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Gas-Phase Structure and Conformational Properties of 3,3,6,6-Tetramethyl-1,2,4,5-Tetroxane

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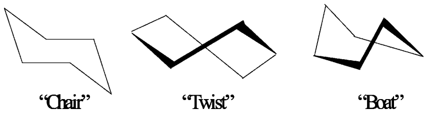
The geometric structure and conformational properties of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane (diacetone diperoxide) have been studied by gas electron diffraction and quantum chemical calculations (MP2 and B3LYP methods with 6-31G(d,p) and 6-311+G(2df,p) basis sets). The molecule possesses a chair conformation with C_{2h} symmetry and the following geometric parameters for the six-membered ring (r_{h1} values) have been determined: O−O = 1.463(5) Å, C−O = 1.432 (4) Å, O−C−O = 108.2(7)°, C−O−O = 107.7(4)°, φ(C−O−O−C) = 63.7(4)°, and φ(O−O−C−O) = −63.9(4)°. A small contribution of less than 3.5% of a twist conformer with C_2 symmetry cannot be excluded. Quantum chemical calculations predict a contribution between 1 and 2%. Additional calculations for the parent compound 1,2,4,5-tetroxane (diformaldehyde diperoxide) demonstrate that methyl substitution at the carbon atoms has a minor effect on the ring geometry but a strong effect on the conformational properties. Methyl substitution reduces the energy difference between twist and chair conformers by more than 5 kcal/mol.

Introduction

The structural and conformational properties of saturated cyclic compounds depend to a large extent on two effects, angle deformation energy (Bayer strain) and torsional energy (Pitzer strain). The magnitude of these effects depends strongly on the conformation of the ring. The chair conformation of cyclohexane with D_{3d} symmetry represents an ideal case where both strain energies are almost zero with C−C−C bond angles close to tetrahedral and adjacent CH_2 groups staggering each other (φ(C−C−C−C) torsion angle close to 60°). In rings which contain heteroatoms, different bond lengths occur and bond angles and dihedral angles deviate more strongly from their ideal values, causing an increase of both strain energies. Saturated six-membered rings can adopt also a twist or boat conformation besides the chair form, which is known to be favored in cyclohexane[1] (see Chart 1).

CHART 1: Conformations of the Six-Membered Ring Molecule



For cyclohexane, an experimental value for the enthalpy difference $\Delta H° = 5.5$ kcal/mol between twist and chair has been reported.[2] Molecular mechanics calculations predict energy differences in a wide range between 4.8 and 7.9 kcal/mol.[3] Low-level ab initio calculations (HF, B3LYP, and MP2 with 3-21G* basis set) result in an energy difference varying from 6.25 to 6.50 kcal/mol.[4] The boat form corresponds to a transition state between two twist conformations. According to molecular mechanics calculations reported by Allinger et al., substitution of hydrogen atoms by methyl groups lowers the energy difference between chair and twist conformers. The energy decreases from 5.3 kcal/mol for the parent compound to 3.1 kcal/mol for 1,1,4,4-tetramethylcyclohexane.[5] However, another molecular mechanics (MM3) calculation predicted the relative energy of the twist conformer to be 5.6 kcal/mol higher than that of the chair form of 1,1,4,4-tetramethylcyclohexane.[6]

In the present work, we report structural and conformational properties of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane $Me_2(C_2O_4)Me_2$, or diacetone diperoxide (DADP), derived by gas electron diffraction (GED) and quantum chemical calculations. This compound belongs to the group of explosive cyclic peroxides, but it was found to be considerably less explosive than triacetone triperoxide, the nine-membered oxygen−carbon ring.[7]

This compound has been studied quite extensively in the solid state and in solution by experimental techniques and also by quantum chemical methods. Two independent X-ray studies resulted in chair structures with near C_{2h} symmetry.[7,8] The study of Dubnikova et al.[7] compares the experimental structural parameters with calculated (B3LYP/cc-pVDZ) values. From photoelectron spectra, a C−O−O−C dihedral angle of 68.3° was derived.[9]

From dynamic proton nuclear magnetic resonance (^1H NMR) spectra, free activation energies $\Delta G^\ddagger = 15.4$ kcal/mol[10] and 15.3 kcal/mol[11] have been determined for chair−chair inversion. Solid-state vibrational spectra (infrared (IR) and Raman) have been recorded and assigned on the basis of calculated DFT frequencies.[12] These calculations yielded an energy difference of about 2.7 kcal/mol between chair and twist conformations.[13]

