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CONFORMATIONAL ANALYSIS OF HEXADECAMETHYLCYCLOOCTASILANE, $(Me_2Si)_8$

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Abstract: Conformational analysis of hexadecamethylcyclooctasilane (1) has been performed using molecular mechanics calculations. Unlike its hydrocarbon analog, cyclooctane, which adopts a boat-chair (BC) conformation in the ground state, 1 is calculated to adopt a twist-chair-chair (TCC) structure as the lowest energy conformation. Other conformations of 1 are relatively close in energy to the TCC form. A comparison between 1 and cyclooctane is reported.

Introduction

Special interest in the class of compounds known as permethylcyclopolysilanes[1] arises, in part, from the unusual electronic properties[2] demonstrated by these molecules. Because of electron delocalization in the σ-framework, permethylcyclopolysilanes exhibit interesting U.V. spectra,[2] they are able to easily form delocalized anion[3] and cation radicals,[4] and they will form charge transfer complexes with Π-acceptors.[5] Despite the level of interest in the chemistry of these compounds, relatively little structural information is available for these systems.[6] In order to partially fill this information gap, we now report a molecular mechanics investigation of the structure and conformational properties of hexadecamethylcyclooctasilane (1).

A number of X-ray crystal and molecular structures for organosilicon ring systems have been reported previously.[6] The results of these studies, together with theoretical investigations,[7,6ℓ] have suggested that the permethylcyclopolysilanes adopt structures which are similar to those found for their hydrocarbon analogs, the cycloalkanes. For example, the derivatives of $(Me_2Si)_5$ adopt C_s conformations,[6c,1] and the six-membered cyclopolysilane ring, $(Me_2Si)_6$, adopts the familiar chair structure associated with cyclohexane.[6b] In further support of this position, recent crystallographic and molecular mechanics investigations[6ℓ] have revealed that both $(Me_2Si)_7$ and cycloheptane adopt the twist-chair (TC) structure in the ground state. Interestingly, however, the conformational energy differences and interconversion barriers calculated for this seven-membered silicon derivative were found to differ substantially from those obtained for cycloheptane.[6ℓ] These findings suggested that the analogy between the structural and conformational behavior of permenthylcyclopolysilanes and cycloalkanes may no longer pertain when one considers such larger ring systems.[6ℓ] In order to test this hypothesis, information on the structure and conformational energies for the next higher permethylcyclopolysilane homolog (i.e., 1) is required. Since attempts to obtain solid-state structural information on 1 have, to date, been unsuccessful (due to disorder in the crystal) we have turned to molecular mechanics calculations in order to predict the stereochemical properties of this compound.

Methods

Calculations were performed with the program MM2[8] using the previously described parameters for permethylpolysilanes.[9] Full relaxation geometry optimizations were performed for all of the conformations under consideration.[10] In certain cases (see below) these geometry optimizations were performed under symmetry constraints.

The ten basic conformations for eight-membered rings have been identified in previous studies of cyclooctane.[11] These conformations have been described as the twist-chair-chair (TCC), chair-chair (CC), crown (CR), twist-boat-chair (TBC), boat-chair (BC), twist-boat (TB), twist-chair (TC), chair (C), boat-boat (B), and boat (B). The BC is of C_s symmetry and this form is generally accepted as the ground-state conformation for cyclooctane. Both the BB and the B are of D_{2d} symmetry and the C and TC both belong to the C_{2h} point group. The TCC and TBC are axially symmetric with D_2 and C_2 symmetries, respectively. The CR, CC and TB are of D_{4d}, C_{2v} and S_4 symmetry. The torsion angles that were obtained for these ten conformations in the study of cyclooctane by Hendrickson[11a] were used as the starting values for the present calculations on these same conformations of 1. Geometry optimization of the TCC, CC, CR, TBC, BC, TB and TC forms were performed without constraint. The C, BB and B conformers were optimized under the the constraint of C_{2h}, C_{2v}, and D_{2d} symmetry, respectively. While the structures of those conformations obtained via optimization without symmetry constraint no longer belong to the same point groups as their input geometries (see above), for simplicity we have retained the same conformational descriptors for the resulting structures.

