the close S–O contacts in sulfuric acid. The other three tetrahedral oxygen atoms have electrostatic bond strengths of $\frac{4}{3}$ to sulfur, $\frac{1}{2}$ to Al and $\frac{1}{6}$ to K. All S–O bonds are shorter than in Hendricks's or Pabst's models.

The environment of potassium is presumably to be considered as octahedral. Six oxygen neighbors from 6 sulfate groups afford a flattened octahedron about each potassium at a bond length of 2·821 Å, while the six OH neighbors of aluminum octahedra in the elongated octahedral arrangement about each potassium are 2·871 Å distant. The 2·821 Å length is comparable to the shorter K–O contacts in Radoslovich's muscovite structure.

The stylized electrostatic bond summations of even fractions conform exactly with Pauling's rules. Inspection of the several bond lengths within each polyhedron indicates that bond strengths actually depart from even fractions but maintain proper sums. In sulfate tetrahedra the 'single' strengths are slightly more than $\frac{4}{3}$ and the 'double' less than 2. In aluminum octahedra, bonds to OH are slightly more than $\frac{1}{2}$ and those to O slightly less than $\frac{1}{6}$. Potassium strengths to O are less than $\frac{1}{6}$ and there is some association with the OH polyhedron, affording a small residual association between protons and the unique sulfate oxygen.

The unique sulfate oxygen has three OH neighbors distant 2·96 Å in directions inclined 32° to the basal plane. These three associations are presumed to be hydrogen bonds. Along them the protons would have positions of the form $x\bar{x}z$ with $x \simeq 0.20$ and $z \simeq 0.11$, so that, with the sulfur, they provide a vague tetrahedral aspect to that oxygen. The calculated amplitude most sensitive to possible allowance for a hydrogen contribution is that for the 003, for which calculated amplitudes would be some 8 or 10 electron units greater, clearly in agreement with the observed data. The number of other observations at small values of $\sin \theta/\lambda$ is inadequate to improve the tentative hydrogen positions cited.

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The Crystal Structure of o-Nitroperoxybenzoic Acid

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The crystal structure of o-nitroperoxybenzoic acid, $C_7H_5NO_5$, has been determined by a three-dimensional structure analysis. The peroxycarboxyl group is shown to have the skewed conformation and the dihedral angle is 146°. Evidence is given suggesting that the intermolecular hydrogen bond largely determines the value of the dihedral angle in the hydrogen bonded peroxides in the solid state. The influence upon the angle exerted by exchange repulsion forces between the lone pair electrons of the peroxide oxygen atoms appears to be small in comparison. The bond lengths in the peroxycarboxyl group are C=O 1·21$_4$, C–O 1·33$_7$, O–O 1·47$_8$ Å, and O–H 1·1$_2$ Å. The valency angles are O=C–O 124·7, C–O–O 108·9, and O–O–H 112°. A 5° torsional angle about the C–O bond displaces the carboxyl oxygen atom 0·09 Å (20σ) from the C–O–O plane, so that the carboxyl oxygen atom and the hydrogen atom are on opposite sides of the plane.

Five of the atoms in the benzene ring are coplanar, and the C atom attached to the NO_2 group is displaced 0·025 Å (5σ) from this plane. The N atom is displaced 0·154 Å (30σ) in the same direction. The C atom of the OCOOH group is displaced 0·074 Å (15σ) on the opposite side of the plane. The plane of the ring atoms makes a 58° angle with the OCO plane and a 28° angle with the ONO plane. There are indications of steric strain between the substituent groups. Glide related molecules are hydrogen bonded into an infinite chain.

Introduction

Swern & Silbert (1963) have given a resume of the information that has been acquired within the past

decade on the structure of several important classes of organic peroxides. They point out that single-crystal studies are needed to establish the structures of the peroxy acids, diacyl peroxides, and tertiary-butyl

