ORGANIC
LETTERS

2004
Vol. 6, No. 4
589−592

[*N*]Chalcogena[*N*]pericyclynes: DFT Studies on Binaric Carbon–Chalcogen Compounds

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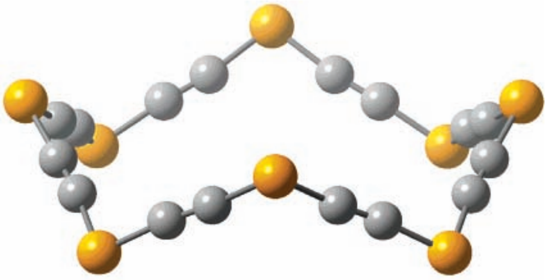
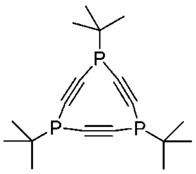
Received December 10, 2003

ABSTRACT



DFT studies on [*N*]chalcogena[*N*]pericyclynes (*n* = 3–6, 8) demonstrate their relative stability and hence their possible existence as stable species. By minimizing repulsive interactions between the chalcogens' lone pairs, the molecules adopt structures that resemble, in shape, cycloalkanes or elemental chalcogens. [3]Chalcogena[3]pericyclynes may be interconverted with their valence tautomers, benzene derivatives with three fused three-membered rings.

Highly symmetric compounds have attracted the interest of chemists for decades. One motivation behind the interest in these compounds is certainly their aesthetic appearance. Many of them are formed by the repetitive arrangement of subunits. Examples are shape-persistent macrocycles,[1] beltphanes,[2] radialenes,[3] or even pericyclynes,[4] just to name a few of them. The term [*N*]pericyclyne connotes the presence of *n* acetylene functionalities on every side of the ring.[4] Furthermore, the numeral prefix [*N*] indicates the number of corners that are saturated moieties, e.g., CMe_2,[5] PR,[6] or S. From a synthetic as well as theoretical point of view, these rather simple molecules are challenging and attractive research targets. In many cases, these cycles are characterized by strong electronic interactions between the subunits.[4,6] In some cases, especially with carbon,[4,5] silicon,[7] and phosphorus[6] as bridging atoms, their synthesis was successful (e.g., **1**). Other pericyclynes such as the tetracation **2** were only investigated by theoretical methods.[8]



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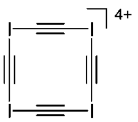

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Attempts to synthesize S_4C_8 have also been in vain.[9] Nevertheless, recently, acyclic oligoacetylenic sulfides with bulky protecting groups have been investigated spectroscopi-

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[1] Reviews: (a) Höger, S. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2685−2698. (b) Grave, C.; Schlüter, A. D. *Eur. J. Org. Chem.* **2002**, 3075−3098.

[2] (a) Haberhauer, G.; Rominger, F.; Gleiter, R. *Angew. Chem.* **1998**, *110*, 3632−3634; *Angew. Chem., Int. Ed.* **1998**, *37*, 3376−3377. (b) Schaller, R. J.; Gleiter, R.; Hofmann, J.; Rominger, F. *Angew. Chem.* **2002**, *114*, 1231−1234; *Angew. Chem., Int. Ed.* **2002**, *41*, 1181−1183.

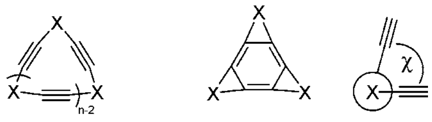
[3] (a) Hopf, H.; Mass, G. *Angew. Chem.* **1992**, *104*, 953−977; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 931−954. (b) Lepetit, C.; Nielsen, M. B.; Diederich, F.; Chauvin, R. *Chem. Eur. J.* **2003**, *9*, 5056−5066.

