

Crystal Structure of 3,6-Spiro-dicyclohexylidene-1,2,4,5-tetraoxacyclohexane ("Dimeric Cyclohexanone Peroxide")

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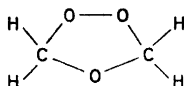
The crystals are triclinic with space group $P\bar{1}$

$$\begin{array}{ll} a = 5.82_7 \text{ \AA} & \alpha = 85.3_7^\circ \\ b = 6.06_1 \text{ \AA} & \beta = 88.5_9^\circ \\ c = 9.48_9 \text{ \AA} & \gamma = 62.6_8^\circ \end{array}$$

and one molecule in the unit cell. The phase problem has been solved by a computer procedure based on direct methods. Full matrix least squares refinement gave the R -value 5.3 % when the 843 observed reflections were included. The O—O distance is found to be 1.48₃ Å while the two independent C—O bond lengths are 1.43₅ Å and 1.44₄ Å, respectively. The environment of the spiro carbon atom is asymmetric; the distortion may possibly be explained by *intramolecular* repulsions of hydrogen atoms from oxygen atoms.

Cyclic organic peroxides and ozonides are not well known from the stereochemical point of view. The only crystal structure analysis reported of a cyclic peroxide is that of hydrated sodium peroxoborate,¹ where the O—O bond length obtained is 1.47 Å while the dihedral angle B—O—O—B is 64°.

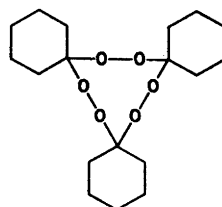
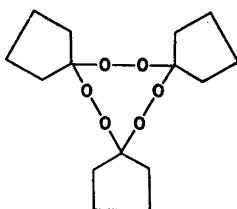
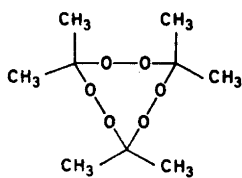
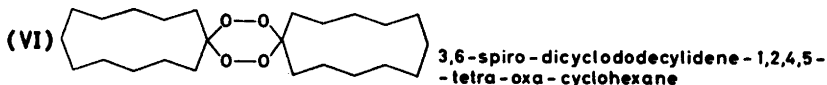
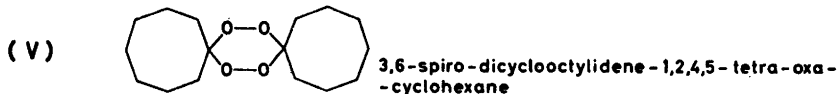
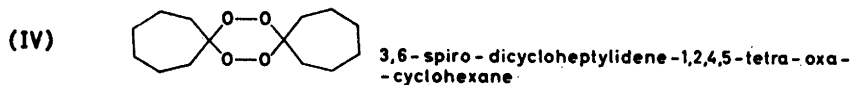
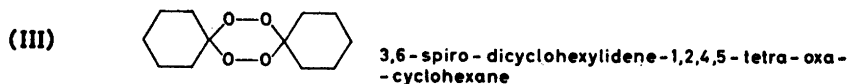
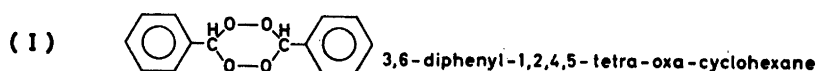
The number of structural information concerning non-cyclic organic peroxides is also limited.²⁻⁵ No structure analyses of ozonides have yet been published. However, an electron diffraction work on the compound 1,2,4-trioxa-cyclo-pentane is in progress at this university.⁶



Baeyer and Villiger⁷ found that treatment of benzaldehyde with hydrogen peroxide and concentrated sulphuric acid gave (I). (II) has been produced from acetone and Caro's acid in ether,⁸ while the oxidation of acetone by means of hydrogen peroxide, in the presence of mineral acids, leads to the trimeric peroxide (VII).⁹ The dimeric peroxides (III), (IV), (V), and (VI)

are obtained by treating the hydroperoxides with propionic acid (added HClO_4) at 0°C . The hydroperoxides are produced by oxidation of the corresponding cyclic ketones in acetonitrile with hydrogen peroxide in the presence of HClO_4 at 20°C .¹⁰

It has been claimed¹¹ that dimeric cyclopentanone peroxide is produced from the ketone and ethereal hydrogen peroxide. Recent attempts made at this university¹⁰ to obtain dimeric cyclopentanone peroxide, have all led to the trimeric form (VIII). Trimeric cyclohexanone peroxide, (IX), has been synthesized from the ketone and hydrogen peroxide in the presence of hydrochloric acid,¹² and by other means.



3,3,6,6,9,9-hexamethyl-
-1,2,4,5,7,8-hexa-
-oxa cyclononane

3,6,9-spiro-tricyclopentylidene-
-1,2,4,5,7,8-hexa-
-oxa cyclononane

3,6,9-spiro-tricyclohexylidene-
-1,2,4,5,7,8-hexa-
-oxa cyclononane

The compounds (I)–(IX) have been synthesized by T. Ledaal at this university. The details are given elsewhere.¹⁰ From the X-ray crystallographic point of view the compounds belong to the “equal atom” group, and according to their moderate complexities, one would expect the phase problems to be solved by direct methods.

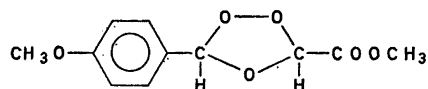
Preliminary X-ray investigations gave the following crystal data:

Compound No.	Space group	Approximate cell dimensions (Å) (°)	Number of molecules in the unit cell
I	$P2_1/c$	$a = 6.09$ $b = 7.85$ $\beta = 93.9$ $c = 12.37$	2
II	Undetermined (twinning)	$V = 800.9 \text{ \AA}^3$	4
III	$P\bar{1}$	$a = 5.85$ $\alpha = 85.4$ $b = 6.06$ $\beta = 88.6$ $c = 9.49$ $\gamma = 62.7$	1
IV	$P2_1/c$	$a = 9.40$ $b = 6.40$ $\beta = 102.4$ $c = 11.68$	2
V	$P2_1/c$	$a = 9.79$ $b = 7.33$ $\beta = 114.2$ $c = 11.78$	2
VI	$P\bar{1}$	$a = 5.62$ $d(010) = 6.97$ $\alpha^* = 85.0$ $d(001) = 14.22$	1
VII	$P2_1/c$	$a = 13.94$ $b = 10.83$ $\beta = 91.6$ $c = 7.95$	4
VIII	$P6_322$	$a = 5.45$ $c = 9.90$	$\frac{2}{3}$
IX	$Pbca$	$a = 9.95$ $b = 11.78$ $c = 31.93$	8

It should be pointed out that several crystals of (I) obtained from benzene and acetonitrile, respectively, were examined, and all turned out to be twins with common (001)-plane. It may also be mentioned that the structure of (VIII) is disordered.