peroxyesters. Compounds in the first two of these classes are currently being investigated in these laboratories. The crystal structure analysis of o-nitroperbenzoic acid (Fig. 1) is reported here as a part of that study. This aromatic peroxy acid was selected because the quality of the crystals indicated that an analysis of this compound would yield more reliable parameters than could be obtained from an aliphatic peroxy acid, although these are also being studied. The main interest in the crystal structure of the peroxy acids stems from the fact that neither the intermolecular hydrogen bonding scheme nor the conformation of the peroxycarboxyl group is known in the solid state (Swern, Witnauer, Eddy & Parker, 1955). In the case of o-nitroperbenzoic acid a closely related and pertinent question concerns the influence of the o-nitro group upon these two structural features. Finally, the aromatic peroxy acids merit attention, for relatively little work has been published on their structures (Swern & Silbert, 1963).
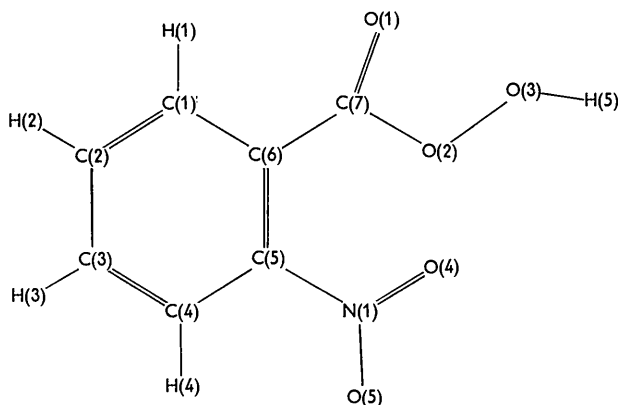

Fig. 1. o-Nitroperoxybenzoic acid: the atomic numbering.

Crystal data

o-Nitroperbenzoic acid, $C_7H_5O_5N$; M.W. 183·118, m.p. 95–96 °C.

Monoclinic:

Cell dimensions (25 °C)

$$a = 13·84 \pm 0·02, \quad b = 8·03 \pm 0·02,$$
$$c = 7·51 \pm 0·02 \text{ Å}; \quad \beta = 112° \pm 30'.$$

Cell dimensions (−15 °C)

$$a = 13·75 \pm 0·02, \quad b = 7·95 \pm 0·01,$$
$$c = 7·47 \pm 0·01 \text{ Å}; \quad \beta = 112° \; 40' \pm 10'.$$

$$V \text{ (25 °C)} = 773·8 \text{ Å}^3, \quad V \text{ (−15 °C)} = 753·5 \text{ Å}^3,$$
$$D_m \text{ (25 °C)} = 1·576 \text{ g.cm}^{-3}.$$
$$Z = 4, \; D_x \text{ (25 °C)} = 1·572 \text{ g.cm}^{-3},$$
$$D_x \text{ (−15 °C)} = 1·614 \text{ g.cm}^{-3}.$$

Space group, $P2_1/c$ from systematic extinctions $h0l$ absent l odd; $0k0$ absent k odd.

Experimental

The crystals of o-nitroperbenzoic acid were supplied to us by Dr L. Silbert of the Eastern Regional Laboratories, U.S. Department of Agriculture. These had well formed faces and were elongated in the c direction. The multifilm equi-inclination Weissenberg photographic method was used, with Cu Kα radiation, for collecting the intensity data. Thermal and chemical instability of the compound required a reduced temperature, ~ -15 °C, for the exposures. Data were obtained from single crystals mounted about the three principal axes. Of the 1575 possible independent reflexions within the limiting sphere for Cu Kα radiation, 94% were indexed and estimated, and 81% were observed above the background.

The uncorrected intensities were estimated visually by comparison with a standard scale. The data reduction, angle corrections, and interlayer correlations were carried out on the IBM 1620 computer. No extinction or absorption corrections were applied.

The unit-cell parameters were determined from equatorial Weissenberg photographs calibrated with NaCl.

Structure determination

The data were placed on the absolute scale by means of a Wilson plot and the structure amplitudes were corrected for thermal vibration and normalized (Hauptman & Karle, 1953). The sign correlation method (Beurskens, 1963, 1965) was used for solving the phase problem. In this method several structure factors are, at first, given signs arbitrarily and these together with an appropriate origin-determining set of structure factors are used to generate other signs relative to these initial choices by means of the sign relation

$$sE(h+k) \sim sE(h).sE(k) . \tag{1}$$

At the time this analysis was carried out, however, the number of arbitrary choices allowed by the computer program was restricted to six and the procedure accordingly was initiated more laboriously.