[4] (a) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1983**, *105*, 7760−7761. (b) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1985**, *107*, 6546−6555. (c) Houk, K. N.; Scott, L. T.; Rondan, N. G.; Spellmeyer, D. C.; Reinhardt, G.; Hyun, J. L.; DeCicco, G. J.; Weiss, R.; Chen, M. H. M.; Bass, L. S.; Clardy, J.; Jørgensen, F. S.; Eaton, T. A.; Sarkozi, V.; Petit, C. M.; Ng, L.; Jordan, K. D. *J. Am. Chem. Soc.* **1985**, *107*, 6556−6562.

10.1021/ol036401b CCC: $27.50

cally.[10] However, to the best of our knowledge, to date no pericyclinic structures that consist only of carbon and chalcogens have been elucidated.

As part of our in-depth study of electron-rich alkynes[11−13] we report here on our ab initio studies of cyclic binaric compounds containing only chalcogens and acetylene units, which we refer to as [*N*]chalcogena[*N*]pericyclynes. A large variety of chalcogen-containing pericyclynes **3(*n*)**−**6(*n*)** (n = 3−6, 8)[14] were optimized by DFT methods (B3LYP/6-311G(d)),[15−17] the calculations were carried out with Gaussian 98.[18] For $n = 3$, the valence tautomers **7**−**10** were also studied by computational means. All the [*N*]chalcogena[*N*]pericyclynes were shown to be minima on the potential energy surface in a singlet ground state by calculating the force constants (NImag = 0). Possible triplet structures are remarkably higher in energy, e.g., **4(4)** = 206 kJ/mol.



3(n) (X = O; n = 3-6,8)
4(n) (X = S; n = 3-6,8)
5(n) (X = Se; n = 3-6,8)
6(n) (X = Te; n = 3-6,8)
7 (X = O)
8 (X = S)
9 (X = Se)
10 (X = Te)

A comparison of their most important geometrical features (distances *d*(CC), angles C−X−C at the corners, X−C−C indicating distortions from the usual acetylene geometry, and torsional angles χ between the XCCX units) is given in Tables 1 and 2. The C≡C bond lengths *d*(CC) are always close to 120 pm. In contrast, the angles C−X−C, X−C−C, and χ vary considerably.

Table 1. Heat of Formation (ΔH_f), Strain Energies E_{strain} (Per XCC Unit), and Bond Lengths and Angles for Oxapericyclynes **3(*n*)** and Thiapericyclynes **4(*n*)** (at the B3LYP/6-311G(d) Level)

compd		ΔH_f [kJ/mol]	E_{strain}(XCC) [kJ/mol]	C−X−C [deg]	X−C−C [deg]	*d*(CC) [pm]	χ [deg][b]
3(3)	D_{3h}	627	214.2	101.2	159.4	119.8	0.0
3(4)	D_{2d}	644	94.4	108.3	170.9	119.1	0.01
3(5)	C_2	729	42.1	112.8	177.6[a]	119.0	0.06
				112.8		119.0	0.08
				112.8		119.0	0.12
3(6)	D_{3d}	844	19.3	115.0	178.6	119.0	42.2
3(8)	D_{4d}	1100	0	117.0	177.2	119.0	77.1
4(3)	D_{3h}	691	41.8	91.6	164.2	121.2	0.0
4(4)	D_{2d}	812	14.5	99.0	170.2	121.4	48.8
4(5)	C_2	986	8.7	100.5	174.6[a]	121.1	31.7
				100.9		121.1	67.4
				101.8		121.4	70.1
4(6)	D_{3d}	1141	1.8	102.5	177.4	121.3	76.9
4(8)	D_{4d}	1506	0	103.9	173.2	121.4	91.4

[a] Mean value. [b] χ describes the torsional angle C−X···X−C.

