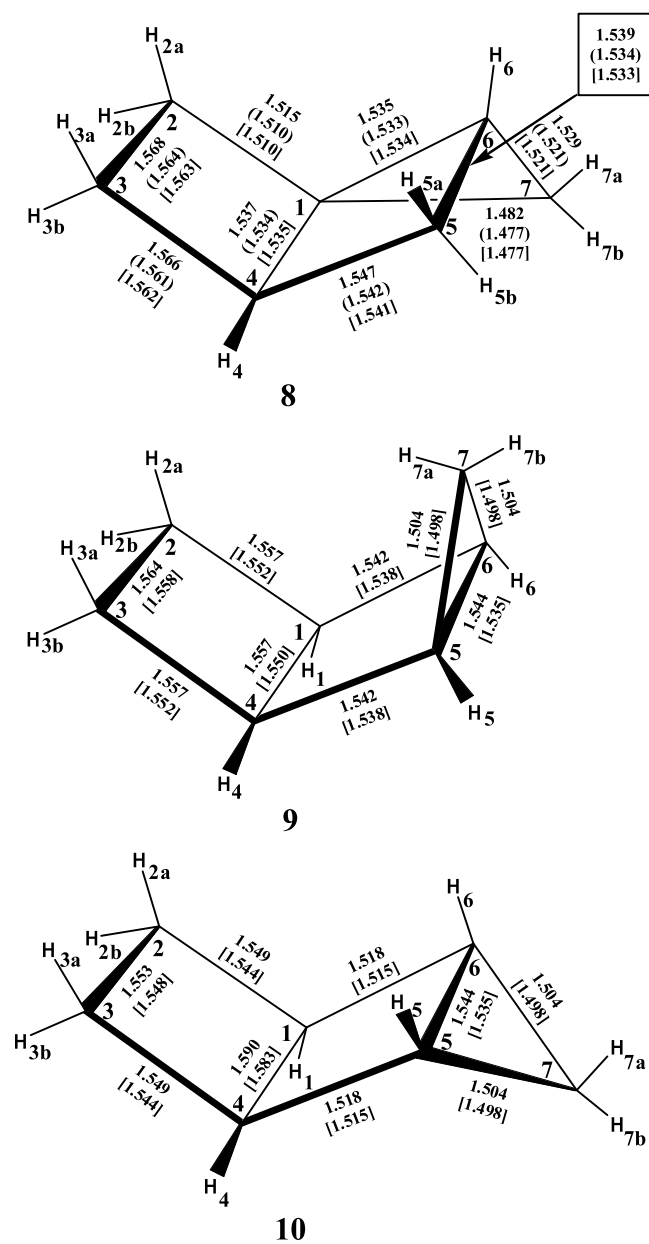


Figure 1. The calculated bond lengths for the molecules **8–10** at the MP2/6-311G** and B3LYP/6-31G** (in square brackets) levels and those calculated for **8** at the MP2/cc-pVTZ (in parentheses) level.

Finally, the calculated energy differences between isomeric molecules **8–10** are given in Table 4.

As mentioned before, **8** is a hypothetical molecule. *syn*-**9**¹³ and *anti*-**10**¹⁴ are known but no data describing their geometry have been reported. Therefore, only the trends in the geometrical parameters among the latter molecules will be discussed. As concerns bond lengths, significantly larger values of the C1C4 and C1C6 bond lengths were obtained for **9** than for **10**. C1C2, C1C6 and C5C6 bond length are calculated smaller in **8** than in **9** while the opposite trend was found for C3C4 and C4C5 bonds. The bond lengths for **8** calculated at the MP2/cc-pVTZ level are slightly smaller than those obtained at the MP2/6-311G** level. The presence of the quaternary C1 atom with arrangements of substituents strongly departing from the tetrahedral

Table 1. The calculated bond angles, $\Sigma=C2C1C6+C4C1C6+C6C1C7$ values, and minimum energies for molecules **8–10**

Method/basis set	HF/6-311G**	MP2/6-311G**	MP2/cc-pVTZ	DFT (B3LYP/6-31G**)
Compound 8				
Angle				
C2C1C6	128.7	128.5	127.6	127.5
C4C1C6	89.6	88.6	88.5	88.4
C6C1C7	61.0	60.9	60.7	60.7
Σ	279.3	278.0	276.8	276.6
C6C1C4H4	−72.4	−76.3	−76.7	−77.0
C2C1C6H6	−39.2	−40.3	−39.6	−39.6
<i>E</i> (a.u.)	−270.843	271.862	−272.041	272.671
Compound 9				
Angle				
H1C1C6H6	−16.1	−16.6	−	−16.6
<i>E</i> (a.u.)	−270.845	−271.862	−	−272.672
Compound 10				
Angle				
H1C1C6H6	−90.2	−90.2	−	−90.3
<i>E</i> (a.u.)	−270.862	−270.878	−	−272.686