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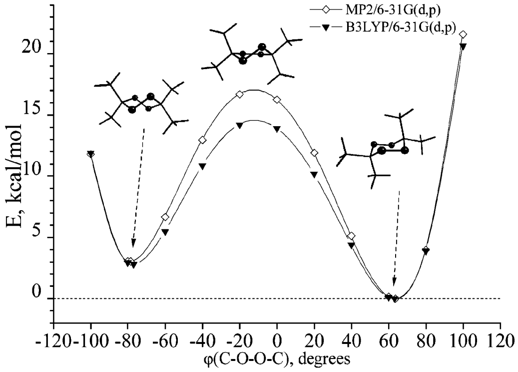

Figure 1. Potential energy curve for the chair-to-twist conversion, obtained by calculations at fixed dihedral angles φ(C−O−O−C) in step of 20° with all other geometric parameters being optimized. Black balls show the oxygen atoms in the molecule drawings.

TABLE 1: Calculated Energy and Gibbs Energy Differences between Twist and Chair Conformers (kcal/mol)

method/basis	ΔE	$\Delta G°$ (298 K)
B3LYP/6-31G(d,p)	2.81	2.30
MP2/6-31G(d,p)	3.04	2.57
B3LYP/6-311+G(2df,p)	2.74	2.29
MP2/6-311+G(2df,p)	3.22	2.88

Our attempt to determine the experimental structure of the parent compound 1,2,4,5-tetroxane $H_2(C_2O_4)H_2$ (or diformaldehyde diperoxide) failed. The experimental radial distribution function showed a very strong peak around 1.2 Å, corresponding probably to C═O bonds. This indicates either an impure sample or decomposition of the sample. To compare our experimental and calculated results for 1,1,4,4-tetramethylcyclohexane with those of the parent compound, we performed quantum chemical calculations. Since rather controversial results for the conformational energy differences of cyclohexane and its tetramethyl substituted analogue have been reported in the literature (see above), calculations have been performed for these molecules, as well.

Quantum Chemical Calculations

All quantum chemical calculations were performed with the Gaussian03 program package.[14] The DFT and MP2 approximations with small (6-31G(d,p)) and large (6-311+G(2df,p)) basis sets were applied. In the first step, the geometries of chair and twist conformers were optimized with the two methods and basis sets. Both conformers correspond to stable structures with no imaginary frequency.

The calculated energy differences and Gibbs free energy differences between chair and twist conformers are summarized in Table 1. These differences depend only slightly on the method and basis sets applied. The HF approximation with 6-31G(d,p) basis sets predicts much smaller values ΔE and $\Delta G°$ (1.60 and 0.98 kcal/mol, respectively, not given in Table 1). From the $\Delta G°$ values in Table 1, a very small contribution of 2% or less of the twist conformer is predicted.

In a second step, the potential for chair−twist conversion was calculated with both computational methods and small basis sets. Energies were calculated at fixed values for one of the two φ(C−O−O−C) dihedral angles in steps of 20° with all other geometric parameters being optimized. The potential curves are shown in Figure 1. In these curves also the energies for fully optimized geometries of both conformers are indicated. The predicted barriers for chair−twist conversion are 14.6 (B3LYP) and 17.1 kcal/mol (MP2).

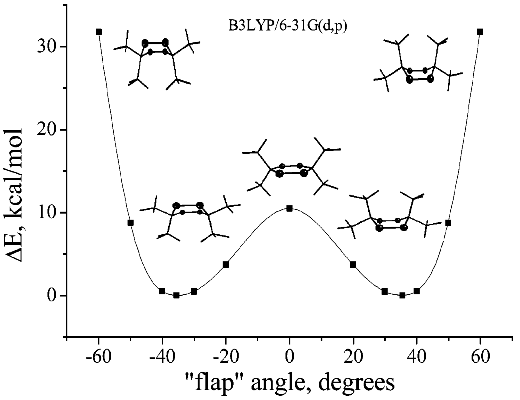

Figure 2. Potential energy for boat-to-boat conversion through the planar ring form. The boat form was found to be a saddle point of second order. Black balls show the oxygen atoms in the molecule drawings.