For the larger cycles, C−X−C and χ tend toward a limit. In the first case (C−X−C), this limit is close to the angles C−X−C in the series of H_2X for X = O, S, Se, and Te. In the latter case, the limit for χ is always close to 90°. This dependency of χ(*n*) can easily be understood by realizing a minimum of repulsion energy between the lone pairs. The minimum is reached when a perpendicular conformation (χ = 90°) is adopted. Furthermore, in Tables 1 and 2 we list for each pericyclyne the heat of formation (ΔH_f) and the strain energy E_{strain}(XCC) per XCC fragment. Concerning ΔH_f, we omitted a BSSE correction;[16] therefore, the values have to be taken with a grain of salt. All the compounds are highly endothermic relative to their elements. To get a reference for the calculation of E_{strain}(XCC), we defined that the largest calculated pericyclynes, the [8]chalcogena[8]pericyclynes, do not have any strain. Therefore, in Tables 1 and 2, $n = 8$ shows a value of 0. Generally, a strong dependency on *n* and X is observed. As anticipated, the larger *n* is, the more E_{strain}(XCC) is reduced. Also, the use of heavier

Table 2. Heat of Formation (ΔH_f), Strain Energies E_{Strain} (Per XCC Unit), and Bond Lengths and Angles for Selenapericyclynes **5(*n*)** and Tellurapericyclynes **6(*n*)** (at the B3LYP/6-311G(d) Level)

compd		ΔH_f [kJ/mol]	E_{strain}(XCC) [kJ/mol]	C−X−C [deg]	X−C−C [deg]	*d*(CC) [pm]	χ [deg][b]
5(3)	D_{3h}	829	32.7	90.1	164.9	121.3	0.0
5(4)	D_{2d}	1021	11.6	96.3	171.9	121.4	48.0
5(5)	C_2	1252	6.8	98.1	175.5[a]	121.2	30.4
				98.3		121.4	66.6
				99.1		121.4	71.0
5(6)	D_{3d}	1469	1.1	99.8	177.0	121.4	78.1
5(8)	D_{4d}	1950	0	101.0	173.1	121.5	93.8
6(3)	D_{3h}	816	26.6	89.3	165.3	121.6	0.0
6(4)	D_{2d}	1019	9.2	94.8	172.0	121.8	50.6
6(5)	C_2	1255	5.6	96.3		121.6	31.8
				96.9	175.3[a]	121.8	69.5
				97.6		121.8	73.6
6(6)	D_{3d}	1478	4.2	98.0	177.0	121.9	80.7
6(8)	D_{4d}	1965	0	99.1	173.3	121.9	96.1

[a] Mean value. [b] χ describes the torsional angle C−X···X−C.

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(5) Scott, L. T.; Cooney, M. J.; Rogers, D. W.; Dejroongruang, K. *J. Am. Chem. Soc.* **1988**, *110*, 7244−7245.

(6) (a) Scott, L. T.; Unno, M. *J. Am. Chem. Soc.* **1990**, *112*, 7823−7825. (b) Märkl, G.; Zollitsch, T.; Kreitmeier, P.; Prinzhorn, M.; Reithinger, S.; Eibler; E. *Chem. Eur. J.* **2000**, *6*, 3806−3820.

(7) (a) Unno, M.; Saito, T.; Matsumoto, H. *Chem. Lett.* **1999**, 1235−1236. (b) Unno, M.; Negishi, K.; Matsumoto, H. *Chem. Lett.* **2001**, 340−341.

(8) Boldyrev, A. I.; Zhdankin, V. V.; Simons, J.; Stang, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 10569−10572.

(9) González, R. M. Ph.D. Thesis, University of Nevada, Reno, NV, 1993.

(10) Lee, A. W. M.; Yeung, A. B. W.; Yuen, M. S. M.; Zhang, H.; Zhao, X.; Wong, W. Y. *Chem. Commun.* **2000**, 75−76.

(11) (a) Benisch, C.; Bethke, S.; Gleiter, R.; Oeser, T.; Pritzkow, H.; Rominger, F. *Eur. J. Org. Chem.* **2000**, 2479−2488. (b) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Org. Chem.* **2002**, *67*, 4290−4297.

(12) (a) Gleiter, R.; Werz, D. B.; Rausch, B. J. *Chem. Eur. J.* **2003**, *9*, 2676−2683. (b) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Am. Chem. Soc.* **2002**, *124*, 10638−10639.