Discussion

The structures that were obtained for the various conformers of 1 after geometry optimization are shown in Figure 1. The ring torsion angles (Si-Si-Si-Si) obtained for these optimized structures are shown schematically in Figure 2. The relative strain energies for the ten conformations of 1 are reported in Table 1 and selected average bond lengths and angles are reported in Table 2.

Inspection of Table 1 reveals that the ground-state structure of 1 is calculated to be the TCC conformation. The CC and CR conformations are not substantially higher in energy than this TCC form, however, since the calculated relative strain energies for these conformations are only 0.4 and 0.9 kcal/mol. Because of this close energy ordering, we feel it is reasonable to expect that the CC and CR conformations, in addition to the TCC, may be observed in ground-state structure determinations for 1. Indeed, the disorder observed in the crystal of 1 may be a result of the presence of a mixture of conformational states for this molecule.[12] The existence of several conformational states below a relatively small strain energy of 1.0 kcal/mol suggests that 1 will exhibit considerable conformational flexibility.

The geometries and relative energies of the C, BB and B conformations of 1 were obtained by optimization under symmetry constraints. Releasing these symmetry constraints on the B and BB conformations followed by geometry optimization yields the TB structure. Optimization of the C structure after removing the symmetry constaints yields the TC form. No intermediates were encountered between the B, BB and TB or C and TC forms. While the C, BB and B conformations are thus relative energy maxima for 1, these structures are relative energy minima for cyclooctane.[11]