The signs of the reflexions $E(\bar{2}73)$, $E(163)$ and $E(061)$ were selected positive to fix the origin and these were used to obtain signs of the seven reflexions listed in Table 1 with relation (1). On the basis of the following four arguments there was no doubt that

Table 1. *The initial reflexions of the set* [0]

hkl	E	Sign
$\bar{2}73$	3·36	[0]+
163	3·13	[0]+
061	2·53	[0]+
002	2·02	[0]−
$\bar{2}75$	2·63	[0]−
$\bar{1}18$	2·50	[0]+
104	2·32	[0]−
$\bar{2}14$	2·20	[0]−
102	2·05	[0]+
$\bar{3}71$	2·03	[0]+

these signs were correct: (1) They were obtained at least once with a high probability ($|E(h)E(k)E(h+k)|$. $N^{-\frac{1}{2}}$ $=Q \geq 2\cdot00$, i.e. with a probability larger than 98%). (2) Each of these was found at least once again in a relation (1) with a good probability ($Q \geq 1\cdot3$). (3) A further expansion to obtain signs for many reflexions ($Q \geq 1\cdot0$) did not give rise to any inconsistent relation (1). (4) The sign of the reflexion $E(002)$ was also found by the Σ_1 relation (Hauptman & Karle, 1953) with a probability $>98\%$. These seven reflexions are therefore registered together with the origin-determining reflexions in correlation set [0] (i.e. the set of reflexions with known signs).

We then arbitrarily selected the signs of six reflexions with a high E value and registered these in the correlation set [1] through [6] (see Table 2); the given signs were not completely arbitrarily selected since they were based upon the results of a preliminary examination using the procedure to be described immediately. Relation (1) was used with the 16 structure factors in Table 1 and 2 to generate many signs and the dependency of the new signs upon initial choices was traced by the computer program so that they were registered into their appropriate correlation sets. A correlation set $[i, j, \ldots]$ is defined as that set of reflexions with signs that are known to

be dependent upon the arbitrary choices numbered $i, j, \ldots$ (Beurskens, 1963). A reflexion which was found several times with a high probability within a particular correlation set was included in the set, and used for further sign generation. Thus 14 signs could be 'accepted' in this way.

From the 385 relations (1) with $Q \geq 1\cdot0$ which were now available the correlation equations [3] $\equiv$ [0] and [2, 6] $\equiv$ [0] were found and consequently the third and the sixth arbitrary choices were eliminated. In other words, all reflexions in correlation set [3] were transferred into set [0] and those in set [6] were transferred to set [2]. Thus, the dependency upon choice three is cancelled and that upon choice six is transferred to a dependency upon choice two. It was now possible to proceed in the same way by 'accepting' more signs and eliminating other arbitrary choices, as given in the consecutive columns of Table 2. The last correlation equation [1]$\not\equiv$[0] indicated that all signs dependent upon choice one should have opposite signs. Thus a single set of 171 signs was obtained and the phase problem was thereby solved.

The list of known phases was extended to 306 structure factors by considering relation (1) with $Q \geq 0\cdot8$. Finally, a total of 441 signs were obtained by applying Σ_2 relations with $Q \geq 0\cdot6$. An E map (Karle, Hauptman, Karle & Wing, 1958), which

Table 2. *The six arbitrary choices and their sign dependency during the course of the analysis*

Correlation equation			[3] $\equiv$ [0]	[2, 6] $\equiv$ [0]	[2, 5] $\equiv$ [0]	[1, 2, 4] $\equiv$ [0]	[2] $\equiv$ [0]	[1] $\not\equiv$ [0]
No. of choice eliminated			3	6	5	4	2	1
hkl	E	Initial sign						
$\bar{1}\bar{1},3,4$	3·03	[1]+	[1]+	[1]+	[1]+	[1]+	[1]+	[0]−
171	2·88	[2]+	[2]+	[2]+	[2]+	[2]+	[0]+	[0]+
$\bar{2}76$	2·93	[3]−	[0]−	[0]−	[0]−	[0]−	[0]−	[0]−
$\bar{1}0,2,6$	2·85	[4]+	[4]+	[4]+	[4]+	[1, 2]+	[1]+	[0]−
366	2·77	[5]−	[5]−	[5]−	[2]−	[2]−	[0]−	[0]−
072	2·75	[6]+	[6]+	[2]+	[2]+	[2]+	[0]+	[0]+

