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The Crystal Structure of *p*-Nitroperoxybenzoic Acid

BY HOON SUP KIM, SHIH-CHEN CHU AND G. A. JEFFREY

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15213, *U.S.A.*

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The crystal structure of *p*-nitroperoxybenzoic acid, $C_7H_5NO_5$, is orthorhombic, $P2_12_12_1$, $a=5{\cdot}81$ (2), $b=5{\cdot}05$ (2), and $c=26{\cdot}34$ (5) Å, $Z=4$. The structure was solved by application of the tangent phase refinement method. The molecule is nearly planar with the nitro and peroxycarboxyl groups inclined at 6 and 8° respectively to the benzene ring. There is one intermolecular hydrogen bond of 2·74 Å between the terminal oxygen atom of the peroxy group and the carbonyl oxygen atom of an adjacent molecule. The peroxycarboxyl group is planar with a dihedral angle about the O–O bond of 170°, based on the assumption of a linear O–H···O hydrogen bond.

Introduction

The crystal structure of *p*-nitroperoxybenzoic acid forms part of a study of the stereochemistry of the peroxy group in peroxy acids. Structures previously studied are the aliphatic peroxypelargonic acid by Belitskus & Jeffrey (1965), and the aromatic *o*-nitroperoxybenzoic acid by Sax, Beurskens & Chu (1965). As in the case of the hydrogen peroxide molecule in perhydrates (Pedersen, 1969), the crystal structural evidence indicates that the potential energy function for rotation about the dihedral angle of the peroxy group was such that this angle was determined by inter- rather than intra-molecular forces in the solid state (Sax & McMullan, 1967). For this reason, a comparison between *ortho* and *para* substituted nitroperoxybenzoic acids was especially interesting.

Crystal data

p-Nitroperoxybenzoic acid, $C_7H_5NO_5$, M.W. 183·1. Orthorhombic: space group $P2_12_12_1$, from systematic absences.

$a=$ 5·81 (2) Å at −15°C	$D_m=1{\cdot}586$ g.cm^{-3}
$b=$ 5·05 (2)	$D_x=1{\cdot}576$ g.cm^{-3}
$c=$ 26·34 (5)	$Z=4$
$V=772{\cdot}8$ Å^3	$\mu_{Cu\ K\alpha}=6{\cdot}07$ cm^{-1}

Experimental

The crystals were supplied by Dr L. S. Silbert of the Eastern Regional Research Laboratory, Department of Agriculture. They were thin, colorless, rectangular plates on (001) and elongated in the *b*-axis direction; they decomposed on heating to 120° and on exposure to Cu *K* radiation at room temperature. At −15°C the crystals were sufficiently stable to radiation damage to permit the collection of a set of diffraction data. The intensities were recorded by the Weissenberg method on four layers about the *a* and *b* axes, and estimated visually. Of the 883 reflexions within the Cu *K* sphere, only 503 could be observed due to the rapid fall-off in intensity with increase of 2θ. The intensities were correlated, scaled and reduced to structure amplitudes using a series of IBM 1620 programs (Shiono, 1963). No absorption corrections were applied.

Structure determination and refinement

Earlier attempts to solve the structure by interpretation of the Patterson synthesis were unsuccessful. The structure was solved by the direct method with the tangent refinement procedure (Karle & Hauptman, 1956) using an IBM 7090 version of the Hall (1968) procedure. The phases of the 147 amplitudes of greatest *E* values were determined from the following starting phases:

H	*K*	*L*	*E*	α in π
0	1	24	3·57	0·5
4	0	11	2·71	0·5
1	0	11	2·63	0·5
0	2	19	2·95	0·0
2	1	10	2·18	1·0

The resulting *E* map revealed thirteen peaks which could be fitted to a chemically feasible structure. The first structure factor calculation gave an agreement index 0·19 for all reflections. The structure was refined anisotropically by block-diagonal least-squares on an IBM 1130 (Shiono, 1968) with a final cycle of full-matrix refinement on an IBM 7090 (Shiono, 1966). The weighting scheme was $\omega^{-1}=1{\cdot}0+0{\cdot}1|F_{obs}|+0{\cdot}002|F_{obs}|^2$. The final *R* value was 0·12, when the coordinate shifts were less than 0·02 Å. The hydrogen atoms could not be located on difference syntheses. The poor quality of the crystals and the limitations of the diffraction data therefore did not warrant further refinement or remeasurement using a diffractometer. The final parameters are given in Table 1 and the observed and calculated structure factors in Table 2. The atomic numbering and the thermal ellipsoids are shown in Fig. 1.