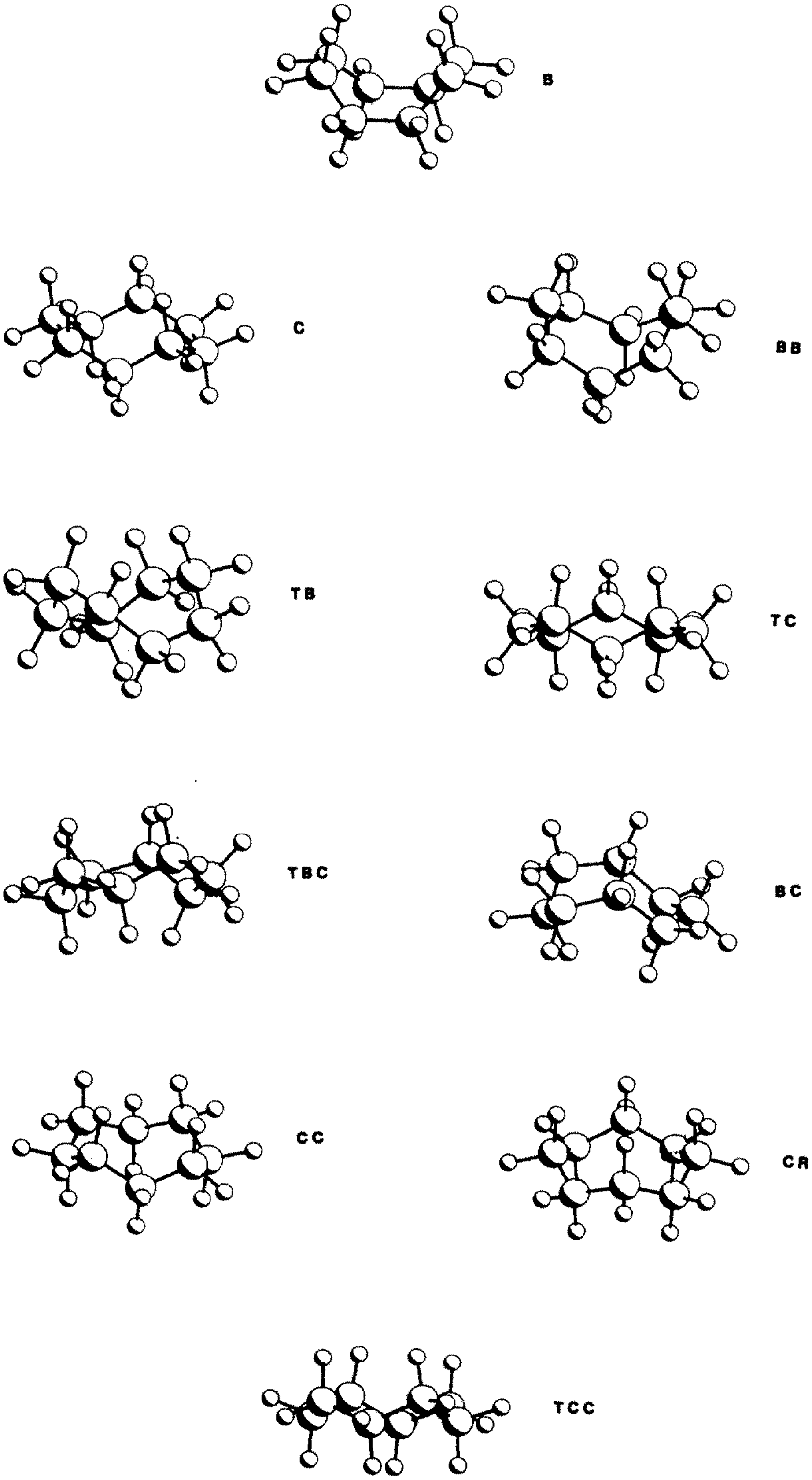

Figure 1. Views of the calculated structures for conformations of 1. Conformational descriptors are shown to the right of the corresponding structure. Hydrogen atoms have been removed for clarity.

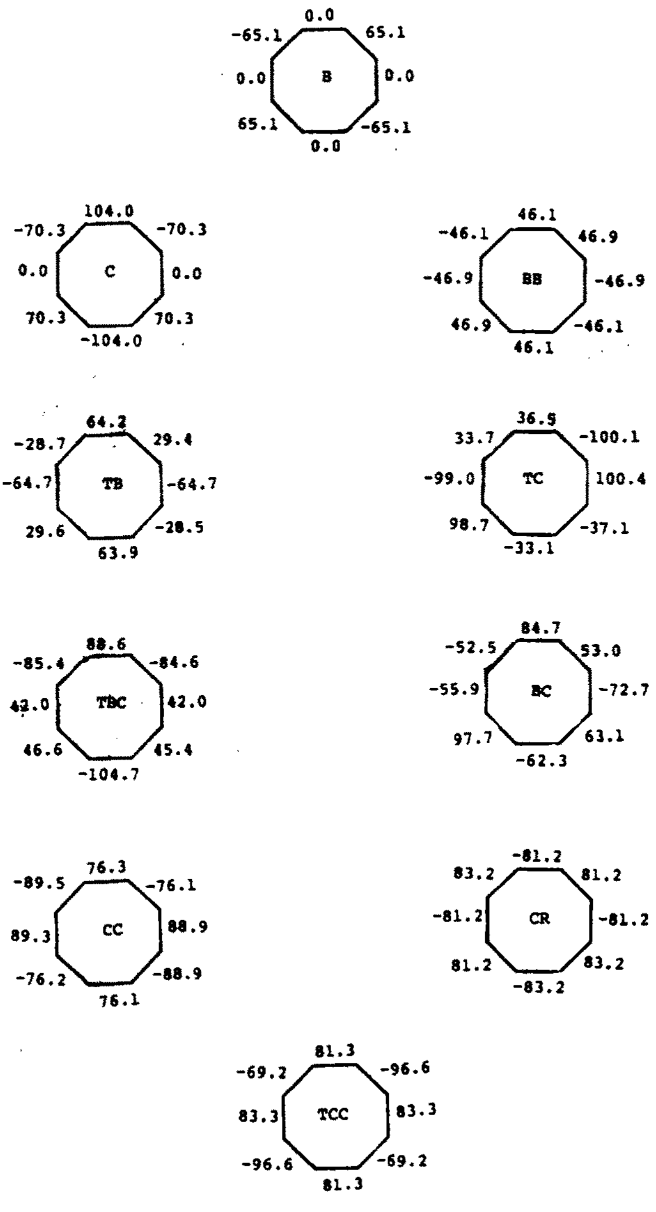

Figure 2. Schematic representation of the calculated conformations of 1 showing ring torsion angles (Si-Si-Si-Si) around the ring perimeter. Conformational descriptors are shown in the center of each structure.