(13) (a) Werz, D. B.; Gleiter, R.; Rominger, F. *Organometallics* **2003**, *22*, 843−849. (b) Werz, D. B.; Gleiter, R. *J. Org. Chem.* **2003**, *68*, 9400−9405.

(14) Due to the low symmetry for $n = 7$, the corresponding potential surfaces are rather complex, showing several local minima that are difficult to localize. Therefore, we abstained from further studies.

(15) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. *J. Chem. Phys.* **1980**, *72*, 650−654.

(16) SDB-cc-pVTZ (with ECP) for Te: (a) Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408−3420. (b) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431−1441.

(17) (a) Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155−2160. (b) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785−789. (d) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989. (e) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, 2000.

chalcogens decreases the strain of the cycles. This observation is in line with the behavior of C−X−C and χ as a function of n: the heavier the chalcogen atom, the smaller the angle C−X−C, the less disfavored are the smaller cycles.

The minimum structures for the calculated [3]pericyclynes **3(3)**, **4(3)**, **5(3)**, and **6(3)** reveal D_{3h} symmetry showing bent triangles. In the case of the [4]pericyclynes **3(4)**, **4(4)**, **5(4)**, and **6(4)**, the minima show D_{2d} symmetry as does cyclobutane (see Figure 1). These envelope-like structures interconvert via a D_{4h} symmetric transition state. The inversion barriers (Table 3) are strongly dependent on the chalcogen in the corners. [4]Oxa[4]pericyclyne **3(4)** shows an almost D_{4h} symmetrical square (Figure 1). This behavior can be rationalized in terms of NBO interactions. Such an analysis reveals that the magnitude of the inversion barriers results essentially as a compromise of two effects: the overlap between the lone pairs at the chalcogen atoms and the π^* orbitals of the triple bonds and the energy difference between these orbitals. The overlap decreases from oxygen to tellurium. The same holds for the energy difference of these orbitals: its largest value is found for oxygen, its smallest for tellurium. As a result, the highest inversion barrier is found for the sulfur congener **4(4)**; for the oxygen congener **3(4)**, the high strain energy overcomes the relatively small repulsion energy between the oxygens' lone pairs. Thus, a structure with only negligible deviations from an exact square results. A similar structure was also proposed for the tetracation **2**.[8]

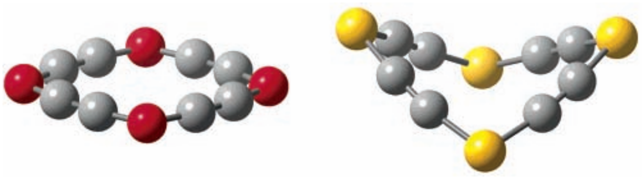

Figure 1. Optimized structures of **3(4)** (left) and **4(4)** (right).

Table 3. Inversion Barriers[a] for [4]Pericyclynes **3(4)**−**6(4)** (at the B3LYP/6-311G(d) Level)

compd	3(4)	4(4)	5(4)	6(4)
inversion barrier[a] [kJ/mol]	0.2	28.5	18.9	18.1

[a] Starting with the D_{2d}-symmetric molecule via a D_{4h}-symmetric transition state.

The favored geometries of the [5]chalcogena[5]pericyclynes show C_2 symmetry also in order to minimize the torsional strain between the chalcogens' lone pairs. Higher pericyclynes behave similarly. For the [6]chalcogena[6]pericyclynes, the global minimum is a chairlike structure (D_{3d}) as shown for **4(6)** in Figure 2. Since pericyclynes can be viewed as expanded cycloalkanes and chalcogenapericyclynes as expanded chalcogen structures, other possible conformations should also be accessible. This reasoning prompted us to explore the inversion process of **4(6)** (Figure 3).

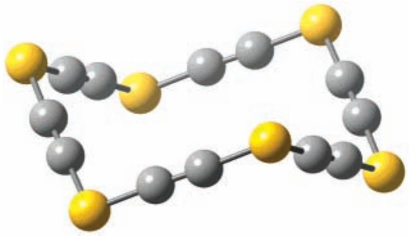

Figure 2. Optimized structure of **4(6)**.