Description of the structure

The molecule is approximately planar with the nitro and percarboxyl groups making angles with the benzene ring of 6 and 8° respectively. This is in contrast to the *ortho* derivative where, owing to the steric interference, the corresponding angles were 28 and 58°. The substituent N and C(7) are coplanar with the benzene ring within the experimental error. Both the percarboxyl and nitro groups, C(7)O(1)O(2)O(3) and

Table 1. *Fractional atomic coordinates, anisotropic temperature factors and estimated standard deviations, in parentheses, for p-nitroperoxybenzoic acid*

The temperature expression used was $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·292 (2)	0·223 (3)	0·1929 (5)	0·025 (5)	0·026 (7)	0·0014 (2)	0·010 (6)	−0·0007 (9)	0·0009 (12)
C(2)	0·433 (3)	0·156 (3)	0·1444 (5)	0·035 (5)	0·028 (8)	0·0012 (2)	−0·005 (6)	0·0003 (10)	0·0018 (13)
C(3)	0·363 (3)	−0·048 (4)	0·1795 (6)	0·025 (5)	0·042 (8)	0·0016 (3)	−0·006 (7)	−0·0004 (9)	−0·0030 (14)
C(4)	0·153 (3)	−0·160 (3)	0·1693 (5)	0·031 (5)	0·039 (8)	0·0007 (2)	0·008 (7)	−0·0007 (9)	−0·0004 (12)
C(5)	0·002 (3)	−0·102 (5)	0·1290 (6)	0·032 (6)	0·075 (13)	0·0016 (3)	0·017 (8)	0·0011 (11)	−0·0018 (18)
C(6)	0·080 (2)	0·096 (4)	0·0951 (6)	0·018 (4)	0·048 (8)	0·0012 (2)	−0·013 (7)	−0·0006 (8)	0·0006 (14)
C(7)	0·389 (3)	0·424 (3)	0·0692 (5)	0·042 (7)	0·026 (7)	0·0010 (2)	0·003 (7)	0·0001 (10)	0·0011 (12)
N	0·068 (3)	−0·379 (3)	0·2040 (5)	0·041 (6)	0·059 (9)	0·0014 (2)	0·002 (7)	0·0017 (10)	−0·0007 (13)
O(1)	0·576 (2)	0·519 (3)	0·0689 (4)	0·037 (4)	0·069 (8)	0·0016 (2)	−0·032 (6)	−0·0005 (7)	0·0043 (11)
O(2)	0·222 (2)	0·490 (3)	0·0345 (4)	0·027 (4)	0·065 (7)	0·0011 (1)	0·005 (5)	0·0000 (6)	0·0039 (10)
O(3)	0·323 (2)	0·691 (3)	0·0001 (4)	0·037 (4)	0·061 (7)	0·0011 (1)	0·011 (5)	−0·0000 (7)	0·0052 (10)
O(4)	0·202 (2)	−0·459 (2)	0·2369 (4)	0·057 (5)	0·043 (7)	0·0015 (2)	0·012 (6)	−0·0025 (9)	0·0051 (9)
O(5)	−0·128 (2)	−0·466 (3)	0·1968 (4)	0·041 (5)	0·077 (9)	0·0016 (2)	−0·025 (7)	0·0009 (8)	0·0007 (12)

Table 2. *Observed and calculated structure amplitudes for* p-*nitroperoxybenzoic acid*

Columns are: index, $10|F_{obs}|$, $10|F_{calc}|$, $10A_{calc}$, $10B_{calc}$. Asterisks indicate unobserved reflections.

