Structure and conformational flexibility of hexamethyldiperoxacyclononane

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3,3,6,6,9,9-Hexamethyl-1,2,4,5-tetraoxacyclononane, one of the most thermally stable organic peroxides, has been studied by X-ray structural analysis. Possible conformations of this compound have been calculated by the molecular mechanics method.

Key words: organic peroxides; 3,3,6,6,9,9-hexamethyl-1,2,4,5-tetraoxacyclononane; X-ray diffraction analysis; conformational analysis; molecular mechanics method.

Organic peroxides are the class of organic compounds most widely used for generating free radicals.[1] In continuation of the studies of structures of organic peroxides, the structure of 3,3,6,6,9,9-hexamethyl-1,2,4,5-tetraoxacyclononane (**1**) has been studied by X-ray structural analysis and the geometry of the molecule has been calculated by the molecular mechanics method. This cyclic peroxide is characterized by high thermal stability and is used as an efficient structure-forming agent.[2]

The nine-membered cycle of molecule **1**, according to Hendrikson's nomenclature,[3] adopts a twisted-boat-chair conformation (Fig. 1, **A**). The related compounds, hexamethyl cyclotrisilperoxane (**2**)[4] and its carbon analog, 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane (**3**),[5] have identical conformations.

It is known that in the absence of steric hindrance, the peroxide group adopts the conformation in which the R—O—O—R angles (τ) are close to 90° (for example, in molecules of hydroperoxides[6] and H_2O_2,[7] τ = 90.2(6)°) or 180° (in particular, in dicumyl peroxide,[8] τ = 180°). Substantial deviations from these values may occur when there are bulky substituents R (for example, in the 1,1-dihydroxydicyclohexyl peroxide molecule,[9] τ = 156.1(4)°) or when the peroxide group enters into relatively small cyclic and cage systems (in six-membered peroxide cycles,[10] τ varies within the range 65—75°). The C(1)—O(1)—O(2)—C(2) torsion angles in cyclic diperoxide **1** have values intermediate between 90° and 180° (Table 1). Apparently, this is attributable to the fact that the COOC groups in cyclic compounds experience Baeyer hindrances caused by the closure of cycles, which results in twisting substantially different from that

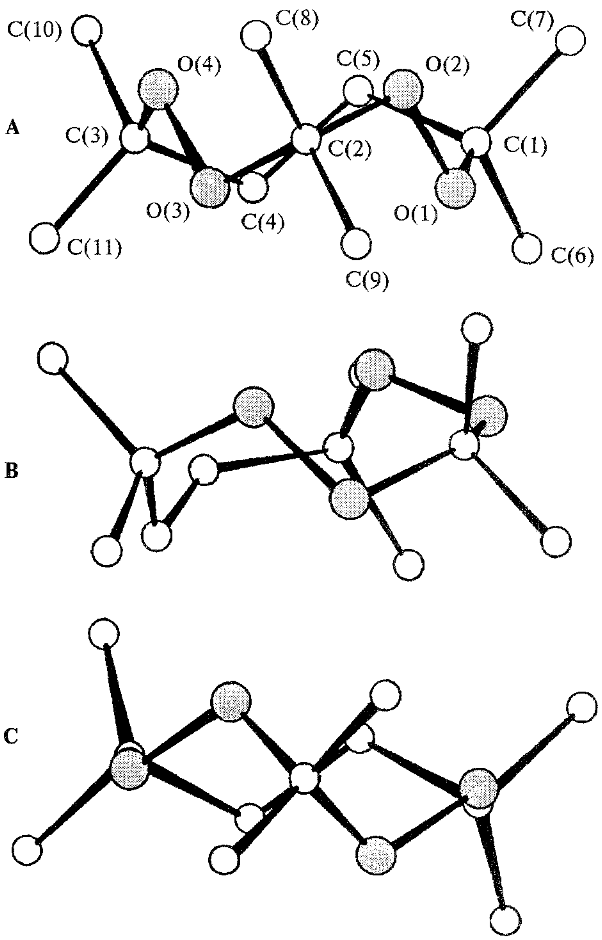

Fig. 1. Equilibrium conformations **A**, **B**, and **C** for molecule **1** (the O atoms are shaded).