It is intended, in forthcoming publications, to give the details of X-ray crystallographic structure determinations of some of these compounds. The crystal structure analysis of (III) is presented in this paper.

Preliminary X-ray investigation of the ozonide: 3-carbomethoxy-5-anisyl-1,2,4-trioxacyclopentane has given the following crystal data:



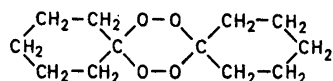
Space group: $Pbca$, $a = 25.39 \text{ \AA}$, $b = 10.96 \text{ \AA}$, $c = 8.17 \text{ \AA}$.

Number of molecules in unit cell: 8.

The compound has been synthesized by P. Kolsaker at this university.¹³

CRYSTAL DATA

Dimeric cyclohexanone peroxide belongs to the triclinic system. The Wilson ratio calculated, is found to be $\rho = 0.586$, theoretical values for centrosym-



metric and non-centrosymmetric distributions, respectively, being $\rho_1 = 0.637$ and $\rho_2 = 0.785$. Both the $N(Z)$ -plot, shown in Fig. 1, and the Wilson ratio correspond to hypercentric intensity distribution, probably due to the approximate centrosymmetrical six-membered ring in general position.¹⁴

The Dirichlets reduced cell has been determined using the method of Balashov and Ursell,¹⁵ and the cell parameters were found by means of $h k 0$, $h 0 l$ and $0 k l$ Weissenberg photographs taken with unfiltered Cu-radiation. Powder diagrams of BaF_2 ($a = 6.2001 \text{ \AA}$) were superimposed on the films for calibration purpose. The 2θ -values of 84 reflections were used in a least squares refinement of the lattice parameters. The programme used has been

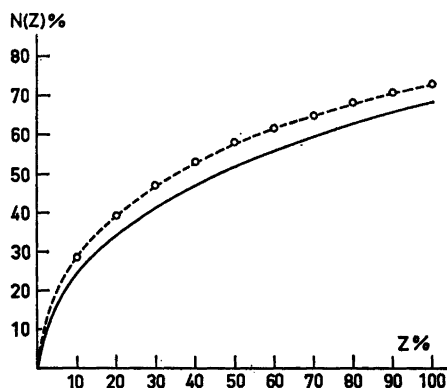


Fig. 1. $N(Z)$ -plot for dimeric cyclohexanone peroxide. Full line corresponds to centrosymmetrical distribution.

written by R. A. Sparks at UCLA. With the wavelengths for CuK-radiation taken as $\bar{\alpha} = 1.54178$, $\alpha_1 = 1.54051$, $\alpha_2 = 1.54433$, and $\beta = 1.39217$ Å, the following cell parameters with their estimated standard deviations resulted:

$a = 5.827$ Å	$\sigma(\text{Å}) = 0.002$
$b = 6.061$ »	$\sigma(\text{Å}) = 0.002$
$c = 9.489$ »	$\sigma(\text{Å}) = 0.001$
$\alpha = 85.37^\circ$	$\sigma(^\circ) = 0.03$
$\beta = 88.58^\circ$	$\sigma(^\circ) = 0.03$
$\gamma = 62.68^\circ$	$\sigma(^\circ) = 0.03$

With one molecule in the unit cell the calculated density is 1.28 g.cm^{-3} . The density measured by floatation was 1.27 g.cm^{-3} . According to the intensity distribution, the space group $P\bar{1}$ was assumed.

The intensity material was obtained from photometric measurements of integrated Weissenberg diagrams corresponding to $h0l$, $hk0$, $hk1$,, $hk8$ (CuK α -radiation) and of $0kl$ -precession diagrams (MoK α -radiation). The number of reflections accessible from these diagrams is 1142, 843 of which were strong enough to be measured.

The intensities were statistically put on an absolute scale, and the overall temperature factor thus obtained, $B = 3.87 \text{ Å}^2$, was used in the calculation of unitary structure factors, and also as starting parameter in the isotropic least squares refinement.

No corrections have been made for absorption or secondary extinction effects.

DETERMINATION OF THE STRUCTURE

The phase problem was solved using a sign determining computer procedure based on the Cochran and Douglas method,¹⁶ the zero-check,¹⁷ and the statistical equivalent of Sayre's equation.¹⁸ The set of programmes, handling two-dimensional data only, has been written in the SPS-language for IBM-1620 by the author.

Projecting along the two shortest periods the sign determination process was carried out for the $0kl$ - and $h0l$ -zone reflections, the corresponding $|U|$ -distributions being listed in Table 1.

Starting with the $0kl$ -projection the origin was specified by giving positive signs to the unitary structure factors $U(0\bar{1}1)$ and $U(010)$ which have absolute values 0.43 and 0.25, respectively. 13 additional large U -values were selected for permutation, 16 sign relationships being found among the 15 reflections which are involved in the expression

$$\chi = \sum_{\mathbf{h}} \sum_{\mathbf{h}'} U_{\mathbf{h}} \cdot U_{\mathbf{h}'} \cdot U_{\mathbf{h} + \mathbf{h}'} \quad (1)$$

16 "small" unitary structure factors ($|U| \leq 0.06$) could be found for the zero-check, and the corresponding number of terms in the sums

$$\psi_0 = \sum_{\mathbf{k}} \left| \sum_{\mathbf{h}} U_{\mathbf{h}} \cdot U_{\mathbf{h} + \mathbf{k}} \right| \quad (2)$$

was 26. χ_e given by

$$\chi_e = \sum_{\mathbf{h}} \sum_{\mathbf{h}'} |U_{\mathbf{h}} \cdot U_{\mathbf{h}'} \cdot U_{\mathbf{h}+\mathbf{h}'}| \cdot \tanh(N |U_{\mathbf{h}} \cdot U_{\mathbf{h}'} \cdot U_{\mathbf{h}+\mathbf{h}'}|) \quad (3)$$

where N is the number of equal atoms in the cell, was calculated, and found to be $\chi_e = 0.911$.