C(4) N O(4) O(5) are planar and are inclined at an angle of 5° to each other about the diameter of the benzene ring C(1)–C(4) (see Table 3). The bond distances and angles are given in Table 4 and Fig. 2. These are less accurate than those for the *o*-nitroperoxybenzoic acid structure and where differences occur they are accountable by experimental errors.

Table 3. *Least-squares planes in p-nitroperoxybenzoic acid*

Equation for plane, $Ax+By+Cz=D$, where x,y,z are in Å.

Atoms included in plane	Atoms not included in plane	Distance from best plane	Constant
C(1)		−0·001 Å	$A=-0·451$
C(2)		0·008	$B=$ 0·695
C(3)		−0·008	$C=$ 0·560
C(4)		0·001	$D=$ 1·535
C(5)		0·006	
C(6)		−0·006	
	C(7)	−0·049	
	O(1)	−0·209	
	O(2)	0·113	
	O(3)	0·043	
	N	−0·032	
	O(4)	−0·180	
	O(5)	0·070	
C(7)		−0·001	$A=-0·319$
O(1)		0·000	$B=$ 0·728
O(2)		0·000	$C=$ 0·607
O(3)		0·000	$D=$ 1·944
	C(1)	−0·019	
	C(2)	0·139	
	C(3)	0·080	
	C(4)	−0·104	
	C(5)	−0·258	
	C(6)	−0·218	

Table 3 (*cont.*)

Atoms included in plane	Atoms not included in plane	Distance from best plane	Constant
C(4)		−0·001	$A=-0·363$
N		0·005	$B=$ 0·681
O(4)		−0·002	$C=$ 0·636
O(5)		−0·002	$D=$ 1·966
	C(1)	−0·091	
	C(2)	0·077	
	C(3)	0·111	
	C(5)	−0·160	
	C(6)	−0·212	
	C(7)	−0·171	
	O(1)	−0·240	
	O(2)	−0·169	
	O(3)	−0·268	

The peroxy dihedral angle is 170°, based on the assumption that the hydrogen atom lies on the line of the hydrogen-bond linking O(3) and O(1) of the adjacent molecule. This compares with 146° in the *ortho* derivative and 133° in peroxypelargonic acid. These differences probably reflect correctly the sensitivity of the peroxy dihedral angle to the intermolecular forces, but more precise data on the position of the hydrogen atoms are necessary to confirm this observation. In all three structures, the molecules are linked by hydrogen bonds of 2·74 Å between O(3)H···O(1), so as to form infinite spirals of percarboxyl groups. The constancy of the O(H)···O distance in the three structures gives support to the assumption that the hydrogen atoms do not deviate far from the oxygen line of centers.

The hydrogen bonding and molecular packing is shown in Figs. 3 and 4 and the intermolecular contacts