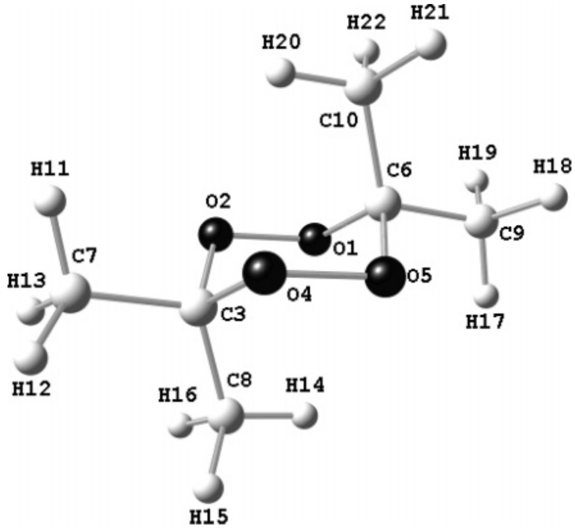

Figure 3. Molecular model of chair conformer of DADP with atom numbering.

The boat structure was considered in our calculations as well, using the B3LYP/6-31G(d,p) method. This structure corresponds to a saddle point of second order and lies about 30 kcal/mol higher than the chair conformation. As it follows from the analysis of the vibration modes, the molecule tends to transform from the boat to the twist and chair structures because of the modes corresponding to the imaginary frequencies of 214*i* and 86*i* cm^{-1}, respectively. In addition, we explored the potential energy profile for one of the possible ways for boat−boat conversion, through the planar ring structure (Figure 2). The energy difference between the planar and boat structures is 10.5 kcal/mol.

The geometrical parameters derived with large basis sets are given together with the experimental values in Table 2. Numbering of the atoms chosen for the chair conformer is indicated in Figure 3. Vibrational amplitudes and corrections were derived from a calculated force field (B3LYP/6-31G(d,p)) using the method of Sipachev,[15] and they are included in Table 3.

Calculations for the parent compound, 1,2,4,5-tetroxane $H_2(C_2O_4)H_2$ (or diformaldehyde diperoxide) were performed with B3LYP and MP2 methods and small basis sets as well as with the MP2 approximation and large basis sets. For cyclohexane and its tetramethyl substituted compound, only the B3LYP/6-31G(d,p) method was applied. Results of these calculations are given in the Discussion.

TABLE 2: Experimental and Theoretical Geometrical Parameters of DADP (Distances in Å, Angles in Degrees)

		chair				twist	
	GED	X-ray		calcd		calcd	
	r_{h1}, $\angle_{h1}$[d]	ref 8	ref 7[a]	B3LYP[b]	MP2[b]	B3LYP[b]	MP2[b]
distances							
O−O	1.463(5) p_1	1.475 (2)	1.471(4)	1.452	1.455	1.441	1.444
C−O	1.432(4) p_2	1.433(2), 1.436 (2)	1.431(5), 1.447(5)	1.429	1.422	1.436	1.430
C3−C7	1.523(6)[e] p_3	1.513(2)	1.509(8)	1.519	1.510	1.518	1.509
C_3−C8		1.518(2)	1.514(6)	1.521	1.512	1.518	1.509
O1···O5	2.320(5) p_4			2.312	2.310	2.326	2.323
C7−H11[c]	1.092 (11) p_5			1.090	1.090	1.091	1.092
C8−H14[c]				*1.086*	*1.087*	*1.089*	*1.090*
bond angles							
O−C−O	108.2(7)	107.6(1)	107.0	108.0	108.7	108.1	108.7
C−O−O	107.7(4)	107.6(1), 107.3(1)	107.6(3), 107.1(3)	108.3	107.0	106.6	105.0
O−C3−C7	104.7(2) p_6	104.7(1), 104.5(1)	104.4(3), 104.1(4)	104.7	104.3	104.7	104.3
O−C3−C8	112.4(2) p_7	112.9(1), 112.9(1)	113.4(3) 112.6(4)	112.5	112.5	112.3	112.2
C−C−C	114.1(3)	113.5(1)	113.4(3)	113.7	113.9	114.7	115.2
<C−C−H>[c]	110.8(2) p_8			110.4	110.3	109.7	109.8
torsion angles							
flap	58.8(3) p_9			57.6	59.9		
C−O−O−C	63.7(4)	64.5(1)	65.2(4)	63.1	63.7	−76.7	−78.3
O−O−C−O	−63.9(4)	−64.7(1)	−65.2(4)	−62.9	−64.8	35.7	36.6