Table 3. *Atomic coordinates*

Atom	Fractional coordinates Differential synthesis			Least squares			e.s.d. (Å)		
	x	y	z	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	0·1785	−0·3014	0·8098	0·1783	−0·3022	0·8096	0·005	0·005	0·005
C(2)	0·2445	−0·4387	0·8216	0·2451	−0·4381	0·8219	0·006	0·005	0·005
C(3)	0·3456	−0·4133	0·8288	0·3454	−0·4130	0·8291	0·006	0·005	0·006
C(4)	0·3837	−0·2505	0·8254	0·3839	−0·2502	0·8259	0·005	0·005	0·005
C(5)	0·3169	−0·1153	0·8163	0·3175	−0·1152	0·8183	0·005	0·005	0·005
C(6)	0·2148	−0·1376	0·8056	0·2145	−0·1377	0·8056	0·005	0·004	0·005
C(7)	0·1381	0·0025	0·7819	0·1383	0·0023	0·7826	0·005	0·005	0·005
O(1)	0·0900	0·0271	0·8868	0·0912	0·0272	0·8872	0·005	0·004	0·004
O(2)	0·1231	0·0882	0·6196	0·1233	0·0881	0·6198	0·004	0·004	0·004
O(3)	0·0477	0·2263	0·6007	0·0475	0·2257	0·5994	0·005	0·005	0·006
O(4)	0·3264	0·1646	0·9078	0·3253	0·1651	0·9061	0·005	0·004	0·006
O(5)	0·4365	0·0759	0·7848	0·4364	0·0759	0·7845	0·005	0·005	0·005
N(1)	0·3631	0·0552	0·8342	0·3628	0·0550	0·8348	0·005	0·004	0·005
H(1)*				0·105	−0·307	0·790			
H(2)*				0·215	−0·552	0·840			
H(3)*				0·395	−0·505	0·815			
H(4)*				0·460	−0·225	0·830			
H(5)*				0·065	0·340	0·530			

* The hydrogen coordinates were obtained from difference maps.

clearly revealed the atomic positions was calculated with the use of these 441 reflexions (Fig. 2). Structure factors calculated with these coordinates and the single overall temperature factor, $B = 2.52$ Å^2, gave an R value of 25·3% on 1277 reflexions.
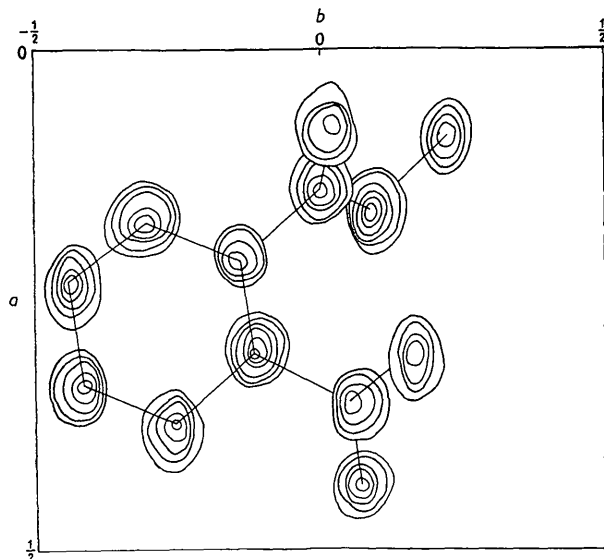

Fig. 2. Composite E map. Scale arbitrary.

Structure refinement

The coordinates obtained from the E map were refined in three cycles of differential synthesis holding the temperature and scale factor constant, the IBM 7070 program of Shiono being used. A cycle of anisotropic differential synthesis lowered the agreement index to 18·1. A difference Fourier synthesis yielded the positions of three of the four hydrogen atoms attached to the aromatic ring, but the acidic hydrogen could not be located unequivocally. Knowledge of the site of this hydrogen was important, for it completes the structural information required to determine the conformation of the peroxycarboxyl group and to estimate the influence of the intermolecular hydrogen bond upon it. Six more cycles of anisotropic differential syntheses lowered the agreement index to 12·9, but the site of the acidic hydrogen was still undetermined although all of the hydrogen atoms attached to the ring could now be located in the difference map.

Up to this point all of the data had been used in the refinement. All reflexions that could not be observed above the background plus forty-one reflexions with observed intensity less than two on the arbitrary scale were dropped from subsequent refinement cycles. The intensity data for the forty-one reflexions were obtained from only one setting of the crystal (about one axis), and the $|F_o - F_c|$ values showed that they were not accurately estimated. Two cycles of anisotropic differential synthesis lowered the agreement index to 12·0 on 1237 reflexions.