Applying the programme to test the $2^{13} = 8192$ possible sign combinations, 24 satisfying $\chi > \chi_e$ resulted. The corresponding values of χ and ψ_0 are listed in Table 2 which shows that only three different values of χ occur. All sets corresponding to the largest χ , 1.127, also have large ψ_0 -values. Signset number 21 associated with the minimum ψ_0 (2.427) and the medium χ (1.019) should be considered the most probable.

Using the sign relationship

$$S(U_{\mathbf{k}}) = S(\sum_{\mathbf{h}} U_{\mathbf{h}} \cdot U_{\mathbf{h}+\mathbf{k}}) \quad (4)$$

where S means "sign of", 16 additional signs of large and moderate unitary structure factors were derived on the basis of set number 21. The 31 signs thus obtained were used in calculating the electron-density map which is shown in Fig. 2 (a) compared to the final map (Fig. 2 (b)). The trial parameters derived from Fig. 2 (a) corresponded to an R -value $R_{0kl} = 50.3\%$. A programme was now written based upon the "minimum residual method"¹⁹ the application of which reduced the R -factor to 14.6%. Two concluding cycles of isotropic least squares refinement reduced it further to 10.3%.

Comparison of the signs determined with those corresponding to $R_{0kl} = 10.3\%$ showed no discrepancies for set number 21 while two had been incorrectly obtained by the application of (4).

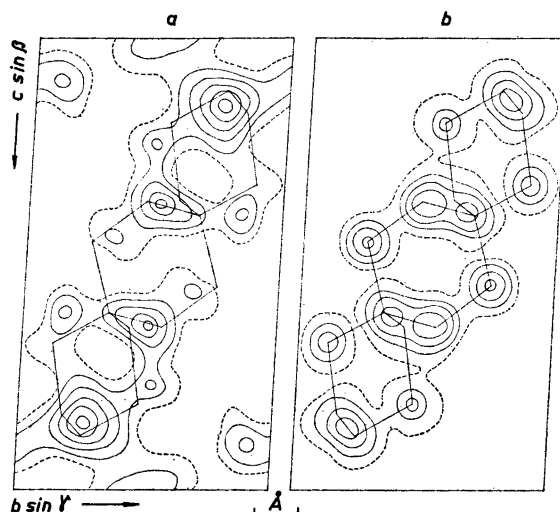


Fig. 2. Fourier projection along the a axis. (a) Calculated with the 31 "most probable signs", (b) final map.

Turning to the $h0l$ -projection $U(100) = 0.44$ and $U(201) = 0.31$ were given positive signs in order to fix the origin. 14 permutable signs were selected, the number of terms in the χ -expression being 27. Corresponding to the 20 unitary structure factors satisfying $|U_h| \leq 0.07$ 46 products for the zero-check could be found. χ_c was calculated by (3) to be $\chi_c = 1.200$.

$2^{14} = 16\,384$ sign combinations were tested by the programme, 18 of which satisfied $\chi > 0.9 \cdot \chi_c$. The results may be found in Table 3 (a). Sign set number 1 consists of 14 positive signs while number 2, 3, and 4 contain one negative sign each; thus these sets may be regarded as unprobable. None of the 14 signsets left are associated with the desired combination of large χ and small ψ_0 .

Therefore each set was used as basis for evaluation of 23 additional signs using (4) in a somewhat special way; the signs being accepted in the order of decreasing probabilities given by

$$P_+(\mathbf{k}) = \frac{1}{2} + \frac{1}{2} \cdot \tanh(N \cdot |U_{\mathbf{k}}| \cdot \sum_{\mathbf{h}} U_{\mathbf{h}} \cdot U_{\mathbf{h}+\mathbf{k}}) \quad (5)$$

and the χ - and ψ_0 -values for the total set, in this case containing 39 signs, being calculated each time. The results are given in Table 3(b) which shows that while χ is practically constant great variations occur for the ψ_0 -values. Among the three sets favoured by the zero-check, with $\psi_0 < 7.0$, that which corresponds to basic signset number 9 has the largest χ -value (3.922).

The corresponding Fourier map is shown in Fig. 3 (a) together with the final map (Fig. 3 (b)). Starting with the z -parameters arrived at for the $0kl$ -projection and the x -coordinates derived from Fig. 3 (a), three cycles of isotropic least squares refinement reduced the R -factor from 26.2 % to 10.2 %.

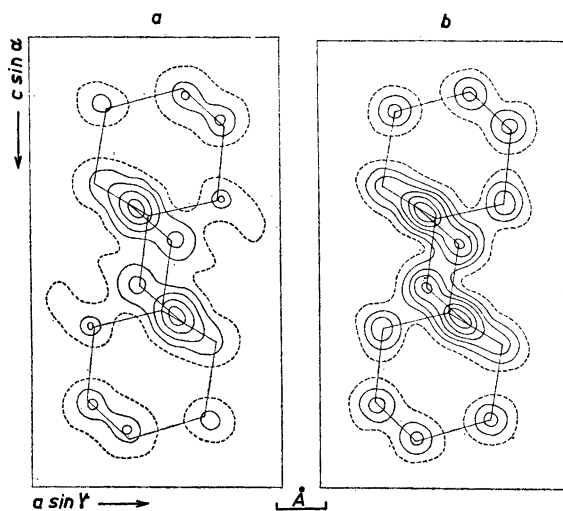


Fig. 3. Fourier projection along the b axis. (a) Calculated with the 39 "most probable signs", (b) final map.

Checking of the 39 signs determined with those corresponding to $R_{h0l} = 10.2\%$ revealed that 6 had been obtained incorrectly, one of which was contained in the set 9 of Table 3 (a). All other sets of this table included more than one wrong sign.

Table 1. $|U|$ -Distributions of the $h0l$ - and $0kl$ -projections.

Range of $ U $	Number of reflections	
	$h0l$ -projection	$0kl$ -projection
0.00–0.01	4	2
0.01–0.02	4	3
0.02–0.03	9	3
0.03–0.04	7	5
0.04–0.05	7	8
0.05–0.10	16	13
0.10–0.15	11	20
0.15–0.20	16	7
0.20–0.25	7	12
0.25–0.30	3	6
0.30–0.35	5	10
0.35–0.40	3	3
0.40–0.45	4	5
0.45–0.50	3	2
0.50–1.00	3	3

Table 2. Most probable signsets for the $0kl$ -projection.