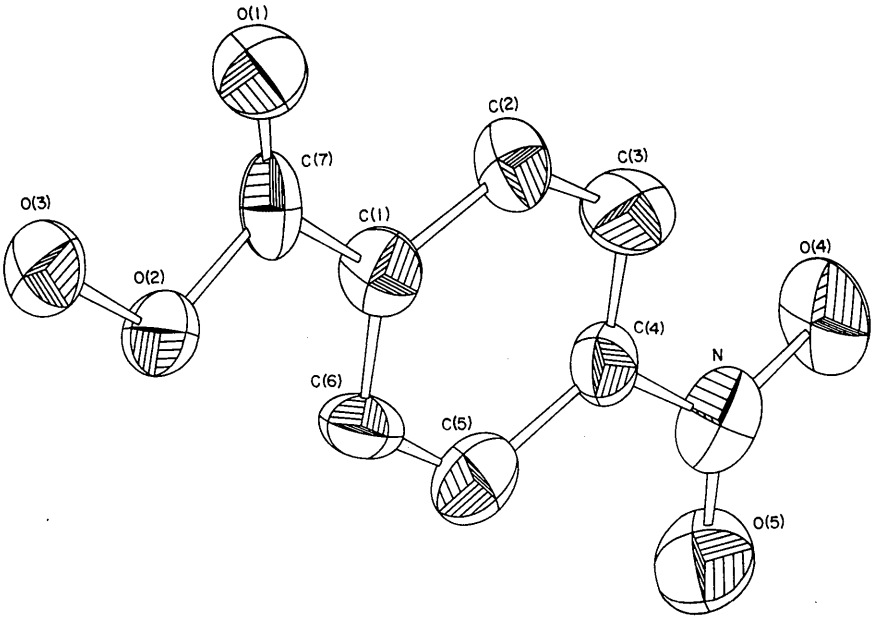

Fig. 1. Molecular conformation observed in the crystal structure of *p*-nitroperoxybenzoic acid, showing atomic numbering used and the anisotropic thermal ellipsoids.

Table 4. *Bond distances and angles and their estimated standard deviations, in parentheses, in p-nitroperoxybenzoic acid*

i	*j*	D_{ij}
C(1)	C(2)	1·41 (2) Å
C(2)	C(3)	1·44 (2)
C(3)	C(4)	1·37 (2)
C(4)	C(5)	1·41 (2)
C(5)	C(6)	1·42 (2)
C(6)	C(1)	1·40 (2)
C(1)	C(7)	1·46 (2)
C(4)	N	1·52 (2)
C(7)	O(1)	1·19 (2)
C(7)	O(2)	1·37 (2)
N	O(4)	1·24 (2)
N	O(5)	1·24 (2)
O(2)	O(3)	1·48 (2)

i	*j*	*k*	∠(*ijk*)
C(1)	C(2)	C(3)	120 (1)°
C(2)	C(3)	C(4)	115 (1)
C(3)	C(4)	C(5)	128 (2)
C(4)	C(5)	C(6)	115 (2)
C(5)	C(6)	C(1)	121 (1)
C(6)	C(1)	C(2)	121 (1)
C(2)	C(1)	C(7)	114 (1)
C(6)	C(1)	C(7)	125 (1)
C(3)	C(4)	N	118 (1)
C(5)	C(4)	N	113 (1)
C(1)	C(7)	O(1)	130 (2)
C(1)	C(7)	O(2)	107 (1)
O(1)	C(7)	O(2)	123 (1)
C(7)	O(2)	O(3)	107 (1)
C(4)	N	O(4)	117 (1)
C(4)	N	O(5)	118 (1)
O(4)	N	O(5)	125 (2)

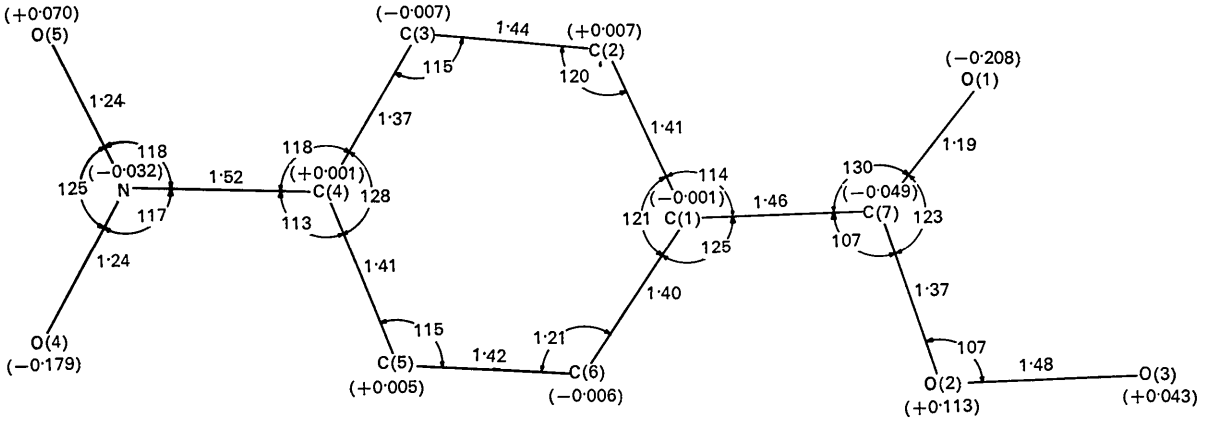

Fig. 2. Bond distances (Å) and angles (°); decimal values in parentheses denote the deviations of atoms from the extended plane of the benzene ring (Å).

