The Crystal and Molecular Structure of p-Dioxanyl

Hydroperoxide

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The crystal structure of p-dioxanyl hydroperoxide has been determined and refined from three-dimensional X-ray photographic data. The unit cell is monoclinic with the cell constants $a = 12.222$, $b = 4.636$, $c = 18.971$ Å, $\beta = 100.85°$. The space group is $C2/c$; there are 8 molecules of p-dioxanyl hydroperoxide ($C_4H_8O_4$) in the unit cell. All atoms occupy 8-fold positions. This investigation has confirmed the general features of the molecule determined from IR and NMR spectra by Gierer and Pettersson.

Crystals of p-dioxanyl hydroperoxide have been prepared by Gierer and Pettersson.[1] The compound was analysed and characterized by means of IR, NMR, mass spectra, and also by reductive degradation. These investigations indicated a chair-formed molecule with its hydroperoxy group axially oriented. In order to check this an X-ray structure determination was suggested.

EXPERIMENTAL

Colourless needle-shaped crystals, suitable for X-ray diffraction studies, were kindly supplied by Dr. J. Gierer. The melting point was determined to 56°C. The sample decomposed slowly, even when kept below 0°C, producing a colourless liquid. At room temperature the crystals could stand X-rays less than half an hour before they changed into a yellowish drop. Therefore it was necessary to cool the crystals down during the radiation.

A powder photograph was taken in a Guinier-Hägg focusing camera with strictly monochromatized $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å) and with KCl ($a = 6.29228$ Å) as an internal standard. All high angle reflections were very diffuse, but from 25 low angle ($\theta < 20°$) powder reflections the unit cell dimensions could be refined with the least-squares program POWDER.[3] The cell constants are shown in Table 1 together with some crystallographic data.

Preliminary Weissenberg and rotation photographs indicated monoclinic symmetry. Systematic absences occurred for hkl with $h + k$ odd, and in addition for $h0l$ with l odd, which is characteristic of the space group Cc (No. 9) and its centrosymmetric equivalence $C2/c$ (No. 15). $C2/c$ was chosen as being the most probable (see below).

Table 1. Crystal data of p-dioxanyl hydroperoxide. The estimated standard deviations are given in parentheses and refer to the last decimal place of the respective value.

Cell constants	$a = 12.222(2)$ Å
	$b = 4.636(1)$ Å
	$c = 18.971(2)$ Å
	$\beta = 100.85(2)°$
Cell volume	$V = 1056$ Å^3
Density (X-ray)	$D = 1.51$ g/cm^3
Molecules per unit cell	$Z = 8$
Space group	$C2/c$

All atoms occupy general equivalent positions $8(f)$: $\pm (x,y,z)$; $\pm (\frac{1}{2}+x, \frac{1}{2}+y, z)$; $\pm (\bar{x}, y, \frac{1}{2}-z)$; $\pm (\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$.

Since the crystals dissolved instantaneously in water and in most organic liquids it was not possible to determine the density of the crystals experimentally. However, it seems most likely to assume 8 molecules in the unit cell which gives a density of 1.51 g/cm^3.

For the Weissenberg equi-inclination exposures $(h0l - h2l)$ a needleshaped crystal with the dimensions 0.40 mm (in the direction of the b axis) × 0.06 mm × 0.08 mm was enclosed in a thin-walled capillary and mounted along the b axis. During the exposures it was cooled down to $-40°C$ by a stream of dry air. The reflections were recorded with the multiple film technique. The intensities of the reflections were estimated visually by comparing with an intensity scale obtained by photographing a reflection with different exposure times. A total of 250 independent reflections were measured. It should be emphasized that the $h2l$ reflections were rather diffuse and only a minor part of these reflections were used henceforth. The net intensities were corrected for Lorentz and polarization effects but not for absorption. However, μ is very low ($\mu = 3.7$ cm^{-1}) and the crystal was rotated about the needle axis.