[a] Data given in the text of ref 7. There is also a somewhat different set of the X-ray data given in Table 1 of that reference. No error limit was indicated for O−C−O angle. [b] Results with 6-311+G (2df,p) basis sets are given for all quantum chemical calculations. [c] According to the calculations, all C−H distances differ less than 0.001 Å, except for the C8H14 (and C10H20 see Figure 3) for which the value is given separately. The differences between the individual C−C−H valence angles are less than 2°, thus the average value is indicated only. In the GED column, the results of least-squares analysis are given with the mentioned differences set to the calculated values (see text). [d] Uncertainties were taken as $\sigma(r_{h1}) = (\sigma_{scale}^2 + (2.5\sigma_{LS})^2)^{1/2}$, where $\sigma_{scale} = 0.002r$ and σ_{LS} is a standard deviation in least-squares refinement. [e] The difference between two different C−C distances was set to 0.002 Å during the GED analysis.

TABLE 3: Experimental and Calculated Vibrational Amplitudes of the Chair Form of DADP and Vibrational Corrections Δ*r* (Å) without Those for Nonbonded Distances Involving Hydrogen Atoms

term[a]	r_{h1}	*l*(GED)	*l*(B3LYP)	$\Delta r = r_{h1} - r_a$
C−H	1.092	0.077(2) l_1	0.076	0.0016
C−O	1.432	0.052(1) l_2	0.051	0.0008
O−O	1.463	0.051(1) l_2	0.050	0.0001
C−C	1.523	0.052(1) l_2	0.051	0.0001
O1···O5	2.320	0.055(1) l_3	0.059	0.0025
O1···C3	2.337	0.064(1) l_3	0.063	0.0031
O2···C7	2.339	0.070(1) l_3	0.070	0.0025
C7···C8	2.555	0.072(1) l_3	0.072	0.0018
C3···C6	2.740	0.061(2) l_4	0.061	0.0040
O1···O4	2.742	0.066(2) l_4	0.066	0.0039
O1···C8	2.837	0.104(2) l_4	0.104	0.0059
C3···C10	3.429	0.098(3) l_5	0.097	0.0073
O1···C7	3.649	0.070(3) l_5	0.068	0.0061
C3···C9	4.058	0.074(7) l_6	0.075	0.0081
C7···C10	4.339	0.144(7) l_6	0.144	0.0126
C8···C10	4.545	0.093(7) l_6	0.096	0.0107
C7···C9	5.483	0.081(22) l_7	0.075	0.0131

[a] See Figure 3 for atom numbering.

Experimental Section

Synthesis. DADP was synthesized according to the method described in the literature.[16] The compound was purified by recrystallizing from ethyl acetate until a constant melting point was obtained. The purity was also checked by GC and IR analyses.

GED/MS. The experiment was performed with the combined Ivanovo GED/MS apparatus[17] consisting of the EMR-100 gas-phase electron diffraction and the APDM-1 monopolar mass spectrometric units. An accurate wavelength $\lambda = 0.04344(4)$ Å of the electrons, accelerated by roughly 74 kV voltage, was determined from the diffraction patterns of polycrystalline ZnO. The sample was evaporated at 18 °C from a molybdenum effusion cell which had the following dimensions of the inner length × diameter: 20 × 7 mm for the cell and 1.2 × 0.6 mm for the effusion nozzle. The scattered electrons were collected on the Kodak Electron Image films of 9 × 12 cm at 1.3 μA primary electron beam intensity and 90-s exposure time. During the experiment, the residual pressure in the diffraction chamber was $2.5 \cdot 10^{-6}$ Torr. The data collected on six photographic films at 338-mm nozzle-to-plate distance were used for the further analysis. The optical densities of the photographs were measured with the computer-controlled microdensitometer[18] on the basis of the Carl Zeiss Jena MD100 model. Experimental molecular scattering intensities curves sM(s) in the *s*-range of 2.4−27.4 $Å^{-1}$ are shown in Figure 4.