Table 4. *Anisotropic temperature coefficients**

Atom	Differential synthesis						Least squares						σ (Å^2)					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	2·03	0·94	1·68	−0·32	0·70	0·23	2·54	1·33	2·06	−0·50	0·89	0·29	0·18	0·18	0·16	0·15	0·14	0·14
C(2)	3·21	0·70	2·40	−0·26	0·95	−0·11	3·62	0·85	2·31	−0·32	1·04	0·08	0·19	0·16	0·17	0·15	0·14	0·15
C(3)	3·02	1·64	2·36	0·48	0·98	−0·40	3·37	1·53	2·82	0·09	1·25	−0·52	0·19	0·16	0·15	0·15	0·13	0·13
C(4)	2·35	1·62	2·34	0·29	1·13	0·04	2·42	1·71	2·60	0·05	1·08	−0·06	0·17	0·20	0·16	0·15	0·13	0·15
C(5)	2·29	1·12	1·85	0·09	0·71	−0·18	2·31	1·35	1·91	−0·13	0·63	−0·13	0·21	0·20	0·19	0·18	0·17	0·16
C(6)	2·26	0·78	1·62	0·13	0·75	−0·25	2·28	0·90	1·67	0·22	0·63	−0·11	0·18	0·21	0·18	0·14	0·15	0·15
C(7)	2·02	0·80	2·22	0·29	0·75	−0·08	2·59	0·97	2·31	0·46	0·75	−0·07	0·22	0·17	0·16	0·16	0·17	0·14
O(1)	3·99	2·56	3·03	1·27	2·12	0·38	4·34	2·76	3·27	1·44	2·36	0·52	0·20	0·18	0·16	0·15	0·15	0·14
O(2)	3·16	1·87	3·54	1·36	2·10	1·53	3·54	2·06	3·79	1·47	2·08	1·57	0·22	0·16	0·29	0·15	0·22	0·18
O(3)	3·70	2·39	7·20	1·91	3·40	3·14	3·68	2·63	7·14	2·05	3·05	3·04	0·17	0·16	0·18	0·14	0·14	0·14
O(4)	4·25	1·69	6·21	−0·43	2·12	−0·87	4·73	1·50	6·65	−0·25	2·42	−0·93	0·21	0·21	0·22	0·17	0·17	0·17
O(5)	3·95	3·02	4·53	−1·51	2·13	0·05	4·27	3·33	4·90	−1·84	2·39	−0·16	0·19	0·18	0·29	0·16	0·19	0·20
N(1)	2·10	1·16	2·87	−0·66	0·39	0·32	2·86	1·60	3·23	−0·63	0·58	0·53	0·18	0·18	0·18	0·14	0·21	0·15

* In the form $f^0(hkl) \exp\left[-\frac{1}{4}(B_{11}.h^2a^{*2}+\ldots+B_{23}.2klb^*c^*)\right]$.

Two cycles of full-matrix least-squares refinement were run with the IBM 704 program of Busing & Levy, with the Hughes weighting scheme. Four reflexions showing extinction were omitted from the refinement. The agreement index on 1237 reflexions including the four low order reflexions was virtually unchanged at 11·9, although there were some changes in the parameters, as shown in Tables 3 and 4. The tabulated e.s.d. are those computed in the least-squares method.

Still the site of the acidic hydrogen was obscured in the difference map by errors in the data. A difference Fourier synthesis was then calculated with 417 selected reflexions, for which $|F_o - F_c| < 4·0$, $\sin \theta < 0·6$, and for which the agreement index was 8·9. A peak of 0·3 e.Å^{-3} containing $\sim$ 0·7 electron occurred in a stereochemically plausible site for the hydrogen bond. A single spurious maximum of 0·3 e.Å^{-3} containing $\sim$ 0·2 electron appeared in a position that gave unreasonable distances and angles for the valence bond and hydrogen bond. The estimated standard deviation in the electron density based upon these selected reflexions was 0·095 e.Å^{-2}. The reason that the acidic hydrogen atom was more difficult to find than the four hydrogen atoms linked to the aromatic ring is probably associated with the large thermal parameters of the oxygen atom to which it is bound.

The hydrogen atoms were assigned the same temperature factors as the atoms to which they are bonded. The carbon, oxygen and nitrogen scattering factors were those given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). Those of McWeeny (1951) were used for the hydrogen atoms. Unobserved reflexions were omitted from calculations of the R value. The observed and calculated structure factors are given in Table 12.*

Discussion of the structure

The atomic coordinates from the two methods of refinement were averaged and the molecular dimensions were calculated from the mean values. The bond lengths and valence angles are listed in Tables 5 and 6. Some non-bonded intramolecular distances are listed in Table 7. The equations of planes of atoms that are useful in the discussion of the molecular structure are given in Table 8.