Signset number	χ	ψ_0
1	1.127	3.907
2	0.983	2.667
3	1.019	3.031
4	1.019	3.293
5	1.127	3.645
6	0.983	2.929
7	1.019	2.913
8	0.983	3.009
9	1.127	2.817
10	0.983	2.747
11	1.127	3.079
12	1.019	2.651
13	1.019	3.517
14	1.127	3.421
15	0.983	2.705
16	1.127	3.683
17	0.983	2.443
18	1.019	3.255
19	0.983	2.971
20	1.127	3.303
*21	1.019	2.427
22	1.019	2.689
23	0.983	3.233
24	1.127	3.041

Table 3. Most probable signsets for the $h0l$ -projection.

(a)			(b)		
Signset number	χ	ψ_0	Basic signset number	χ	ψ_0
1	1.518	4.063	5	4.015	9.631
2	1.193	3.185	6	4.211	10.926
3	1.289	2.638	7	3.849	6.207
4	1.197	2.526	8	3.651	7.116
5	1.148	2.020	*9	3.922	6.718
6	1.215	2.179	10	3.823	7.730
7	1.136	2.165	11	3.999	7.222
8	1.102	2.171	12	3.890	6.711
*9	1.148	2.184	13	3.919	7.178
10	1.090	2.026	14	4.031	7.983
11	1.201	2.132	15	3.846	8.686
12	1.145	2.215	16	3.889	8.129
13	1.213	2.217	17	3.980	8.947
14	1.268	2.135	18	3.825	8.064
15	1.141	2.174			
16	1.111	1.903			
17	1.123	2.049			
18	1.129	2.028			

REFINEMENT OF THE STRUCTURE

With the final coordinates from the two-dimensional analysis and the statistically determined overall B -value as starting parameters, a three-dimensional full-matrix least squares refinement was carried out using a programme written by Gantzel, Sparks and Trueblood²⁰ (revised for UNIVAC 1107 by cand. real. Christian Rømming at this university). The weighting scheme No. 1:

$$\text{for } F_o \leq \text{FB}, \quad W = A1(F_o)^{B1}$$

$$\text{for } F_o > \text{FB}, \quad W = A2(F_o)^{B2}$$

was adapted by taking

$$A1 = 10.0, \quad A2 = 15.0, \quad B1 = 0.0, \quad B2 = -0.5 \text{ and } \text{FB} = 2.0.$$

The atomic form factors used were those of Hanson, Herman, Lea and Skillman.²¹

After 3 cycles of isotropic refinement, anisotropic thermal vibrational parameters were introduced for the oxygen and carbon atoms. The hydrogen atom positions were calculated assuming tetrahedral C—H bonds of lengths 1.05 Å, and reflections corresponding to $\sin \theta/\lambda < 0.45$ were included in the isotropic refinement of these atoms. The R -value arrived at for the 843 observed reflections was 5.3 %.

The 299 accidentally absent reflections had previously been given the value $\frac{1}{4}I_{\min}$ and had been scaled along with the rest of the data although not used

in any calculations of the scale factors. Allowance for the inclusion of these reflections in the least squares refinement was made by applying weighting scheme No. 3 ($W = 1/\sigma$). Satisfactory weight analysis²² was obtained by giving all unobserved reflections the same constant weight $W = A1/3$.

With the inclusion of the accidental absences, it would be roughly expected that the standard deviations (estimated from the inverse matrix of the normal equations) would decrease by a factor $(842/(834 + 299))^{1/2} = 0.86$. The actual improvement in the average coordinate E.S.D.'s corresponded to a factor 0.91. The R -value arrived at for all data was 6.9 %.

A final difference Fourier map, calculated with the observed data and with phases determined by the parameters corresponding to $R = 5.3$ % contained no positive or negative areas greater than $0.23 \text{ e}\cdot\text{\AA}^{-3}$, the E.S.D. of the electron density²³ being $\sigma(\rho) = 0.06 \text{ e}\cdot\text{\AA}^{-3}$.

The fractional atomic coordinates and the thermal vibration parameters arrived at are given in Tables 4, 5, 6; the expressions for the anisotropic and isotropic vibrations, respectively, being:

$$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$$

and $\exp[-B\sin^2\theta/\lambda^2]$

A comparison between calculated and observed structure factors is presented in Table 7. The accidental absences (with F_u -values corresponding to I_{\min}) and the calculated values, are given in Table 8.

Table 4. Fractional atomic coordinates for oxygen and carbon atoms.^a (Estimated standard deviations in parantheses).

	x	y	z
O ₁	-0.0965 (0.0003)	-0.0373 (0.0003)	0.1282 (0.0002)
O ₂	-0.0774 (0.0003)	0.2458 (0.0003)	-0.0456 (0.0002)
C ₁	-0.0264 (0.0004)	0.1592 (0.0004)	0.1015 (0.0002)
C ₂	-0.2224 (0.0004)	0.3750 (0.0004)	0.1798 (0.0003)
C ₃	-0.1810 (0.0005)	0.3236 (0.0005)	0.3393 (0.0003)
C ₄	0.0968 (0.0006)	0.2553 (0.0005)	0.3817 (0.0003)
C ₅	0.2858 (0.0004)	0.0321 (0.0005)	0.3050 (0.0003)
C ₆	0.2508 (0.0004)	0.0841 (0.0004)	0.1446 (0.0003)

^a For numbering of atoms, see Fig. 4(a).

Table 5. Anisotropic thermal vibration parameters. (Estimated standard deviations in parantheses).

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O_1	0.0342 (0.0006)	0.0293 (0.0005)	0.0110 (0.0002)	-0.0330 (0.0009)	0.0058 (0.0005)	-0.0059 (0.0005)
O_2	0.0368 (0.0006)	0.0237 (0.0005)	0.0111 (0.0002)	-0.0252 (0.0009)	0.0008 (0.0005)	-0.0010 (0.0005)
C_1	0.0321 (0.0008)	0.0256 (0.0007)	0.0107 (0.0003)	-0.0290 (0.0012)	0.0002 (0.0007)	-0.0003 (0.0007)
C_2	0.0328 (0.0008)	0.0297 (0.0008)	0.0138 (0.0004)	-0.0216 (0.0013)	0.0005 (0.0008)	-0.0064 (0.0008)
C_3	0.0458 (0.0010)	0.0373 (0.0009)	0.0135 (0.0004)	-0.0284 (0.0016)	0.0061 (0.0009)	-0.0113 (0.0009)
C_4	0.0553 (0.0013)	0.0430 (0.0010)	0.0136 (0.0004)	-0.0351 (0.0019)	0.0068 (0.0011)	-0.0102 (0.0010)
C_5	0.0374 (0.0009)	0.0375 (0.0009)	0.0138 (0.0004)	-0.0256 (0.0015)	0.0086 (0.0009)	-0.0033 (0.0009)
C_6	0.0321 (0.0008)	0.0337 (0.0008)	0.0127 (0.0004)	-0.0305 (0.0013)	0.0001 (0.0008)	-0.0053 (0.0008)