below 3·5 Å are given in Table 5. As in the case of the *ortho* derivative, this is a comparatively close-packed structure with a density greater than 1·5 g.cm^{-3}, and there are, in addition to the hydrogen bond, several O···O and a N···O separation less than 3·2 Å.

Table 5. *Intermolecular distances less than* 3·5 Å *in p-nitroperoxybenzoic acid*

i	*j*	D_{ij}
C(2)	O(4), *b*	3·39 Å
C(2)	O(5), *c*	3·47
C(3)	O(4), *b*	3·47
C(3)	O(4), *f*	3·38
C(4)	O(4), *e*	3·37
C(5)	O(2), *a*	3·47
C(6)	O(3), *g*	3·26
N	O(4), *e*	3·06
N	O(5), *e*	3·36
O(1)	O(3), *h*	2·74 (hydrogen bond)
O(2)	O(3), *k*	2·96
O(3)	O(3), *h*	2·97

Table 5 (*cont.*)

i	*j*	D_{ij}
O(4)	O(5), *e*	3·07
O(4)	O(5), *d*	3·13

Symmetry operation:

i,	*x*	*y*	*z*
j, *a*	*x*	$-1+y$	*z*
b	*x*	$1+y$	*z*
c	$1+x$	$1+y$	*z*
d	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
e	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
f	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
g	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$
h	$\frac{1}{2}+x$	$1\frac{1}{2}-y$	$-z$
k	$-\frac{1}{2}+x$	$1\frac{1}{2}-y$	$-z$

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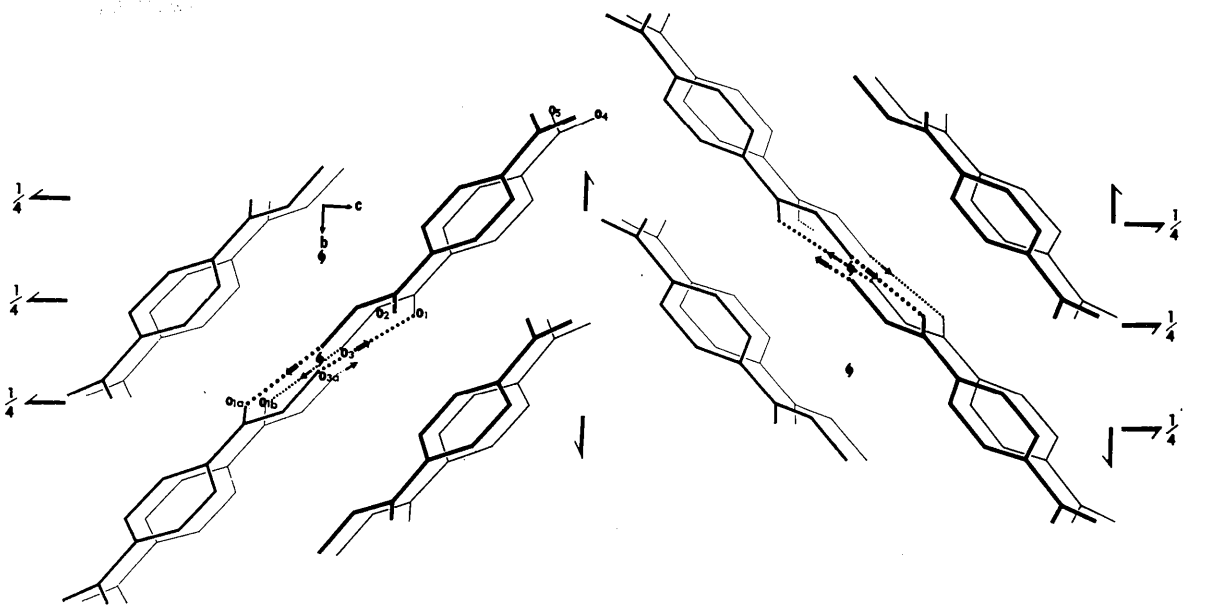