The dihedral angle between the COO and the OOH planes is 146°, which is significantly larger than has been reported for other organic peroxides from their

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* Table 12 has been deposited as Document number 7999 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and remitting $3·75 for photoprints, or $2·00 for 35 mm microfilm. Advance payment is required. Make check or money order payable to Chief, Photoduplication Service, Library of Congress.

Table 5. *Bond lengths in o-nitroperoxybenzoic acid*

Bonded atoms	Distance	σ
C(1)–C(2)	1·399 Å	0·007 Å
C(2)–C(3)	1·379	0·008
C(3)–C(4)	1·401	0·007
C(4)–C(5)	1·397	0·007
C(5)–C(6)	1·390	0·007
C(6)–C(1)	1·401	0·007
C(6)–C(7)	1·495	0·007
C(7)–O(1)	1·214	0·007
C(7)–O(2)	1·337	0·006
O(2)–O(3)	1·478	0·007
C(5)–N(1)	1·478	0·007
N(1)–O(4)	1·236	0·007
N(1)–O(5)	1·215	0·007
C(1)–H(1)	0·96	0·12
C(2)–H(2)	1·02	0·12
C(3)–H(3)	1·03	0·12
C(4)–H(4)	1·06	0·12
O(3)–H(5)	1·12	0·15

Table 6. *Bond angles and their e.s.d. in o-nitroperoxybenzoic acid*

Angle		σ
C(6)C(1)C(2)	119·7°	0·4°
C(1)C(2)C(3)	120·7	0·5
C(2)C(3)C(4)	120·8	0·5
C(3)C(4)C(5)	117·8	0·5
C(4)C(5)C(6)	122·4	0·5
C(5)C(6)C(1)	118·6	0·4
C(1)C(6)C(7)	117·1	0·4
C(5)C(6)C(7)	124·2	0·4
C(6)C(7)O(1)	125·1	0·5
C(6)C(7)O(2)	109·9	0·4
O(1)C(7)O(2)	124·7	0·5
C(7)O(2)O(3)	108·9	0·4
C(5)N(1)O(4)	116·8	0·5
C(5)N(1)O(5)	118·3	0·5
C(6)C(5)N(1)	120·7	0·4
C(4)C(5)N(1)	116·8	0·4
O(4)N(1)O(5)	124·8	0·5
H(1)C(1)C(2)	127	7
C(6)C(1)H(1)	113	7
H(2)C(2)C(3)	125	7
C(1)C(2)H(2)	114	7
H(3)C(3)C(4)	113	7
C(2)C(3)H(3)	126	7
H(4)C(4)C(5)	119	6
C(3)C(4)H(4)	123	6
O(2)O(3)H(5)	112	6

electric moments in dilute solution (Verderame & Miller, 1962; Rittenhouse, Lobunez, Swern & Miller, 1958; Lobunez, Rittenhouse & Miller, 1958). A stereochemical feature of the hydrogen bonded peroxides is the relation between the molecular dihedral angle and the dihedral angle calculated with the O–O · · · O plane, that is with the hydrogen bond acceptor atom. These angles are compared in three hydrogen bonded peroxide structures in Table 9. In each case the dihedral angle based upon the acceptor oxygen is greater by a few degrees than the molecular dihedral angle. Nevertheless, in all of these cases the hydrogen atom lies nearly on the line that joins the hydrogen bonded oxygen atoms, even though the molecular dihedral angle is found at values scattered between