Table 6. Fractional coordinates and isotropic thermal vibration parameters for hydrogen atoms^a (Estimated standard deviations in parantheses).

	x	y	z	B (\AA^2)
H_{2e}	-0.403 (0.004)	0.407 (0.004)	0.159 (0.002)	3.2 (0.5)
H_{2a}	-0.205 (0.004)	0.519 (0.003)	0.147 (0.002)	1.3 (0.4)
H_{3e}	-0.310 (0.004)	0.471 (0.004)	0.398 (0.002)	2.8 (0.5)
H_{3a}	-0.223 (0.005)	0.174 (0.005)	0.380 (0.003)	5.8 (0.7)
H_{4e}	0.125 (0.004)	0.221 (0.004)	0.490 (0.002)	3.0 (0.5)
H_{4a}	0.136 (0.004)	0.409 (0.004)	0.348 (0.002)	3.4 (0.5)
H_{5e}	0.457 (0.004)	-0.018 (0.004)	0.334 (0.002)	2.2 (0.4)
H_{5a}	0.271 (0.004)	-0.126 (0.003)	0.347 (0.002)	1.9 (0.4)
H_{6e}	0.374 (0.004)	-0.069 (0.003)	0.094 (0.002)	1.9 (0.4)
H_{6a}	0.272 (0.004)	0.234 (0.004)	0.121 (0.002)	2.7 (0.5)

^a Referring to Fig. 4(a), the hydrogen atoms H_{ne} and H_{na} are, respectively, equatorially and axially bonded to C_n .

THERMAL MOTIONS

The principal axes of the thermal vibration ellipsoids for the oxygen atoms and the carbon atoms were derived from the temperature parameters in Table 5. Root mean square amplitudes for the atomic anisotropic thermal vibrations along the principal axes as well as the components of these axes along the crystal axes are given in Table 9. Fig 4(b) shows the ellipsoids of vibration viewed along [100].

However, the atomic anisotropic vibration parameters given in Table 5 may be supposed to arise primarily from rigid-body oscillations of the whole molecule,²⁴ and a programme written by Hirschfeld²⁵ has been used in carrying out the following calculations:

- (1) An orthogonal coordinate system L, M, N was chosen with axes along the principal axes of inertia, and origin in the centre of gravity. The moments of inertia, the direction cosines of L, M, and N with respect to the crystallographic axes, and the coordinates of the origin are given in Table 10.
- (2) Atomic coordinates and vibration tensors were transformed to the molecular coordinate system.

Table 9. Root mean square amplitudes for the atomic anisotropic thermal vibrations along the principal axes (Fig. 4(b)), and the components of these axes along the crystal axes.

Atom	Principal axis	$(\bar{u}^2)^{\frac{1}{2}}(\text{Å})$	P_x	P_y	P_z
O ₁	1	0.197	0.061	0.130	-0.012
	2	0.204	0.140	-0.105	-0.064
	3	0.234	0.120	-0.081	0.083
O ₂	1	0.185	0.068	-0.185	0.016
	2	0.225	0.068	0.004	0.094
	3	0.229	0.167	-0.025	-0.044
C ₁	1	0.186	0.008	0.160	-0.025
	2	0.209	0.190	-0.087	0.020
	3	0.223	0.030	-0.040	-0.101
C ₂	1	0.200	0.151	-0.166	-0.010
	2	0.228	0.118	0.066	0.030
	3	0.252	0.017	0.052	-0.101
C ₃	1	0.212	0.111	-0.144	-0.055
	2	0.260	0.083	-0.102	0.089
	3	0.268	0.135	0.058	-0.008
C ₄	1	0.225	0.012	0.082	0.085
	2	0.252	0.147	-0.160	0.038
	3	0.303	0.124	0.049	-0.051
C ₅	1	0.209	0.168	-0.096	0.053
	2	0.239	0.032	-0.150	-0.050
	3	0.272	0.091	0.051	-0.077
C ₆	1	0.207	0.180	-0.025	0.012
	2	0.220	0.069	-0.175	-0.027
	3	0.242	0.000	0.059	-0.102

- (3) Rigid-body parameters were calculated (the centre of libration of course being fixed at $L = 0$, $M = 0$, $N = 0$) and the final values are given in Table 11. From these parameters the components of the atomic vibration tensors were calculated. Table 12 shows the results together with the corresponding values obtained by the least squares refinement. Principal components of the rigid-body vibrations and their direction cosines with respect to molecular axes are given in Table 13.
- (4) Atomic coordinates were corrected for rigid-body libration.²⁶ The corrections obtained, together with the estimated standard deviations of the coordinates are listed in Table 14.

Since the programme requires the components U_{ij} of the thermal vibration tensor U , these quantities must be calculated from the B_{ij} 's obtained by the

Table 10. Moment of inertia (on relative scale), origin and directional cosines of the axes L, M, N of the molecular system with respect to the crystallographic axes.

L	134.726	0.2623	-0.5131	-0.8959
M	675.671	0.7113	0.2859	-0.1010
N	711.275	0.6521	-0.8093	0.4327

Centre of gravity at (0,0,0)

Table 11. Final rigid-body translation parameters T_{ij} and libration parameters ω_{ij} . (U_{ij} calculated according to Cruickshank).

	LL	MM	NN	LM	MN	LN
$T(\text{\AA}^2)$	0.0451	0.0403	0.0431	-0.0034	0.0040	-0.0088
$\omega(\text{rad}^2)$	0.00294	0.00262	0.00105	0.00031	-0.00016	-0.00049

(U_{ij} calculated according to Scheringer)

$T(\text{\AA}^2)$	0.0515	0.0477	0.0440	0.0014	0.0011	0.0015
$\omega(\text{rad}^2)$	0.00699	0.00299	0.00190	-0.00039	-0.00049	0.00034

least squares refinement. Scheringer²⁷ has shown that the formula for the transformation of thermal vibration tensors given by Cruickshank:

$$U_{ij} = \frac{(1 + \delta_{ij})B_{ij}}{4\pi^2 a_1^* a_j^*}$$

where a_1^* , a_2^* , a_3^* are the reciprocal axis lengths and δ_{ij} is the Kronecker delta, has to be modified for oblique crystal systems, the correct expression being:

$$U_{ij} = \frac{(1 + \delta_{ij})B_{ij}a_1a_j}{4\pi^2}$$

where a_1 , a_2 , a_3 are the lengths of unit cell axes.