Table 1. Calculated Relative Conformational Energies for 1 and Cyclooctane[a]

Conformation	1	Cyclooctane[b]
TCC	0.0	c
CC	0.4	c
CR	0.9	1.22
TBC	2.3	2.37
BC	2.6	0.0
TB	3.7	c
TC	4.3	9.96
C	6.3	9.51
BB	9.2	1.67
B	10.7	12.13

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[a] In kcal/mol

[b] Taken from reference 11c

[c] Not an energy extremum on the MM2′ potential energy surface.[11c]

Table 2. Selected Average Calculated Bonding Parameters for Conformations of 1

Conformation	Average Si-Si Bond Length[a]	Average Si-Si-Si Angle[b]
TCC	2.351	118.3
CC	2.351	118.5
CR	2.352	118.9
TBC	2.352	119.4
BC	2.354	119.6
TB	2.354	120.2
TC	2.353	119.2
C	2.354	120.5
BB	2.354	122.3
B	2.358	123.0

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[a] In Angstrom units

[b] In degrees

Further accentuating the differences between cyclooctane and 1 is the observation that while the TB, TCC and CC forms are found not to be energy extrema for the former,[11c] for the latter these conformations are relative energy minima.

In order to allow for a detailed comparison of relative conformational energies between 1 and cyclooctane, we have also assembled the calculated relative energies[11c] for this hydrocarbon in Table 1. The BC conformation is both calculated and observed to be the ground-state structure for cyclooctane.[11] These calculations thus reveal that structurally as well as energetically, 1 differs substantially from its hydrocarbons analog. While, as mentioned previously, the CC and CR conformations of 1 are relatively close in energy to the ground-state TCC, for cyclooctane the CR conformation resides 1.22 kcal/mol above the lowest energy structure. The TBC and BC structures of 1 have comparable strain energies of 2.3 and 2.6 kcal/mol as do the TB and TC structures with relative strain energies of 3.7 and 4.3 kcal/mol. While the strain energy of 2.37 kcal/mol found for the TBC conformation of cyclooctane is thus comparable to the value obtained for the corresponding conformation of 1, the relative energies for the BC structures of these two molecules differ substantially. The C and BB forms reside 6.3 and 9.2 kcal/mol above the TCC for 1. While the strain energy of the C forms are therefore reasonably comparable for these two molecules, the BB conformation of cyclooctane has a strain energy of only 1.67 kcal/mol. Evidently, steric interactions between the bulky methyl groups in 1 are responsible for the higher relative energy found for this form of 1. The B conformation is found to be highest in strain energy for both compounds with a relative strain energy of 10.7 kcal/mol for 1 and 12.13 for cyclooctane.

Selected average bond lengths and angles for the various conformations of 1 are shown in Table 2. It is particularly interesting to note that while all of the average Si-Si bond lengths are calculated to reside within the 2.351-2.358 Å range and thus compare well with the unstrained value of 2.345 Å the Si-Si-Si angles in each of these conformations are considerably larger than the unstrained value of 111.7° and average 118.3°-123.0°. While exceptions exist, a general trend is observed for both of these bonding parameters with the longer bond lengths and larger angles being demonstrated by those structures with the highest relative strain energies. The average Si-Si-Si angles in these structures are all somewhat expanded relative to those values calculated (ca. 117.2°) and observed (116.2°) for tetradecamethylcycloheptasilane. The expansion of internal bond angles from strain-free values has been noted previously for medium-ring hydrocarbons[13] (see also, Table 3). Based on the results obtained for $(Me_2Si)_7$,[6ℓ] it was suggested that the higher homologs of permethylcyclopolysilanes may also demonstrate a similar trend. The present calculations suggest that the expansion of internal Si-Si-Si angles relative to strain-free values will be a general phenomena for these higher homologs.