Table 7. *Non-bonded intramolecular distances less than 3 Å*

C(1)	H(2)	2·04 Å		C(5)	O(2)	2·98 Å
C(1)	C(5)	2·40		C(6)	H(1)	1·99
C(1)	C(3)	2·41		C(6)	O(2)	2·32
C(1)	C(7)	2·47		C(6)	O(1)	2·41
C(1)	C(4)	2·81		C(6)	N	2·49
C(2)	H(1)	2·12		C(6)	O(4)	2·79
C(2)	H(3)	2·15		C(7)	O(3)	2·29
C(2)	C(4)	2·42		C(7)	H(1)	2·51
C(2)	C(6)	2·42		C(7)	O(4)	2·71
C(2)	C(5)	2·76		C(7)	N	2·99
C(3)	H(2)	2·14		O(1)	O(2)	2·26
C(3)	H(4)	2·17		O(1)	O(3)	2·54
C(3)	C(5)	2·40		O(1)	H(1)	2·78
C(3)	C(6)	2·80		O(2)	H(5)	2·16
C(4)	H(3)	2·03		O(2)	O(4)	2·85
C(4)	C(6)	2·45		O(4)	O(5)	2·17
C(4)	N	2·45		O(5)	H(4)	2·42
C(4)	O(5)	2·74		N	H(4)	2·60
C(5)	H(4)	2·12		H(1)	H(2)	2·40
C(5)	O(4)	2·32		H(2)	H(3)	2·57
C(5)	O(5)	2·32		H(3)	H(4)	2·38
C(5)	C(7)	2·55				

Table 8. *Some planes of atoms*

Atoms	Coefficients* in $AX + BY + CZ + D = 0$			
	A	B	C	D
C(1), C(2), C(3), C(4), C(6)	− 0·0447	0·0387	0·9983	5·473
O–C = O	0·5341	0·6611	0·5269	2·666
C–O–O	0·6072	0·6079	0·5117	2·552
O–O–H	0·2658	0·3494	0·8985	4·059
O–O ⋯ O′ =	0·3476	0·4156	0·8405	3·850
Nitro group	0·3099	− 0·2670	0·9125	5·934

* Referred to the orthogonal axes *abc**.

89° and 146°. In this respect it is noteworthy that in the hydrogen bonded peroxide structures, peroxypelargonic acid and $CONH_2.H_2O_2$, the angle is ~ 133° and ~ 106°, respectively, based upon the acceptor oxygen position (Belitskus & Jeffrey, 1965; Lu, Hughes & Giguère, 1941).* These data strongly suggest that the intermolecular hydrogen bond determines the value of the dihedral angle, for the most part, in these peroxides in the solid state. Certainly the exchange repulsions between the lone pair electrons

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* Also the *trans* configuration for the H_2O_2 molecule has been reported by Pedersen & Pedersen, 1963, in a preliminary discussion of the crystal structure of $Na_2C_2O_4.H_2O_2$. They point out that the *trans* configuration could well be stabilized by two hydrogen bonds to the oxalate ions.

on the peroxide oxygen atoms have a much weaker effect upon the assumed molecular conformation. The estimates of the rotational barrier appearing in the literature have been summarized (Amako & Giguère, 1962). The empirical values listed for the *trans* barrier are 0·32 kcal.m^{-1} from microwave spectra and 0·86 kcal.m^{-1} from infrared rotation spectra. Indeed these results are consistent with the aforementioned point of view.

The torsional angle about the C–O bond, which is the dihedral angle between the OCO and COO planes, has been the subject of speculation in connection with the interpretation of the electric moment data obtained from the monomeric aliphatic peroxyacids in dilute non-polar solvents (Verderame & Miller, 1962). In crystalline *o*-nitroperoxybenzoic acid its value is 5°. The sense of the angle is such that the H atom and the carboxyl oxygen atom are on opposite sides of the COO plane. The oxygen atom is displaced 0·09 Å out of the plane. The bond lengths and valence angles in the peroxycarboxyl group indicate that resonance in the OCO group is not as pronounced as in the carboxylic acid dimers.

A χ^2 test (Hoel, 1947) showed the distances of the ring atoms from a calculated least-squares plane to be significant at the > 99% level. Five of the ring atoms are coplanar but the carbon atom bearing the nitro substituent is 0·025 Å (5σ) from this plane. The
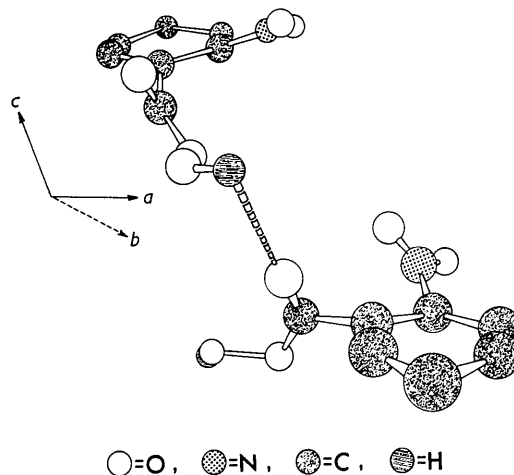

$\bigcirc$=O , ⊛=N , ⊚=C , ⊜=H

Fig. 3. Perspective view of glide related molecules in a hydrogen bonded chain.