The programs for the IBM 360/75 of the Stockholm Data Centre used in all calculations involved in the present work are described in a paper by Brandt and Nord.[4]

STRUCTURE DETERMINATION AND REFINEMENT

An ordinary Wilson plot [5] and some tests for centric distribution from intensity statistics were performed with the programs WILP and ZTEST, written by one of the authors (A.G. N.). From the Wilson plot an approximate scale factor and an overall temperature factor were calculated. With the program FAME (Dewar & Stone, Chicago, USA) normalized structure factors, $|E|$, were calculated and rescaled to set the average of $|E|^2$ equal to 1. The

Table 2. Statistical averages and distributions of the normalized structure factors.

| | Experimental | Theoretical values | |
		Centric	Acentric
$\langle|E|\rangle$	0.81	0.798	0.886
$\langle|E|^2 - 1\rangle$	0.94	0.968	0.736
$\langle|E|\rangle^2$	1.00	1.000	1.000
$|E| > 1$	35 %	32 %	37 %
$|E| > 2$	3.5 %	5.0 %	1.8 %
$|E| > 3$	0.47 %	0.30 %	0.01 %

distribution of the $|E|$' s after rescaling is given in Table 2. The result of the $N(z)$ test [6] is shown in Fig. 1. This test and the results presented in Table 2 indicate a centric distribution. For this reason the space group $C2/c$ (No. 15) was chosen as being the most probable.
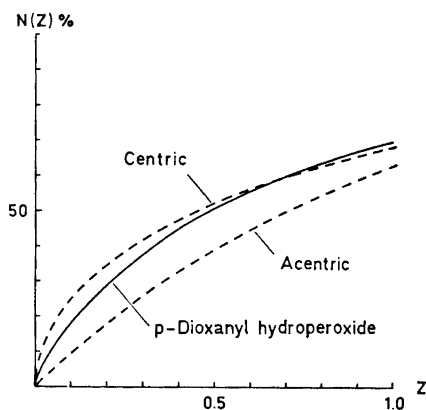

Fig. 1. $N(z)$ test. Distribution for p-dioxanyl hydroperoxide compared with theoretical curves for centric and acentric distribution.

The 45 highest $|E|$ values ($|E| > 1.27$) were used to generate 57 triple relations. The reflections 519 ($E = +2.59$) and $71\bar{6}$ ($E = +1.72$) were used to specify the origin of the unit cell. The signs of 44 $|E|$ values could then be determined by symbolic addition of the triple-product sign relationships.[7] 42 of these signs proved to be correct. The E map calculated for this solution (44 E values) clearly revealed the positions of all the eight non-hydrogen atoms in the asymmetric unit.

The structure was refined by a combination of full-matrix least-squares (program LALS) and Fourier methods. Isotropic temperature factors were always used. The scattering factor curves applied were those given by McMaster *et al.*[8] corrected for the real part of the anomalous dispersion coefficient. Hughes' weighting function [9] with $h=4$ and $F_{o,min}=7.5$ was applied. After 3 cycles of refinement a three-dimensional difference Fourier synthesis was calculated. The interpretation of the Fourier maps was hampered by the presence of spurious maxima. Of the eight hydrogen atoms in the asymmetric unit it was only possible to locate four (H1, H2, H3, H5). However, the calculated C–H bond distances were rather unreliable, nor was it possible to refine the hydrogen atom positions. Therefore the seven hydrogen atoms H1 − H7 were introduced geometrically assuming a C–H bond distance of 1.10 Å, tetrahedral angles, and a temperature factor of 1.50 Å². The eight non-hydrogen atoms were further refined improving the R value ($R = \sum ||F_{obs}| - |F_{calc}||/\sum |F_{obs}|$) to 11 %. From the subsequent difference Fourier maps it was now possible to determine the position of the last hydrogen atom, H8.

The weighting scheme obtained in the final cycle of refinement is shown in Table 3. Zero weight was given to 10 reflections with $|F_{obs}|/|F_{calc}|$ less than 0.5 or greater than 2. A list of the observed and calculated structure factors is presented in Table 4. Owing to its somewhat uncertain position the

Table 3. Weight analysis obtained in the final cycle of the least-squares refinement. w = weighting factor, $\Delta = ||F_{obs}| - |F_{calc}||$. Zero weight was given to 10 reflections.