Mass spectra of the effusing molecular beam were recorded simultaneously with collecting the diffracted electrons. Electron impact (50 eV) was applied to ionize the neutral species. The mass spectrometric section was evacuated down to $4.9 \cdot 10^{-7}$ Torr. The mass spectrum contains very few peaks. The major ion present in the mass spectrum with a mass of 43 amu (100%) corresponds to the fragment $[CH_3-C\equiv O]^+$. Two peaks occur at *m*/*e* 58 and 59 amu with equal intensities of about 14% each. The most probable assignment of these peaks may be $[(CH_3)_2-C=O]^+$ (58) and $[CH_3-C(O)=O]^+$ (59). The highest observed mass was 101 amu (3%), corresponding probably to the loss of a methyl radical and an oxygen molecule by the molecular ion (*m*/*e* 148). Neither molecular ion nor other ions with *m*/*e* higher than 101 were detected at the relative intensity level of 10^{-3} comparing to that of *m*/*e* 43. Peaks at *m*/*e* 16 (O^+) and 28 (CO^+) were of about 2% each.

The only mass spectrometric investigation of diacetone diperoxide reported so far presents only plotted data with no numerical relative intensities given.[19] Visually, this mass spectrum recorded at 70 eV ionizing electron energy agrees with ours, except for the peak at 59 amu which was not observed in the cited study. This may possibly be because the ionizing

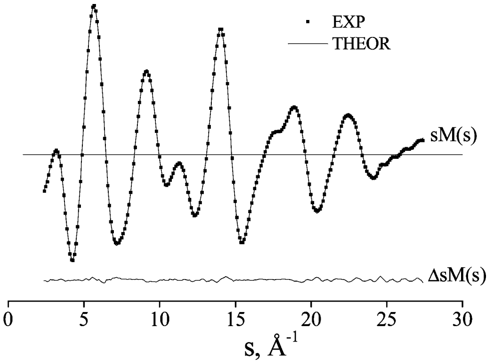

Figure 4. Experimental (dots) and calculated (full line) molecular scattering intensities sM(s) and the difference (exp − theor) for the refined chair structure. Agreement factor $R_f = 2.2\%$.

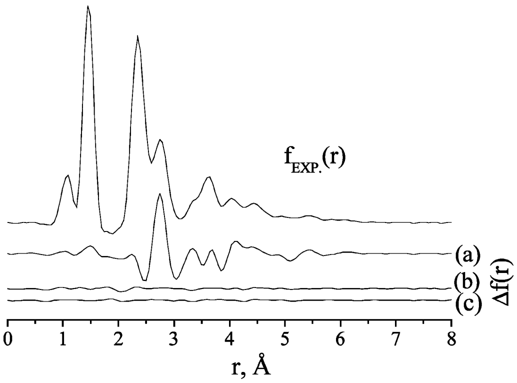

Figure 5. Experimental radial distribution curve (above) and the differences (exp − theor): (a) and (b) for the twist and chair structures from B3LYP/6-31G(d,p) calculations ($R_f = 29.2$ and 3.0%, respectively) and (c) for the chair conformation after least-squares refinement of the all geometric parameters and vibrational amplitudes ($R_f = 2.2\%$).

voltage is different from ours. The peak for the molecular ion is absent in both electron impact mass spectra. The very low stability of the molecular ion of tetroxane rings with different substituents was confirmed also by high-resolution mass spectrometry.[20] The thermal decomposition of gaseous DADP in the presence of *n*-octane was studied at temperatures of 403−523 K[21] which are significantly higher than the temperatures the sample was exposed to in our studies.

The relative intensities of the ions in the mass spectra showed no change during the course of the experiment until complete evaporation of the sample from the container. After the sample was completely sublimed, no visible traces of any possible impurity or decomposition product was detected on the inner walls of the sample container.