The present calculations establish that the ground-state structures and relative conformational energies differ substantially between 1 and cyclooctane. Thus, the hypothesis that the analogy between the conformational behaviour of permethylcyclopolysilanes and cycloalkanes will dissolve upon consideration of the higher homologs finds full support in the present work. Despite this disparity in the stereochemical behaviour of 1 and cyclooctane, a comparison of structural parameters leads to some interesting similarities. It is interesting, for example, to compare the twist angles in the conformations of 1 with those obtained for the same conformations of cyclooctane. To allow for such a comparison we have assembled structural information from the most recent molecular mechanics calculations on cyclooctane[11c] in Figure 3. Only seven out of the ten possible conformations are presented in this Figure since the MM2′ force field used in these previous calculations did not locate the TB, CC and TCC conformations as energy extrema on the cyclooctane hypersurface. In Table 3 we have also assembled the torsional information from the X-ray structural determinations of previously reported cyclooctane derivatives.[14] In this assemblage we have included only those derivatives which do not contain substituents that would lead to further ring formation in the molecule (i.e., cyclooctane fused ring systems and bicyclic derivatives were excluded).

Table 3. Selected Structural Parameters for Cyclooctane Derivatives[14]

Compound	Ring Torsion Angles[a,b]				Average C-C-C Angle[a]
A	-70.3	101.0	-43.4	-63.1	116.0
	70.7	-105.8	46.8	62.1	
B	-67.4	104.8	-48.2	-60.1	116.8
	65.7	-96.1	37.9	68.8	
C	-63.0	100.3	-41.2	-67.2	116.3
	60.65	-100.7	48.2	62.1	
D	-65.4	97.9	-46.4	-63.5	117.1
	67.2	-98.0	40.5	67.2	
E	-59.8	105.7	-52.2	-62.1	115.4
	61.5	-108.5	50.3	63.9	
	-61.8	107.6	-50.8	-61.8	115.5
	60.1	-105.8	51.0	62.9	
	-58.0	107.2	-55.7	-58.7	115.7
	61.3	-106.6	45.9	65.1	
F	-74.9	101.4	-38.7	-69.5	114.8
	73.2	-103.5	45.4	64.8	
G	-64.4	102.6	-46.5	-62.5	116.0
	65.3	-102.6	46.6	63.5	
	-63.2	-101.3	45.5	62.6	116.2
	62.1	102.4	-46.9	-62.8	
H	-62.8	99.3	-41.8	-67.8	116.4
	63.3	-101.4	44.1	66.3	
I	-61.9	108.2	-50.3	-62.4	115.3
	60.5	-107.6	52.9	60.8	
	-61.5	105.6	-45.3	-64.4	115.7
	58.2	-107.6	57.1	57.1	
	-57.8	105.6	-52.3	-62.2	115.8
	59.9	-107.9	52.0	61.1	
J	-69.2	107.6	-47.5	-62.9	115.7
	67.3	-104.9	50.0	59.6	
K	-63.8	102.2	-40.6	-68.5	116.4
	62.8	-104.5	52.2	59.5	

L	-65.4 69.9	104.6 -92.9	-57.1 21.0	-55.7 80.2	116.2
M	-66.5 66.4	103.8 -99.2	-45.3 40.9	-64.2 66.5	116.2
N	-61.9 61.9	100.5 -104.6	-49.5 50.0	-57.6 59.5	117.0