In Tables 11–14 are also given the results according to Cruickshank's formula. As one would expect with $\gamma = 62.68^\circ$, the U_{ij} 's differ appreciably from those obtained with Scheringer's formula. The tables illustrate that the results of the rigid-body motion analysis and the corrections in fractional coordinates deviate considerably, both with respect to magnitudes and directions, from Scheringer's.

Table 12. Components of atomic vibration tensors V^2 in \AA^2 as found by the least squares refinement (exp) and as calculated from the rigid-body parameters (RB). (U_{ij} calculated according to Cruickshank).

Atom	V_{LL}	V_{MM}	V_{NN}	V_{LM}	V_{MN}	V_{LN}
O_1 (exp)	0.0377	0.0456	0.0509	-0.0063	0.0018	-0.0122
O_1 (RB)	0.0482	0.0436	0.0451	-0.0035	0.0032	-0.0063
O_2 (exp)	0.0483	0.0451	0.0436	0.0024	0.0083	-0.0044
O_2 (RB)	0.0486	0.0442	0.0452	-0.0031	0.0067	-0.0094
C_1 (exp)	0.0479	0.0428	0.0370	0.0000	0.0024	-0.0044
C_1 (RB)	0.0453	0.0427	0.0481	-0.0030	0.0047	-0.0096
C_2 (exp)	0.0497	0.0405	0.0646	-0.0032	0.0040	-0.0124
C_2 (RB)	0.0471	0.0469	0.0654	0.0001	0.0076	-0.0090
C_3 (exp)	0.0415	0.0545	0.0866	-0.0074	0.0094	-0.0133
C_3 (RB)	0.0468	0.0530	0.0823	0.0003	0.0057	-0.0029
C_4 (exp)	0.0466	0.0662	0.0920	-0.0066	0.0120	-0.0077
C_4 (RB)	0.0451	0.0590	0.0885	-0.0048	0.0061	-0.0095
C_5 (exp)	0.0601	0.0476	0.0674	-0.0021	0.0024	-0.0021
C_5 (RB)	0.0471	0.0506	0.0720	-0.0080	0.0033	-0.0084
C_6 (exp)	0.0479	0.0438	0.0573	-0.0062	-0.0013	-0.0102
C_6 (RB)	0.0480	0.0472	0.0542	-0.0062	0.0016	-0.0121
(U_{ij} calculated according to Scheringer)						
O_1 (exp)	0.0491	0.0610	0.0486	0.0054	-0.0025	0.0009
O_1 (RB)	0.0552	0.0576	0.0462	0.0027	0.0001	0.0041
O_2 (exp)	0.0514	0.0572	0.0521	0.0026	0.0108	0.0001
O_2 (RB)	0.0554	0.0560	0.0484	0.0018	0.0070	0.0008
C_1 (exp)	0.0508	0.0542	0.0443	-0.0010	0.0034	-0.0003
C_1 (RB)	0.0517	0.0512	0.0495	0.0019	0.0022	0.0006
C_2 (exp)	0.0583	0.0533	0.0694	0.0043	0.0022	-0.0014
C_2 (RB)	0.0550	0.0582	0.0717	0.0073	0.0050	0.0008
C_3 (exp)	0.0585	0.0739	0.0855	0.0120	0.0044	0.0071
C_3 (RB)	0.0545	0.0754	0.0871	0.0093	0.0036	0.0080
C_4 (exp)	0.0540	0.0856	0.1054	-0.0021	0.0131	0.0034
C_4 (RB)	0.0517	0.0809	0.0983	-0.0012	0.0100	0.0001
C_5 (exp)	0.0608	0.0593	0.0856	-0.0084	0.0052	0.0011
C_5 (RB)	0.0553	0.0663	0.0909	-0.0070	0.0075	-0.0012
C_6 (exp)	0.0554	0.0571	0.0624	-0.0015	-0.0039	-0.0007
C_6 (RB)	0.0561	0.0575	0.0634	-0.0024	-0.0025	-0.0044

The amplitudes of translational motion in direction of the principal axes are

L	0.229 \AA
M	0.218 »
N	0.209 »

Table 13. Principal components of rigid-body vibrations, with direction cosines, and coordinates of libration centre, referred to molecular axes. (U_{ij} calculated according to Cruickshank).

	L	M	N
$T_1^2 = 0.0548 \text{ \AA}^2$	-0.6934	0.3378	0.6363
$T_2^2 = 0.0386 \text{ \AA}^2$	-0.3716	-0.9243	0.0857
$T_3^2 = 0.0351 \text{ \AA}^2$	-0.6172	0.1770	-0.7665
$\omega_1^2 = 0.0032 \text{ rad}^2$	0.8497	0.4771	-0.2241
$\omega_2^2 = 0.0024 \text{ \AA}^2$	0.4752	-0.8773	-0.0660
$\omega_3^2 = 0.0009 \text{ \AA}^2$	0.2281	0.0503	0.9723
Libration centre at (0,0,0) (U_{ij} calculated according to Scheringer)			
	L	M	N
$T_1^2 = 0.0523 \text{ \AA}^2$	0.9190	0.3320	0.2122
$T_2^2 = 0.0473 \text{ \AA}^2$	0.3664	-0.9182	-0.1501
$T_3^2 = 0.0435 \text{ \AA}^2$	0.1450	0.2158	-0.9656
$\omega_1^2 = 0.0070 \text{ rad}^2$	0.9918	0.1032	-0.0749
$\omega_2^2 = 0.0031 \text{ \AA}^2$	0.1228	-0.9313	0.3427
$\omega_3^2 = 0.0017 \text{ \AA}^2$	0.0344	0.3491	0.9364

Table 14. Corrections in fractional atomic coordinates due to rigid-body motion, compared with the estimated standard deviation. The corrections obtained with U_{ij} calculated according to Cruickshank and Scheringer are labeled *c* and *s*, respectively. (The σ 's and Δ 's have been multiplied by 10^4).