GED Analysis

The modified KCED-35 program was applied for the analysis of the electron diffraction intensities.[22] The experimental radial distribution function *f*(r) derived by Fourier transformation of the molecular intensities is shown in Figure 5, together with the difference curves between experimental and calculated (B3LYP/6-31G(d,p)) *f*(r) functions for twist and chair structures. The difference curves for twist (a) and chair (b) confirm the very strong preference for the chair conformer predicted by our calculations. A detailed analysis of the terms contributing to the radial distribution curves indicates that the strongest difference between chair and twist occurs in the range 2.5−3 Å. This range corresponds predominantly to differences in $(O\cdots O)_{diagonal}$, $(C\cdots C)_{ring}$, and (O···C) distances. The preliminary geometry of the chair form was then refined by least-squares fitting of the molecular scattering intensities. In the analysis, overall C_{2h} symmetry and local C_{2v} symmetry for the methyl groups were assumed. The following independent geometric parameters were used for describing the geometry of the ring: *r*(O−O), *r*(O−C), *r*(O1···O5), and the "flap" angle between the OCO plane and the rectangle, formed by the oxygen atoms (see Figure 3 for atom numbering). The difference between axial and equatorial C−C bond lengths was constrained to the calculated value (see Table 2). The OCC angles for equatorial and axial methyl groups were refined separately. On the basis of the quantum chemical calculations, all C−H bond lengths were assumed to be equal, except for the bonds C8−H14 and C10−H20 which were constrained to be shorter by 0.004 Å. A mean value of C−C−H angles was refined and differences between angles were set to calculated values.

Vibrational amplitudes have been collected in seven groups and the differences between amplitudes within each group were constrained to the calculated values. With these constraints, nine independent parameters (p_1−p_9) and seven groups of vibrational amplitudes ((l_1−l_7) were refined simultaneously. Geometric parameters and vibrational amplitudes derived with the B3LYP/6-31G(d,p) method were used as starting values. Vibrational corrections, $\Delta r = r_{h1} - r_a$, calculated with the method of Sipachev,[15] were incorporated in this refinement. The following correlation coefficients had absolute values larger than 0.6: $p_1/p_2 = -0.83$, $p_2/p_3 = 0.60$, $p_3/p_4 = -0.67$, $p_2/l_2 = 0.80$, $p_3/l_2 = -0.73$, and $p_6/l_3 = -0.63$. The final geometric parameters derived by the GED analysis are included in Table 2, together with X-ray data and quantum chemical results. The vibrational amplitudes are given in Table 3, together with calculated amplitudes and vibrational corrections. The difference curve (c) in Figure 5 corresponds to these refined values.

In a final step, least-squares analyses were performed for mixtures of chair and twist conformers. Since the calculated (B3LYP/6-31G(d,p)) structure for the chair conformer reproduces the experimental radial distribution function surprisingly well (see difference curve b in Figure 5), the calculated parameters for the twist conformer are expected to reproduce the real structure of this form equally well. For this reason, only the parameters for the chair form were refined in these analyses. Refinements were carried out for different fixed contributions of the twist conformer. The *R*-factor decreases slightly from 2.21 to 2.16% for a contribution of 1% twist form and increases noticeably for higher contributions (Figure 6). According to the Hamilton criterion, the contribution of the twist conformer is less than 3.5% at a significance level of 0.05,[23] corresponding to $\Delta G^0 > 2.0$ kcal/mol. This confirms the calculated values given in Table 1.

Discussion

The GED analysis results in a chair conformation of DADP six-membered ring, with a negligible contribution of the twist form at room temperature. This result is in agreement with our quantum chemical calculations which predict a contribution of less than 2% twist. In the crystal, slightly distorted chair structures were found.[7,8] Considering experimental uncertainties and systematic differences between geometric parameters derived by X-ray diffraction on crystals and GED, the values obtained with the two methods are in very good agreement (Table 2). Similarly, both quantum chemical methods, B3LYP and MP2, reproduce the gas-phase structure very satisfactorily. Calculated bond lengths (r_e values) are systematically shorter

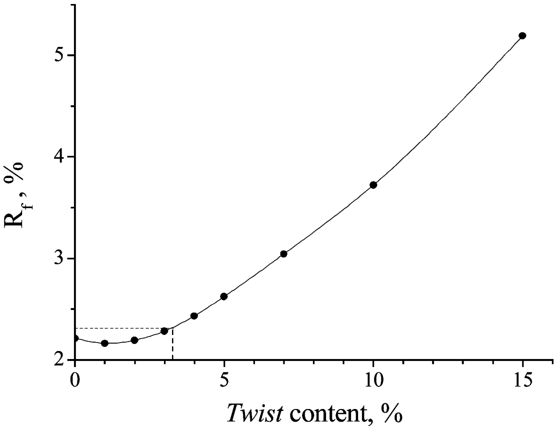

Figure 6. Agreement factor R_f for different molar contribution of the twist form. Geometrical parameters of the chair form were refined while those for the twist were kept fixed. The dashed lines correspond to the uncertainty in the twist content according to the Hamilton's criterion[23] at significance level 0.05.