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Table 1. Bond (ω) and torsion (τ) angles in the cycle of molecule **1** (which are not presented in Fig. 2)

Angle	ω/deg	Angle	τ/deg
O(1)—C(1)—C(6)	101.7(1)	C(1)—O(1)—O(2)—C(2)	137.8(2)
O(1)—C(1)—C(7)	109.6(1)	O(1)—O(2)—C(2)—O(3)	−59.3(1)
C(5)—C(1)—C(6)	112.3(1)	O(2)—C(2)—O(3)—O(4)	−64.9(1)
C(5)—C(1)—C(7)	110.9(1)	C(2)—O(3)—O(4)—C(3)	140.2(2)
C(6)—C(1)—C(7)	111.5(1)	O(3)—O(4)—C(3)—C(4)	−59.9(2)
O(2)—C(2)—C(8)	103.0(1)	O(4)—C(3)—C(4)—C(5)	−49.1(2)
O(2)—C(2)—C(9)	113.2(1)	C(3)—C(4)—C(5)—C(1)	126.3(2)
O(3)—C(2)—C(8)	113.0(1)	C(4)—C(5)—C(1)—O(1)	−53.1(2)
O(3)—C(2)—C(9)	102.2(1)	C(5)—C(1)—O(1)—O(2)	−60.0(1)
C(8)—C(2)—C(9)	113.6(1)		
O(4)—C(3)—C(10)	100.8(1)		
O(4)—C(3)—C(11)	110.0(1)		
C(4)—C(3)—C(10)	112.4(1)		
C(4)—C(3)—C(11)	111.1(1)		
C(10)—C(3)—C(11)	111.3(1)		

typical of acyclic peroxides. In related compound **3**, the C—O—O—C torsion angles (135.4—136.0°) are identical to those in peroxide **1**.

The O(1)—O(2) and O(3)—O(4) bond lengths in molecule **1** are 1.474(2) and 1.477(2) Å, respectively (Fig. 2), which are typical of observed torsion angles τ (the standard O—O bond lengths[11] at τ = 90° and 180° are 1.464 and 1.482 Å, respectively).

In molecule **1**, the distortions of the tetrahedral coordination of the C(1), C(2), and C(3) atoms reported previously[12] are well reproduced: the O(1)—C(1)—C(6), O(2)—C(2)—C(8), O(3)—C(2)—C(9), and O(4)—C(3)—C(10) bond angles are 101.7(1)°, 103.0(1)°, 102.0(1)°, and 100.8(1)°, respectively; the torsion angles in the corresponding essentially planar transoid fragments, O(2)—O(1)—C(1)—C(6) [179.4(2)°], O(1)—O(2)—C(2)—C(8) [178.8(2)°], O(4)—O(3)—C(2)—C(9) [173.5(2)°], and O(3)—O(4)—C(3)—C(10) [179.1(2)°], are substantially smaller than the remaining bond angles at the C(1), C(2), and C(3) atoms (see Table 1). Other geometric parameters for molecule **1** are also given in Table 1 and in Fig. 2.

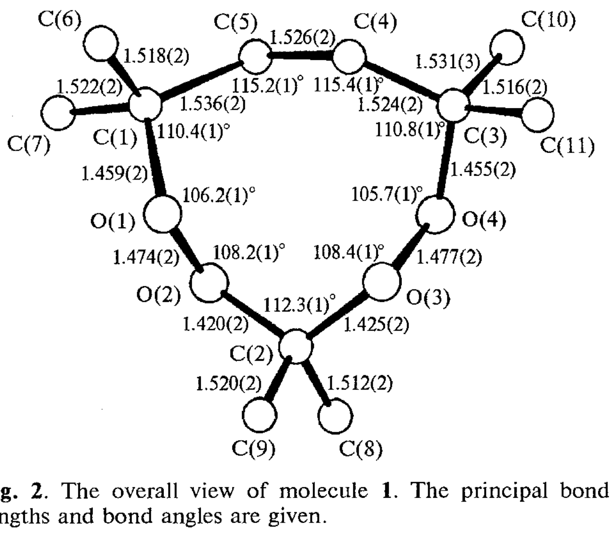

Fig. 2. The overall view of molecule **1**. The principal bond lengths and bond angles are given.

Table 2. Calculations of the conformations of the nine-membered cycle in conformers **A**, **B**, and **C** of molecule **1**

Torsion angle	τ/deg		
	A (0)*	**B** (13.4)*	**C** (18.0)*
C(1)—O(1)—O(2)—C(2)	137.6	−118.1	120.3
O(1)—O(2)—C(2)—O(3)	−60.8	37.7	−75.3
O(2)—C(2)—O(3)—O(4)	−60.8	−71.0	−75.3
C(2)—O(3)—O(4)—C(3)	137.6	155.1	120.3
O(3)—O(4)—C(3)—C(4)	−57.9	−60.3	−58.2
O(4)—C(3)—C(4)—C(5)	−53.8	−55.0	79.2
C(3)—C(4)—C(5)—C(1)	129.0	78.3	−132.7
C(4)—C(5)—C(1)—O(1)	−53.8	−62.6	79.2
C(5)—C(1)—O(1)—O(2)	−57.9	136.1	−58.2

* Conformational energies (E/kJ mol^{-1}) are given in parentheses.