Table 2. The calculated (MP2/6-311G**) frequencies and relative intensities for molecules **8–10**

8	<i>syn-9</i>	<i>anti-10</i>
187.2 (0.2)	206.5 (0.1)	75.1 (0.0)
276.7 (0.7)	320.3 (0.2)	276.9 (0.2)
370.4 (0.2)	344.8 (0.0)	336.8 (0.8)
383.6 (0.4)	517.3 (0.7)	480.8 (0.4)
561.5 (1.5)	638.7 (0.1)	603.2 (0.0)
644.3 (3.5)	724.6 (9.6)	744.1 (0.2)
709.5 (3.0)	737.1 (0.9)	770.1(9.4)
788.8 (1.5)	744.4 (4.2)	778.9 (7.3)
791.9 (1.7)	800.4 (2.1)	824.4 (1.3)
855.6 (3.9)	881.1 (8.6)	831.0 (1.5)
880.5 (4.4)	896.2 (3.9)	923.6 (4.4)
914.2 (0.8)	900.4 (3.1)	942.7 (6.3)
929.2 (0.8)	929.5 (1.9)	943.2 (0.5)
957.2 (1.0)	946.5 (0.2)	989.5 (0.8)
960.9 (2.1)	970.6 (1.0)	1004.7 (2.3)
1017.8 (0.9)	999.6 (2.4)	1029.3 (1.0)
1035.2 (0.9)	1028.5 (7.8)	1039.7 (1.2)
1053.8 (6.4)	1056.1 (0.1)	1059.9 (1.2)
1080.9 (2.3)	1062.6 (0.8)	1082.8 (2.0)
1095.7 (1.0)	1091.6 (4.3)	1087.3 (3.4)
1136.8 (0.5)	1104.0 (0.9)	1104.7 (2.3)
1183.0 (1.0)	1115.6 (1.9)	1143.9 (2.2)
1191.5 (1.2)	1153.4 (1.6)	1167.8 (1.0)
1214.6 (0.3)	1181.9 (1.8)	1193.9 (1.1)
1232.5 (1.3)	1193.6 (2.4)	1219.6 (0.4)
1245.8 (0.7)	1228.6 (0.4)	1240.0 (0.1)
1268.7 (1.6)	1248.2 (0.9)	1257.9 (0.1)
1279.4 (8.7)	1255.9 (1.9)	1270.6 (3.5)
1290.4 (0.7)	1281.1 (0.1)	1278.8 (3.0)
1324.1 (0.3)	1309.8 (6.4)	1319.9 (2.0)
1428.7 (0.9)	1327.9 (1.6)	1338.2 (4.9)
1482.9 (0.6)	1368.8 (0.4)	1373.8 (0.5)
1492.2 (4.4)	1482.1 (2.4)	1485.5 (1.6)
1504.3 (0.6)	1498.9 (4.1)	1504.0 (2.3)
1521.2 (4.2)	1518.2 (6.9)	1511.1 (4.5)
3071.3 (57.2)	3092.5 (32.7)	3089.3 (23.4)
3078.8 (45.0)	3098.1 (39.0)	3096.1 (53.8)
3094.8 (33.5)	3136.0 (18.8)	3103.4 (54.3)
3102.0 (50.2)	3147.5 (19.6)	3114.9 (38.5)
3133.9 (23.4)	3151.7 (2.1)	3145.3 (17.9)
3140.5 (24.9)	3165.1 (8.5)	3147.6 (0.7)
3145.5 (12.9)	3169.6 (61.2)	3167.4 (50.9)
3170.3 (40.9)	3208.5 (18.9)	3200.0 (19.4)
3205.2 (14.5)	3218.6 (17.0)	3210.3 (12.6)
3238.5 (11.9)	3256.6 (12.2)	3252.1 (12.5)

configuration (see below) causes significant changes in bond lengths of **8** in comparison to **9** and **10**. The most important differences include a considerable shortening of the C1–C2 bond and changes in the bond lengths in the cyclopropane ring. In the latter, a very low value of the C1–C7 bond length and a relatively high value of the C1–C6 and C6–C7 bond lengths are remarkable.