A) Cyclooctane-1,2-trans-dicarboxylic acid. Dobler, M.; Dunitz, J. D.; Mugnoli, A. Helv. Chim. Acta 1966, 49, 2492. B) Cyclooctane-cis-1,2-dicarboxylic acid. Burgi, H. -B.; Dunitz, J. D. Helv. Chim. Acta 1968, 51, 1514. C) trans-1,4-Dichlorocyclooctane. Van Egmond, J.; Romers, C. Tetradehron 1969, 25, 2693. D) 1-Aminocyclooctane carboxylic acid hydrobromide. Srikrishnan, T.; Srinivasan, R.; Zand, R. J. Cryst. Mol. Structure 1971, 1, 199. E) Cyclooctane-1,5-dione dioxime. Winkler, F. K.; Seiler, P.; Chesick, J. P.; Dunitz, J. D. Helv. Chim. Acta 1976, 59, 1417. F) cis-3,7-Di-t-butylcyclooctyl-cis-p-bromobenzoate. Hoge, R.; Lehnert, R.; Fischer, K. F. Cryst. Struct. Comm. 1977, 6, 363. G) Bis(p-acetoxyphenyl)cyclooctylidenemethane. Precigoux, G.; Busetta, B.; Courseille, C.; Hospital, M.; Miquel, J. F. Acta Crystallogr., Sect. B 1978, B34, 3300. H) cis-Cyclooctane-1,5-diol. Miller, R. W.; McPhail, A. T. J. Chem. Soc., Perkin 2 1979, 1527. I) Cyclooctane-1,5-dione-dioxime. Miller, R. W.; McPhail, A. T. J. Chem. Res. 1979, 285, 3122. J) Cyclooctane-1,5-dione. Miller, R. W.; McPhail, A. T. J. Chem. Soc., Perkin 2 1979, 1527. K) Cyclooctane oxime. Groth, P. Acta Chem. Scand. Ser. A 1981, A35, 117. L) Cyclooctane phenylsemicarbazone. Groth, P. Acta Chem. Scand. Ser. A. 1981, A35, 117. M) 1-Ethyl-3-((4-cyclooctyl-pyrid-3-yl)-sulfonyl)-urea hydrogen nitrate. DuPont, L.; Lewinski, K.; Stadnicka, K.; Delarge, J. Cryst. Struct. Commun. 1981, 10, 925. N) 5-(3',5'-Dinitrobenzoyloxy)-cyclooctanone. Jones, P. G.; Sheldrick, G. M.; Kirby, A. J.; Glenn, R.; Halstenberg, M. Z. Kristallogr. 1983, 163, 75.

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[a] In degrees

[b] Following the notation of Hendrickson[11a]

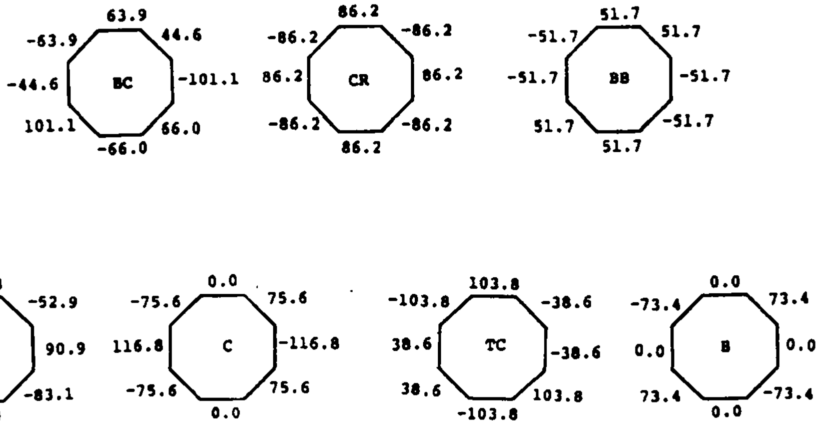

Figure 3. Schematic representation of the calculated[11c] conformations of cyclooctane showing ring torsion angles (C-C-C-C) around the ring perimeter. Conformational descriptors are shown in the center of each structure.

Inspection of Figures 2 and 3 reveals that the CR, TC, C, BB and B conformations are very similar in terms of ring torsion angles for 1 and cyclooctane. Angles in these structures differ on average by ca. 5°, 3°, 8°, 5° and 8° and are consistently smaller in 1 than in cyclooctane. By contrast, the TBC and BC conformations differ substantially between 1 and cyclooctane with differences in ring torsion angles ranging as high as ca. 30°.

The assemblage of X-ray crystallographic data on cyclooctane derivatives indicates that all of the cyclooctanes adopt the BC conformation in the ground state[11] and the torsion angles for these molecules are similar. Also shown in Table 3 is a list of average C-C-C angles for these eight-membered ring systems. Inspection of these angles clearly reveals their expansion relative to strain-free values[13] (see above). A comparison of the BC conformation obtained for 1 with those observed for cyclooctane reveals that the calculated BC conformation of 1 differs substantially from the observed BC conformation of cyclooctane derivatives. Thus the experimental torsion angles obtained for the cyclooctanes also differ from those calculated for 1.

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