by about 0.005 Å (C−O, O−O, and C−C bonds) and by about 0.010 Å (C−H bonds) than experimental r_{h1} values. Bond angles in the DADP ring (108.2(7) and 107.7(4)°) are slightly smaller than those in cyclohexane (111.3(2)°), whereas dihedral angles in DADP (63.7(4) and −63.9(4)°) are somewhat larger than those in cyclohexane (55.1(7)°).[24] The latter angle is close to the ideal value in the open-chain molecule $CH_3-CH_2-CH_2-CH_3$ which implies minimal torsional strain. In the tetroxane ring, however, the torsional angle around the O−O bond of 63.7(4)° deviates strongly from the ideal value observed for the open-chain molecule $CH_3-O-O-CH_3$, for which a C−O−O−C dihedral angle of 119(4)° has been determined.[25] Thus, considerable torsional strain is expected to be present in the tetroxane ring. Since the C−O−O angle in the ring (107.4(4)°) is close to the value in dimethyl peroxide (105.2(5)°)[25] and the O−C−O angle (108.2(7)°) is close to the tetrahedral, angle strain is negligible. Also, the bond lengths in the ring, $r(O-O) = 1.463(5)$Å and $r(C-O) = 1.432(4)$Å, are almost equal to those in dimethyl peroxide, $r(O-O) = 1.457(12)$Å and $r(C-O) = 1.420(7)$Å, within the combined error limits.

Information about the structural properties of the twist conformer of DADP and its relative energy has been derived from quantum chemical calculations. Bond lengths and bond angles are very similar in chair and twist conformers (Table 2). Torsional angles, however, differ appreciably. The dihedral angle around the O−O bond changes from about 64° in the chair form to about −77° in the twist form, and the angle around the C−O bond changes from about −64° to 36°. The change of this torsional angle by about 30° is expected to increase the torsional strain in the twist form. The geometry and conformational properties of ring compounds which contain oxygen atoms, such as tetroxane, depend also on orbital interactions between the oxygen electron lone pairs and vicinal antibonding orbitals (anomeric effect) in addition to angle and torsional strain.

The calculated energy difference between twist and chair conformers is between 2.8 and 3.2 kcal/mol. On the other hand, this energy difference is considerably larger for the parent compound 1,2,4,5-tetroxane, for which calculations predict values between 8.1 and 8.8 kcal/mol. Thus, methyl substitution at the opposite carbon atoms lowers this energy difference by more than 5 kcal/mol. On the other hand, methyl substitution has a minor effect on the ring geometry of the chair conformer. The C−O bonds lengthen by about 0.02 Å, the O−C−O angles decrease by about 2°, the O−C−O angles increase by the same amount, and the torsional angle around the C−O bond, $\varphi(O-C-O-O)$, decreases by about 3° upon methyl substitution. The O−O bond length and torsional angle around this bond, $\varphi(C-O-O-C)$, are almost unchanged. The predicted barriers for chair−twist conversion 14.6 (B3LYP) and 17.1 kcal/mol (MP2) obtained in this work are comparable to the experimental values $\Delta G^{\ddagger} = 15.4$ kcal/mol[10] and 15.3 kcal/mol[11] from dynamic ^1H NMR spectra.

The effect of methyl substitution on opposite carbon atoms in cyclohexane has been studied by molecular mechanics methods. Whereas the calculations of Allinger et al.[5] predict a conformational energy difference of 5.3 kcal/mol for cyclohexane and 3.1 kcal/mol for 1,1,4,4-tetramethylcylohexane, MM3 calculations by Weiser et al.[6] result in a value of 5.6 kcal/mol for the latter compound. Because of these inconclusive results, we performed B3LYP/6-31G(d,p) calculations for both compounds. These calculations predict conformational energy differences of 6.4 kcal/mol for cyclohexane and 4.2 kcal/mol for 1,1,4,4-tetramethylcylohexane. These results are in agreement with the MM calculations of Allinger et al.[5] and predict a decrease of the energy difference upon methyl substitution, although considerably less than that derived for the tetroxane rings.

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