Table 3. The calculated (GIAO/MP2/631G**) and experimental chemical shifts molecules **8–10** relative to TMS (ppm)

Atom	8 , Calcd	<i>syn 9</i>				
		Calcd	Exp. ^a	Calcd	Exp. ^a	Exp. ¹⁴
C1	34.32	34.91	31.60	41.26	39.88	
C2	32.72	25.62	23.17	27.52	25.31	
C3	33.27	as C2		as C2		
C4	36.67	as C1		as C1		
C5	32.13	20.63	17.52	22.07	19.69	
C6	15.81	as C5		as C5		
C7	21.66	9.73	7.37	14.33	12.27	
H1	–	2.69	2.97	2.51	2.35	2.32
H2a	2.16	1.89	1.80	2.11	2.05	2.05 ^b
H2b	2.9	2.00	1.80	2.42	2.35	2.32
H3a	2.45	as H2a		as H2a		
H3b	2.45	as H2b		as H2b		
H4	2.23	as H1		as H1		
H5	–	1.85	1.80	1.69	1.60	1.59 ^b
H5a	1.97	–		–		
H5b	1.77	–		–		
H6	1.38	as H5		as H5		
H7a	0.94	1.96	1.80	0.70	0.65	0.65
H7b	1.03	0.67	0.62	0.32	0.25	0.23

Calculated isotropic shieldings of TMS at MP2/6-31G** level equal to 207.55 ppm (C) and 31.96 ppm (H).

^a The data from Ref. 13 assigned according to our calculations.

^b The assignment of these signals is reversed on the basis of our calculations.

Table 4. The calculated relative energies (kcal/mol) between the most stable **10** and other molecules under study

Method/basis set	10	9	8
HF/6-311G**	0.00	10.73	12.00
MP2/6-311G**	0.00	9.86	10.17
B3LYP/6-311G**	0.00	9.12	9.95

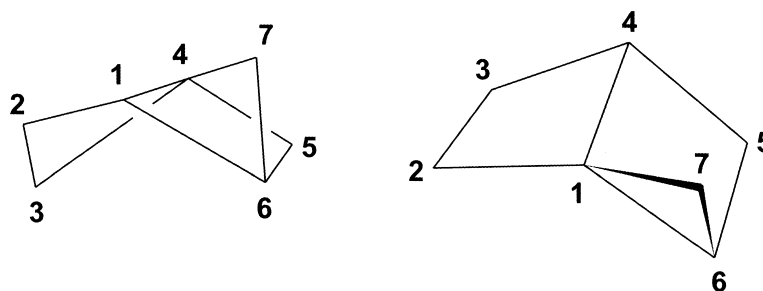


Figure 2. Two projections of the optimized MP2/cc-pVTZ structure of **8**.

As mentioned in Section 2, a value of the Σ parameter (equal to the sum of the C2–C1–C6, C4–C1–C6, and C6–C1–C7 bond angles) indicates whether the configuration at the quaternary C1 atom is close to the tetrahedral or the pyramidal configuration. The intermediate case is characterized by $\Sigma=270^\circ$. The Σ values given in Table 1 are slightly bigger than this value but decrease when the larger basis sets and higher level of theory are applied. Therefore, **8** is expected to have a configuration at the C1 carbon atom that is very close to the intermediate case between the tetrahedral and pyramidal arrangements of bonds around it similar to those in **6** and **11**. This configuration is clearly seen in the projection shown on the left side of Figure 2.

An analysis of the harmonic vibrational frequencies reveals that only real frequencies were calculated for **8**–**10**. Thus, the calculated structures represent the minima on the potential energy surfaces. The predicted vibrational frequencies and intensities for **9** and **10** are given in Table 2 but cannot be compared with the reported experimental data since the experimental data were obtained from the old solution spectra of low resolution.

To get an insight into the kinetic stability of **8**, the dependence of its minimized energy on the elongation of C1–C4, C1–C6 and C1–C7 bonds was studied. The corresponding bond lengths were changed in the increments of 0.05 Å from the optimum values of 1.534, 1.534 and 1.477 Å, respectively, to 3.034 Å for the first two bonds and

to 2.977 Å for the third one. This was followed by full geometry optimization and vibrational frequency calculations for the best obtained structures. The lengthening of the C1–C6 and C1–C7 bonds did not result in stable structures while that of C1–C4 produced a shallow minimum corresponding to a more stable structure **12** (Fig. 3) than that of **8** by 8.71 kcal/mol with the transition state **13** at C1–C4 distance of 2.534 Å lying by 56.9 kcal/mol higher than **8**. Thus, the latter molecule is expected to be a stable molecule. Interestingly, the value of 56.9 kcal/mol corresponding to the barrier of decomposition of **8** is slightly smaller than the energy of one C–C bond although two bonds are broken in **13** in comparison to **8**.