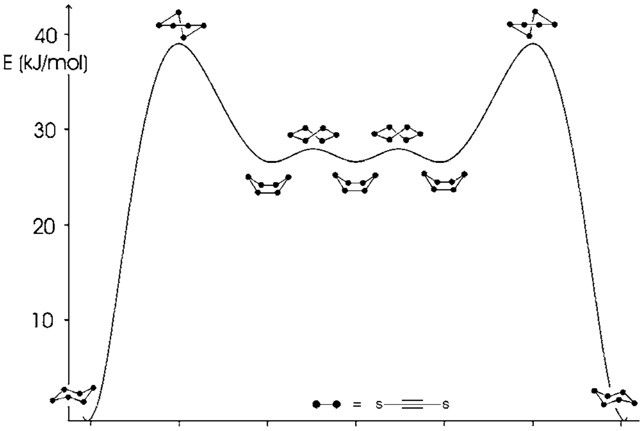

Figure 3. Energy profile of [6]thia[6]pericyclyne (**4(6)**).

On the potential surface, we located the chair conformation (D_{3d}) as global minimum and the boat conformation (C_{2v}) as a local minimum. The transition state between chair and boat conformation, the half-chair conformation (C_2), is 39.0 kJ/mol higher in energy than the chair and 12.4 kJ/mol higher in energy than the boat conformation. Between the flexible boat conformations, we find as a transition state a twist conformation. A comparison with the well-known energy profile of cyclohexane[19] shows similarities and differences. The value of the activation energy for both inversion processes (cyclohexane about 45 kJ/mol)[19] and the conformation of the transition state is similar. In variance with the energy profile of cyclohexane is the finding that the boat conformation is a local minimum and the twist conformation is a transition state between the boat conformations. The energy difference for both was calculated to be 1.4 kJ/mol.

In particular, the [8]chalcogena[8]pericyclynes illustrate the structural relationships to chalcogens such as S_8 and Se_8. Exploded crown-like structures (D_{4d}) are observed where the acetylene unit serves as a rigid and (concerning the repulsion of the lone pairs) electronically active relais. The crownlike structure is shown for the selenium congener **5(8)** in Figure 4.

In the case of the [3]pericyclynes, their valence tautomers **7**−**10**, the corresponding benzene derivatives with three

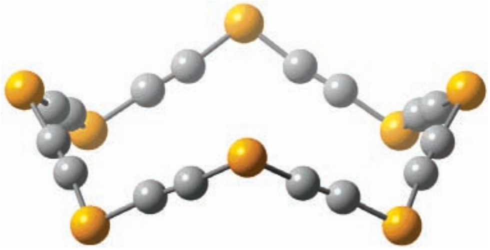

Figure 4. Optimized structure of **5(8)**.

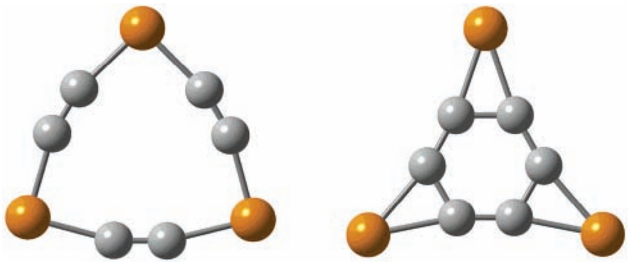

Figure 5. Optimized structures of the pericyclyne **6(3)** and the benzene derivative **10**.