Interval $|F_{obs}|$	$\overline{w\Delta^2}$	Number of independent reflections	Interval sin θ	$\overline{w\Delta^2}$	Number of independent reflections
0 — 10	0.57	23	0.00 — 0.37	1.20	55
10 — 14	0.94	20	0.37 — 0.47	1.08	51
14 — 18	1.24	22	0.47 — 0.54	0.92	48
18 — 22	1.17	25	0.54 — 0.59	1.11	21
22 — 26	1.05	25	0.59 — 0.64	0.60	26
26 — 31	1.19	26	0.64 — 0.68	1.18	16
31 — 39	1.18	24	0.68 — 0.71	0.31	6
39 — 48	1.20	25	0.71 — 0.74	0.61	8
48 — 67	0.76	25	0.74 — 0.77	1.68	6
67 — 140	0.67	25	0.77 — 0.80	0.40	3

Table 4. Observed and calculated structure factors. Reflections marked with an asterisk were assigned zero weight in the final cycles of least-squares refinement.

H8 atom was not included in the calculation of the structure factors, nor was it included in the final cycles of least-squares refinement. The atomic parameters and temperature factors are given in Table 5. Note that no hydrogen atoms were refined. (The atoms H1 – H7 were introduced geometrically, and H8 had been located from the last ΔF synthesis.) The parameters in Table 5 were also used to calculate the structure factors for the unobserved reflec-

Table 5. Fractional atomic coordinates and thermal parameters. The estimated standard deviations are given in parentheses and refer to the last decimal places of the respective values. Note that the hydrogen atoms were not refined.

Atom	x	y	z	B
O1	0.1037(5)	0.2422(21)	0.0404(3)	1.60(10)
O2	0.1692(5)	0.0937(24)	0.1848(4)	1.23(9)
O3	0.3131(6)	0.3061(23)	0.1331(4)	1.69(10)
O4	0.3963(6)	0.3019(24)	0.2008(4)	2.45(11)
C1	0.1776(8)	0.0076(36)	0.0587(6)	1.26(13)
C2	0.2445(9)	0.0682(40)	0.1353(6)	2.01(14)
C3	0.0906(8)	0.3320(38)	0.1655(5)	0.96(13)
C4	0.0273(8)	0.2645(36)	0.0910(6)	1.94(14)
H1	0.2345	− 0.0084	0.0203	1.50
H2	0.1304	− 0.1946	0.0582	1.50
H3	− 0.0170	0.0585	0.0920	1.50
H4	− 0.0332	0.4375	0.0734	1.50
H5	0.0330	0.3451	0.2035	1.50
H6	0.1356	0.5374	0.1656	1.50
H7	0.2983	− 0.1194	0.1517	1.50
H8	0.3260	0.4780	0.2130	1.50

tions. This revealed no $|F_{calc}|$ value greater than 10. Furthermore, the ΔF Fourier synthesis showed no peak or hole greater than 0.5 eÅ^{-3}. These facts, together with the statistical tests and the reasonable molecular dimensions presented below, enable the authors to assume, with a high degree of probability, that the crystal possesses the centric space-group symmetry *C2/c*.
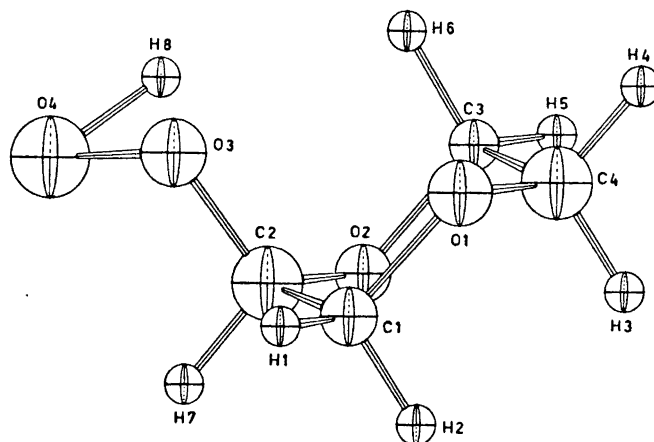

Fig. 2. Three-dimensional model of a molecule of *p*-dioxanyl hydroperoxide.