Table 9. *Molecular dihedral angle in H-bonded peroxides and the dihedral angle based upon the H-bond acceptor atom*

Compound	Molecular dihedral angle		Dihedral angle based on acceptor O		
	Atomic planes	Angle	Atomic planes	Angle	
H_2O_2	H–O–O and O–O–H	89°	O ⋯ O–O and O–O ⋯ O	93·8°	Busing & Levy, 1958; Abrahams, Collin & Lipscomb, 1951
$H_2O_2.2H_2O$	H–O–O and O–O–H	130	O ⋯ O–O and O–O ⋯ O	139	Olovsson & Templeton, 1960
o-Nitroperbenzoic acid	C–O–O and O–O–H	146	C–O–O and O–O ⋯ O	153	

nitrogen atom is displaced 0·154 Å (30σ) in the same direction. The bond joining the benzene ring to the peroxycarboxyl carbon atom is directed toward the opposite side of plane but toward the same side as the peroxide group (Figs. 2 and 3), and 0·074 Å (15σ) is the distance of the peroxycarboxyl carbon atom from the plane. Evidently steric repulsion exists between the substituent groups. The plane of the ring atoms makes a 58° angle with the OCO plane and a 28° angle with the ONO plane. The valence angles within the benzene ring average 120° (e.s.d. 0·5°) but the angles involving the carbon atom bearing the nitro group deviate significantly (4σ) from this value. Two of the bonds on opposite sides of the ring average 1·385 Å and the other four bonds average 1·399 Å. The significance (2σ) of this difference is questionable. The largest of the three angles subtended at C(5) is C(6)C(5)N and at C(6) it is C(5)C(6)C(7) (Table 6), again an indication of steric strain involving the substituents. The NO distances in the nitro group average 1·226 Å.

Table 10. *Hydrogen bonding distances and angles*

Distance	(Å)	Angle	(°)
H(5)(I) $\cdots$ O(1)(II)	1·63	O(3)(I)–H(5)(I) $\cdots$ O(1)(II)	166
O(3)(I) $\cdots$ O(1)(II)	2·73	H(5)(I)–O(3)(I) $\cdots$ O(1)(II)	8
		O(2)(I)–O(3)(I) $\cdots$ O(1)(II)	107

Table 11. *Shortest distances between atoms in neighboring molecules*

H(1)–O(3′)	2·54 Å	(2$_1$, 0$\bar{1}\bar{1}$)*
H(2)–H(5)	2·58	(1, 0$\bar{1}$0)
H(3)–O(5)	2·77	(2$_1$, 1$\bar{1}$1)
H(4)–O(5)	2·49	(2$_1$, 1$\bar{1}$1)
H(5)–O(1)	1·63	(c, 00$\bar{1}$)
O(1)–O(3)	2·73	(c, 000)
O(2)–H(2)	2·84	(c, 0$\bar{1}\bar{1}$)
O(4)–H(2)	2·66	(1, 010)
N–H(2)	3·46	(c, 0$\bar{1}\bar{1}$)
N–H(3)	3·47	(c, 0$\bar{1}$0)
C(1)–H(5)	3·34	($\bar{1}$, 001)
C(2)–H(5)	3·13	(1, 0$\bar{1}$0)
C(3)–O(5)	3·40	(c, 0$\bar{1}$0)
C(4)–O(5)	3·20	(2$_1$, 1$\bar{1}$1)
C(5)–C(2)	3·47	(c, 0$\bar{1}\bar{1}$)
C(6)–C(1)	3·57	(c, 0$\bar{1}\bar{1}$)
C(7)–H(5)	2·73	(c, 000)

* The tabulated distance is from the atom in the first column with coordinates as in Table 3 to the atom in the second column with coordinates from Table 3 transformed according to the parenthesized symmetry operation. The first symbol refers to a $P2_1/c$ group operator for the second setting, and the three integers refer to the lattice translational operation to be applied in the transformation.

Glide related molecules are hydrogen bonded in an infinite chain nearly parallel to the c axis (Fig. 3). The distances and angles between atoms involved in the hydrogen bonding system are given in Table 10. The closest intermolecular contacts at each atom are listed in Table 11.

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