The calculated NMR shifts for **9** and **10** are collected in Table 3 and compared with the corresponding experimental data. The results of the calculations are in semiquantitative agreement with the data reported by Roth et al.¹³ who did not give the signal assignments. They also indicate that the tentative old assignment by the Tanida group¹⁴ has to be changed.

The stabilities of **8** and **9** relative to the most stable **10** are shown in Table 4. In all calculations, the former molecule was found to be only slightly less stable than known **9** and the energy difference diminishes at higher levels of the calculation. These results and the analysis of the dependence of the energy of **8** upon distortions of C1–C4, C1–C6 and C1–C7 bonds indicate that **8**, having a quite unusual

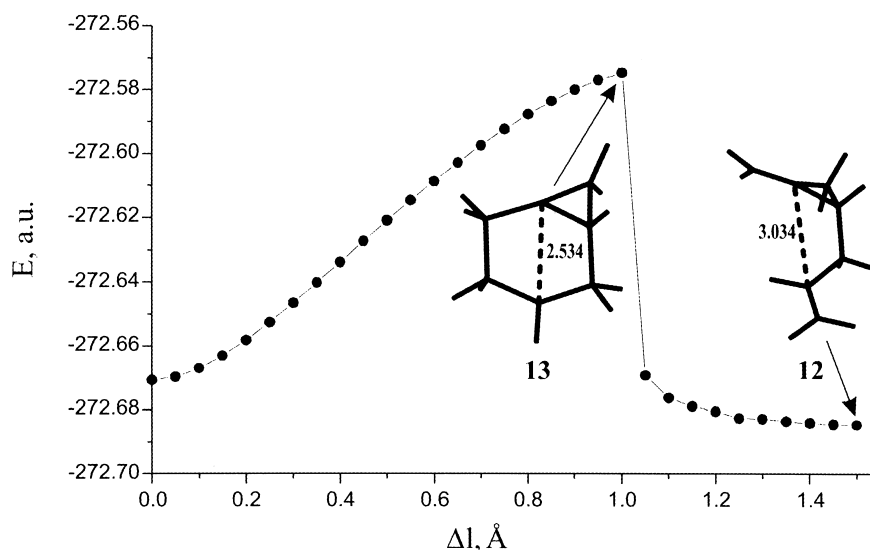


Figure 3. The dependence of the DFT (B3LYP/6-31G**) energy of **8** on the elongation of C1–C4 bond.

configuration at the quaternary carbon atom, could be a plausible synthetic target. Recent advances in the stabilization of short-lived species in ‘molecular flasks’¹⁸ might pave the way to the observation of this species, even though it will be not very stable.

4. Conclusion

The results of ab initio calculations at different levels of theory indicate that tricyclo[3.2.0.0^{1,3}] heptane **8** has a quaternary carbon atom with a very unusual configuration. This configuration is very close to the intermediate configuration between the tetrahedral and pyramidal ones. At all applied levels the relative energy of **8** is only slightly higher than the energy predicted for the stable isomer **9**. This finding as well as the analysis of the plausible routes of decomposition of **8** indicate that this unusual molecule could be a plausible synthetic target.

Acknowledgements

This project was supported by NSF EPSCoR grant.

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.
- Dodziuk, H. *J. Mol. Struct.* **1990**, 239, 167–172.
- Dodziuk, H.; Lipkowitz H. A communication to the Second 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.
- Wiberg, K. B.; Snoonian, J. R. *J. Org. Chem.* **1998**, 63, 1390–1401.
- Ref. 4, pp 90–93.
- Roth, W. R.; Klärner, F.-G.; Grimme, W.; Köser, H. G.; Bush, R.; Muskulus, B.; Breuckmann, R.; Scholz, B. P.; Lennartz, H. W. *Chem. Ber.* **1983**, 116, 2717–2737.
- Tanida, H.; Teratake, S.; Hata, Y.; Watanabe, M. *Tetrahedron Lett.* **1969**, 5345–5347.
- 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.
- Schindler, M.; Kutzelnigg, W. *Mol. Phys.* **1983**, 48, 781–798.
- Helgaker, T.; Jaszunski, M.; Ruud, K. *Chem. Rev.* **1999**, 99, 293–352.
- (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.