Table 4. Stabilization Energies E_{stab} (vs Corresponding Pericyclyne) and Bond Lengths and Angles for Benzene Derivatives **7**−**10** (at the B3LYP/6-311G(d) Level)

	7[a]	**8**	**9**	**10**
ΔH_{f} [kJ/mol]	780	719	805	799
E_{stab} [kJ/mol][b]	−153.4	−28.2	+24.0	+17.2
d(C−C) [pm] (WBI)[c]	139.9 (0.92)	140.4 (1.14)	139.3 (1.24)	139.1 (1.31)
d(C═C) [pm] (WBI)[c]	130.4 (1.78)	133.0 (1.59)	134.1 (1.55)	135.0 (1.50)
Δd [pm]	9.5	7.4	5.2	4.1
d(C−X) [pm]	144.0	179.6	195.0	212.3
X−C−X [°]	58.1	46.0	41.8	38.3
NICS [ppm]	−14.6	−10.2	−12.1	−12.9

[a] From ref 22. [b] Positive sign (+) indicates that the benzene derivative is more stable than the pericyclyne. [c] WBI: Wiberg bond index.

annelated three-membered rings, were also investigated. The compounds **7**−**10** might be formed from the corresponding pericyclynes via an allowed [π^2s + π^2s + π^2s] cycloaddition process. Figure 5 shows a comparison between the planar structures of **6(3)** and **10**. In Table 4 we list the most relevant geometrical parameters calculated. It is seen that the lighter the chalcogen is, the more a bond-localized cyclohexatriene structure is adopted. In benzotrisoxirene **7**, the difference (Δd) between the C═C double-bond and C−C single-bond lengths amounts to 9.5 pm, whereas in the corresponding tellurium congener **10**, this value decreases to 4.1 pm. This result can be rationalized by considering electronic effects. The smaller the chalcogen is, the better the orbital overlap between the p orbitals of the chalcogen and the carbon atoms. To avoid an unfavored (antiaromatic) 4π system in the three-membered rings, bond localization in the central benzene ring is favored. An NBO analysis and a comparison of the corresponding bond indices confirm this view. These computational results are in line with experimental studies of cyclobutadiene fused benzenes,[20] which also adopt cyclohexatriene-like structures. To our surprise, the NICS values,[21] calculated in the center of the six-membered ring (Table 4), were not reduced at all relative to that of benzene (−9.4). This result confirms the relative insensitivity of NICSs to geometry variations in aromatic systems.[21] It is interesting to note that for the heavier chalcogens (Se, Te), the benzene derivatives **9** and **10** should be more stable than the corresponding pericyclynes, whereas for C_6O_3 and C_6S_3, structures with triple bonds should be favored.

An NBO analysis of **3(3)**−**6(3)** reveals that only **3(3)** possesses transannular interaction (homoaromaticity for **3-(3)**). As a result of this interaction, the bond index of the triple bond is reduced from 2.7 to 1.8. For **4(3)**−**6(3)**, the homoaromatic interaction was found to be negligible.

Our investigations demonstrate that [*N*]chalcogena[*N*]-pericyclynes are local minima on their potential energy surface possessing a singlet ground state. Most of their structures are determined by interactions between the chalcogens' lone pairs. Due to a minimum of repulsion, an almost perpendicular arrangement of their p orbitals is, whenever possible, favorable. Many of their molecular structures resemble, in shape, cycloalkanes or elemental chalcogens such as S_8. In the case of [3]chalcogena[3]pericyclynes, for the heavier chalcogens (Se, Te), a benzene-like structure is calculated to be more stable than the acetylenic one. All these highly remarkable molecules are still waiting to be synthesized.

Acknowledgment. D.B.W. thanks the Deutsche Forschungsgemeinschaft (Graduiertenkolleg 850: "Molecular Modelling") for a graduate fellowship.

Supporting Information Available: Gaussian archive entries of all calculated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) 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.; 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.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) (a) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; J. Wiley & Sons: New York, 1994. (b) Juaristi, E., Ed. *Conformational Behavior of Six-membered Rings*; VCH: New York, 1995.

(20) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150−3152.

(21) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Eikema Hommes, N. J. R. v. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318.

(22) HF/6-31G* calculation on the geometry of this structure was carried out before: Lewars, E. *Can. J. Chem.* **2000**, *78*, 297−306.