	$(\Delta x)_c$	$(\Delta x)_s$	σx	$(\Delta y)_c$	$(\Delta y)_s$	σy	$(\Delta z)_c$	$(\Delta z)_s$	σz
O ₁	-3	-5	3	-1	-3	3	3	5	2
O ₂	-1	-3	3	6	10	3	-1	-3	2
C ₁	-1	-1	4	4	5	4	2	2	2
C ₂	-5	-10	4	9	11	4	3	4	3
C ₃	-5	-8	5	7	7	5	6	9	3
C ₄	1	5	6	7	4	5	6	10	3
C ₅	5	13	4	2	-4	5	5	8	3
C ₆	5	12	4	3	1	4	2	3	3
H _{3e}	-9	-18	40	9	13	40	3	4	20
H _{2a}	-4	-8	40	12	18	30	2	2	20
H _{3e}	-7	-11	40	11	1	40	7	12	20
H _{3a}	-6	-14	50	3	12	50	7	10	30
H _{4e}	1	7	40	5	10	40	8	8	20
H _{4a}	3	6	40	12	1	40	5	13	20
H _{5e}	9	21	40	1	-6	40	5	9	20
H _{6a}	4	12	40	-2	-11	40	6	11	20
H _{6e}	8	18	40	0	-4	40	1	2	20
H _{6a}	6	14	40	7	7	40	1	1	20

and the amplitudes of libration about principal axes are

L	4.8°
M	3.2°
N	2.4°

From Table 13 it may be seen that the maximum libration occurs about an axis approximately parallel to the molecular L-axis, which is the principal axis corresponding to the smallest moment of inertia.

Table 15. Interatomic distances and angles before and after correcting for librational effects, and their estimated standard deviations (Fig. 4 (a)).

Bond	Uncorr. (Å)	Corr. (Å)	σ (Å)
O ₃ -O ₃	1.478	1.482	0.002
O ₁ -C ₁	1.429	1.435	0.003
O ₂ -C ₁	1.439	1.444	0.003
C ₁ -C ₂	1.520	1.525	0.003
C ₂ -C ₃	1.523	1.528	0.004
C ₃ -C ₄	1.531	1.538	0.006
C ₄ -C ₅	1.524	1.529	0.004
C ₅ -C ₆	1.529	1.534	0.003
C ₆ -C ₁	1.520	1.527	0.005
C ₁ -H _{2c}		1.00	0.03
C ₂ -H _{2a}		0.96	0.02
C ₃ -H _{3e}		1.06	0.02
C ₃ -H _{3a}		1.09	0.03
C ₄ -H _{4c}		1.04	0.02
C ₄ -H _{4a}		1.08	0.03
C ₅ -H _{5e}		0.94	0.03
C ₅ -H _{5a}		1.05	0.02
C ₆ -H _{6e}		1.03	0.02
C ₆ -H _{6a}		0.98	0.03
Angle	Uncorr. (°)	Corr. (°)	σ (°)
O ₃ -O ₃ -C ₁	107.6	107.5	0.2
O ₄ -O ₁ -C ₁	107.1	107.1	0.2
O ₁ -C ₁ -O ₂	108.1	108.2	0.2
O ₁ -C ₁ -C ₂	105.6	105.5	0.2
O ₂ -C ₁ -C ₂	104.5	104.4	0.2
O ₁ -C ₁ -C ₆	113.2	113.2	0.4
O ₂ -C ₁ -C ₆	112.3	112.2	0.3
C ₆ -C ₁ -C ₂	112.7	112.8	0.3
C ₁ -C ₂ -C ₃	111.6	111.5	0.3
C ₂ -C ₃ -C ₄	111.5	111.4	0.4
C ₃ -C ₄ -C ₅	110.0	110.1	0.4
C ₄ -C ₅ -C ₆	111.4	111.4	0.3
C ₅ -C ₆ -C ₁	110.6	110.5	0.3
C ₁ -C ₁ -H _{2c}		111	1
C ₁ -C ₁ -H _{2a}		107	1
H _{2c} -C ₁ -H _{2a}		108	2
H _{2c} -C ₂ -C ₃		107	1
H _{2a} -C ₂ -C ₃		111	1
C ₂ -C ₃ -H _{3e}		114	1
C ₂ -C ₃ -H _{3a}		112	1
H _{3e} -C ₃ -H _{3a}		101	2
H _{3e} -C ₃ -C ₄		109	2
H _{3a} -C ₃ -C ₄		108	2
C ₃ -C ₄ -H _{4c}		112	2
C ₃ -C ₄ -H _{4a}		109	2
H _{4c} -C ₄ -H _{4a}		108	2
H _{4c} -C ₄ -C ₅		111	1
H _{4a} -C ₄ -C ₅		107	1
C ₄ -C ₅ -H _{5e}		111	1
C ₄ -C ₅ -H _{5a}		109	1
H _{5e} -C ₅ -H _{5a}		98	2

Angle	Uncorr. (°)	Corr. (°)	σ (°)
H _{5c} -C ₅ -C ₆		112	1
H _{5a} -C ₅ -C ₆		115	1
C ₅ -C ₆ -H _{6c}		111	1
C ₅ -C ₆ -H _{6a}		106	1
H _{6c} -C ₆ -H _{6a}		115	2
H _{6c} -C ₆ -C ₁		110	2
H _{6a} -C ₆ -C ₁		105	2

The standard deviation of the thermal vibration components transformed to the molecular coordinate system was calculated to average $\langle\sigma(V)\rangle = 0.0019 \text{ \AA}^2$. The mean value of the differences between V_{exp} and V_{BR} in Table 12 being 0.0026 \AA^2 thus supports the assumption of regarding the molecule as an oscillating rigid body.

DISCUSSION

The interatomic distances and angles, referring to Fig. 4, before and after correcting for librational effects, are listed in Table 15. Standard deviations in bond lengths and angles were calculated from the standard deviations given in Tables 4 and 6 without taking into account the cell dimension E.S.D.'s.