DESCRIPTION AND DISCUSSION OF THE CRYSTAL STRUCTURE

According to the present X-ray structure investigation, the configuration of the p-dioxanyl hydroperoxide molecule is in good agreement with the results by Gierer and Pettersson.[1] The molecule has a pronounced chair form with the hydroperoxy group axially oriented. Fig. 2 shows a three-dimensional model of one molecule with all hydrogen atoms (H1 − H8). It has been produced by the plot program ORTEP [10] and its graphic display version.[11] Fig. 3 shows the contents of a unit cell with eight molecules. Only the oxygen and carbon atoms are drawn.
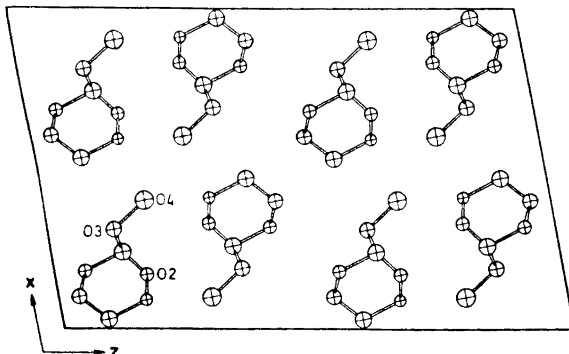

Fig. 3. The contents of one unit cell projected along the b axis. Only oxygen and carbon atoms are drawn.

Table 6. Interatomic distances (Å) with standard deviations ($\pm \sigma$ in Å) and some angles in p-dioxanyl hydroperoxide. The e.s.d. of the angles are $\pm 1°$ or less. For comparison the corresponding average values in 1,4-dioxane (Ref. 2) are within parentheses and marked by an asterisk.

Intramolecular distances and angles

C1 − C2	1.55(2)		C1 − O1 − C4	110.5°	
C3 − C4	1.51(2)		C2 − O2 − C3	111.7°	
Average:	1.53	(1.523)*	Average:	111.1°	(112.5°)*
C1 − O1	1.41(2)		O1 − C1 − C2	106.9°	
C2 − O2	1.44(1)		O2 − C2 − C1	109.7°	
C2 − O3	1.39(2)		O2 − C3 − C4	105.9°	
C3 − O2	1.46(2)		O1 − C4 − C3	110.6°	
C4 − O1	1.46(1)		O3 − C2 − C1	109.2°	
Average:	1.43	(1.423)*	Average:	108.5°	(109.2°)*
O3 − O4	1.48(1)		O4 − O3 − C2	106.5°	
			O2 − C2 − O3	114.7°	

Some interatomic distances and angles concerning the hydrogen bond. Atom denotations used: (x,y,z) without subscript; subscript (ii) denotes $(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$.

O4 − O2	2.90(1)		O4 − O2(ii)	2.80(1)
O3 − O4 − O2	55.0°		O3 − O4 − O2(ii)	115.6°

Table 6 contains some interatomic bond distances with estimated standard deviations (σ) and a few interesting angles. The C–C and C–O bond distances are all among the usual covalent bond length distances in the literature.[12] The average interatomic distances and two kinds of angles (C–O–C and O–C–C) are also compared in Table 6 with the corresponding values obtained from electron diffraction studies of 1,4-dioxane.[2] The agreements between all averaged values are always within the standard deviations. The O–O distance of the hydroperoxy group (1.48 Å) is also in good agreement with earlier results, *i.e.* from the crystal structure analysis (X-ray) of hydrogen peroxide [13] with a reported O–O distance of 1.49 Å.

The hydrogen atom H8 is likely to form a weak hydrogen bond in connection with two oxygen atoms. This hydrogen bond would involve the atoms O4 and H8 from one molecule, and one O2 atom. Looking at the pertinent O2 – O4 distances and the O3 – O4 – O2 angles in Table 6, an intermolecular hydrogen bond seems to be far more likely than an intramolecular one as suggested by Gierer and Pettersson.[1] Intramolecular hydrogen bonds are relatively rare, and the present hydrogen bond dimensions assuming an intermolecular bond would be more within the range of ordinary O–H–O hydrogen bonds.[14] As a matter of fact, Abrahams *et al.* also reported an O–O hydrogen bond distance of 2.78 Å in hydrogen peroxide.[13] The sharp bending of the present hydrogen bond (about 125° for the intermolecular O–H–O hydrogen bond angle) might well be caused by the uncertainty of the H8 hydrogen atom position. If its position was well established, the hydrogen bond could almost be regarded to be bifurcated.

All other interatomic distances between atoms in neighbouring molecules are long enough to allow only van der Waals bondings between the molecules. Compared with the melting point and density of ordinary 1,4-dioxane (12°C resp. 1.03 g/cm³), the corresponding values for p-dioxanyl hydroperoxide (56°C resp. 1.51 g/cm³) indicate a slightly higher degree of stability which could be caused by weak intermolecular hydrogen bonds.

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