Molecular mechanics calculations of geometry demonstrated that molecule **1** adopts three equilibrium conformations, **A**, **B**, and **C** (see Fig. 1). Structure **A**, which was determined in the crystal, corresponds to the absolute energy minimum (Table 2).

Experimental

Compound 1 was obtained by condensation of acetone with 2,5-bis(hydroperoxy)-2,5-dimethylhexane.[13]

Crystals of **1** are monoclinic; at −120 °C a = 6.053(2) Å, b = 14.983(6) Å, c = 14.159(5) Å, β = 100.82(3)°, V = 1261.4(7) Å^3, Z = 4, M = 218.29, d_{calc} = 1.150 g cm^{-3}, the space group is $P2_1/n$. The unit-cell parameters and intensities for 2278 independent reflections were measured on an automated four-circle Syntex P2$_1$ diffractometer (−120 °C, Mo-Kα radiation, a graphite monochromator, $\theta/2\theta$ scanning technique, θ_{max} = 28°). The structure was solved by the direct

Table 3. Atomic coordinates for nonhydrogen atoms ($\times 10^5$ for O atoms; $\times 10^4$ for C atoms) in molecule **1**

Atom	*x*	*y*	*z*
O(1)	38402(18)	24324(7)	49716(7)
O(2)	14208(18)	26453(7)	47503(7)
O(3)	21813(20)	40151(7)	55748(7)
O(4)	9361(20)	37411(7)	63298(7)
C(1)	4096(3)	1716(1)	5683(1)
C(2)	1185(3)	3588(1)	4699(1)
C(3)	2632(3)	3610(1)	7193(1)
C(4)	4307(3)	2891(1)	7034(1)
C(5)	3269(3)	2024(1)	6591(1)
C(6)	6617(3)	1560(1)	5864(1)
C(7)	2807(3)	896(1)	5249(1)
C(8)	−1336(3)	3716(1)	4449(1)
C(9)	2440(3)	4014(1)	3980(1)
C(10)	1162(4)	3316(1)	7907(1)
C(11)	3815(4)	4484(1)	7496(1)

Table 4. Atomic coordinates for hydrogen atoms ($\times 10^3$) in molecule **1**

Atom	*x*	*y*	*z*
H(4.1)	526(3)	275(1)	764(1)
H(4.2)	522(3)	317(1)	661(1)
H(5.1)	161(2)	206(1)	643(1)
H(5.2)	356(3)	150(1)	704(1)
H(6.1)	701(3)	105(1)	633(1)
H(6.2)	739(3)	205(1)	611(1)
H(6.3)	713(3)	134(1)	529(1)
H(7.1)	321(3)	37(1)	565(1)
H(7.2)	336(3)	69(1)	465(1)
H(7.3)	107(3)	99(1)	508(1)
H(8.1)	−163(2)	434(1)	443(1)
H(8.2)	−211(3)	341(1)	485(1)
H(8.3)	−196(3)	352(1)	381(1)
H(9.1)	203(3)	463(1)	391(1)
H(9.2)	202(3)	367(1)	342(1)
H(9.3)	410(3)	394(1)	421(1)
H(10.1)	219(3)	323(1)	853(1)
H(10.2)	39(3)	271(1)	774(1)
H(10.3)	11(3)	375(1)	796(1)
H(11.1)	496(3)	446(1)	808(1)
H(11.2)	280(3)	491(1)	757(1)
H(11.3)	478(3)	469(1)	702(1)

method (the MULTAN program) and refined by the block-diagonal least-squares method with anisotropic thermal parameters for nonhydrogen atoms. Positions of H atoms were calculated geometrically and refined isotropically. The final values of R factors are $R = 0.044$ and $R_w = 0.040$ (from 2130 reflections with $I > 3\sigma(I)$). All calculations were carried out on an Eclipse S/200 computer using the INEXTL program package.[14] Atomic coordinates are given in Tables 3 and 4.

Molecular mechanics calculations of the geometry of molecule **1** were performed with the use of MMP2 potentials[15] (the lengths of chemical bonds were fixed; the conformational energy was minimized in the space of independent bond and torsion angles; in calculations, angular, torsion, and van-der-Waals components were taken into account).

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