The O—O distance is, within the limit of probable errors, in agreement with earlier investigations.^{1,2,5}

To test the significance of the difference between two distances (or angles), regarded as independently determined from large samples of observations, we define:²⁸

$$t = \frac{|d_1 - d_2|}{(\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}}}$$

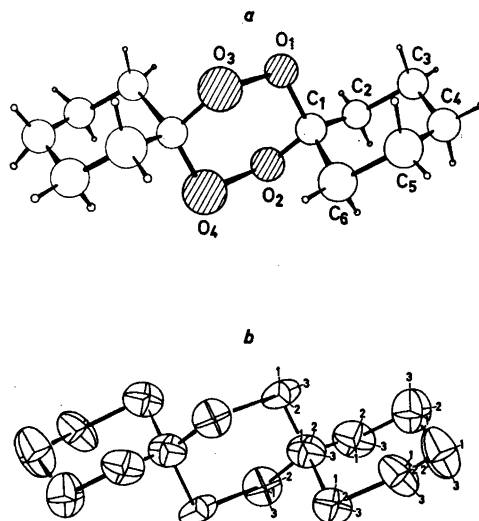


Fig. 4. (a) Schematical drawing of the molecule, (b) view along [100] of the ellipsoids of vibration.

where d_1 and d_2 are the distances (or angles), and σ_1 and σ_2 their estimated standard deviations. Criteria commonly used are:

$t > 1.96$	<i>possibly significant</i>
$t > 2.58$	<i>significant</i>
$t > 3.29$	<i>highly significant</i>

The t -value for the two distances C_1-O_1 and C_1-O_2 is 2.11 and the difference is thus possibly significant. On the other hand, the angles $C_1-O_1-O_4$ and $C_1-O_2-O_3$, corresponding to $t = 1.40$, are not significantly different.

Tables 16 and 17 contain t -values for differences in bond distances and angles of the cyclohexylidene ring. Except for the distances C_1-C_2 and C_5-C_6 , which have a possibly significant difference, the criterion $t < 1.96$ is satisfied for all distance differences. The mean value of the C—C bond lengths is 1.530 Å with E.S.D. equal to 0.0017, in close agreement with the

Table 16. t -Values for differences in bond distances of the cyclohexylidene ring.

	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_1
C_1-C_2	0	0.60	1.94	0.80	2.12	0.34
C_2-C_3	0.60	0	1.39	0.18	1.20	0.16
C_3-C_4	1.94	1.39	0	1.25	0.60	1.41
C_4-C_5	0.80	0.18	1.25	0	1.00	0.31
C_5-C_6	2.12	1.20	0.60	1.00	0	1.20
C_6-C_1	0.34	0.16	1.41	0.31	1.20	0

Table 17. t -Values for differences in angles of the cyclohexylidene ring.

	$C_6-C_1-C_2$	$C_1-C_2-C_3$	$C_2-C_3-C_4$	$C_3-C_4-C_5$	$C_4-C_5-C_6$	$C_5-C_6-C_1$
$C_6-C_1-C_2$	0	3.06	2.80	5.40	3.30	5.42
$C_1-C_2-C_3$	3.06	0	0.20	2.80	0.24	2.36
$C_2-C_3-C_4$	2.80	0.20	0	2.30	0.00	1.80
$C_3-C_4-C_5$	5.40	2.80	2.30	0	2.60	0.80
$C_4-C_5-C_6$	3.30	0.24	0.00	2.60	0	2.12
$C_5-C_6-C_1$	5.42	2.36	1.80	0.80	2.12	0

value reported for the free cyclohexane molecule,²⁹ 1.528 ± 0.005 Å. The angle $C_6-C_1-C_2$ is, however, significantly greater than the five other C—C—C angles which have a mean value 111.0° ($111.55^\circ \pm 0.15$ is found for free cyclohexane).

The shortest H—H distance between hydrogens not bonded to the same carbon atom is 2.38 Å.

The environment of the spiro carbon atom, C_1 , is asymmetric in the sense that the angles $O_1-C_1-C_2$ and $O_2-C_1-C_2$ are about 8° smaller than the

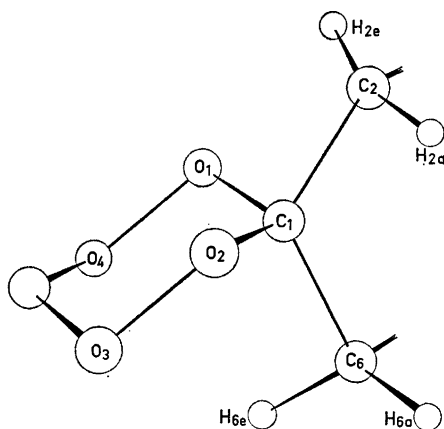


Fig. 5. Schematical drawing of the environment of the spiro carbon atom.

angles $O_1-C_1-C_6$ and $O_2-C_1-C_6$. This deformation may roughly be described as a "rotation" of the cyclohexylidene ring, through an angle close to 4° , about an axis through C_1 approximately normal to the plane defined by the carbon atoms C_1 , C_2 , and C_6 .

It seems possible that this distortion may be explained by the *intramolecular* hydrogen-oxygen atom contacts. These contacts, referring to Fig. 5, are given in Table 18. Taking the sum of the van der Waals' radii of oxygen and hydrogen as 2.6 Å, some of the contacts are significantly shorter than this distance.

Table 18. Hydrogen-oxygen contacts (Fig. 5) and their estimated standard deviations. (The values are corrected for librational effects).

Bond	Distance (Å)	σ (Å)
$H_{2e}-O_1$	2.50	0.02
$H_{2e}-O_2$	2.60	0.03
$H_{2a}-O_1$	3.17	0.02
$H_{2a}-O_2$	2.44	0.02
$H_{6e}-O_1$	2.69	0.03
$H_{6e}-O_2$	2.75	0.02
$H_{6e}-O_3$	2.55	0.02
$H_{6e}-O_4$	2.49	0.03
$H_{6a}-O_1$	3.26	0.03
$H_{6a}-O_2$	2.59	0.03
$H_{6a}-O_3$	3.13	0.02
$H_{6a}-O_4$	3.71	0.03

However, if one calculates the hydrogen-oxygen contacts assuming tetrahedral $O-C-C$ angles and $C-C-H$ angles, and substitutes for the two distances C_1-C_2 and C_1-C_6 their mean value (1.526 Å), the (equal) $H_{6e}-O_3$ and $H_{6e}-O_4$ distances become 2.35 Å.

It seems therefore reasonable to suggest that the deformation is caused by the repulsions of the hydrogen atom H_{6c} from the oxygen atoms O_3 and O_4 .

Regarding the large E.S.D.'s of the C—C—H and H—C—H angles, the degree of distortion of these angles cannot be estimated.

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