Fig. 3. The crystal structure of *p*-nitroperoxybenzoic acid viewed down the *a* axis. Solid lines indicate primary C–C, C–O, N–C, N–O and O–O bonds. Dotted lines indicate hydrogen bonds with arrows pointing in the donor direction.

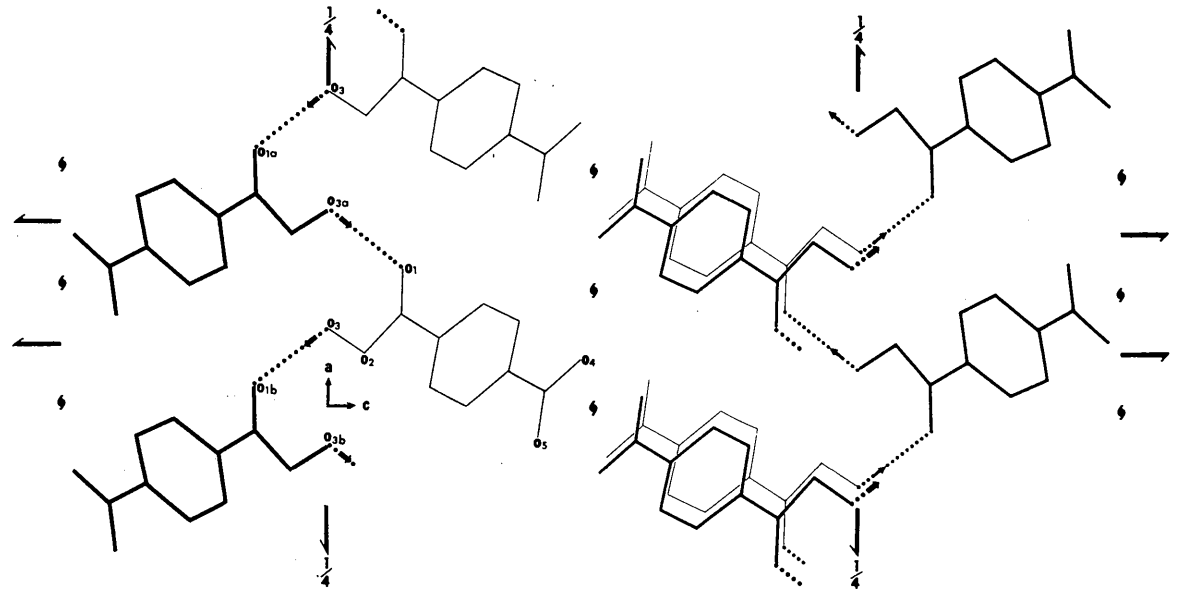

Fig. 4. The crystal structure of *p*-nitroperoxybenzoic acid viewed down the *b* axis. Solid and dotted lines are as in Fig. 3.

References

BELITSKUS, D. & JEFFREY, G. A. (1965). *Acta Cryst.* **18**, 458.

HALL, S. R. (1968). *Direct Phasing Methods Program*, UWAC-17. The University of Western Australia, revised for the IBM 7090 by H. M. Berman, Crystallography Laboratory, University of Pittsburgh.

KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.

PEDERSEN, B. F. (1969). *Acta Cryst.* A**25**, S104, XII-16.

SAX, M., BEURSKENS, P. & CHU, S. (1965). *Acta Cryst.* **18** 252.

SAX, M. & MCMULLAN, R. K. (1967). *Acta Cryst.* **22**, 281.

SHIONO, R. (1963). Technical Report No. 43, University of Pittsburgh Computation and Data Processing Center.

SHIONO, R. (1966). *Oak Ridge Least-Squares Program*, modified for the Crystallography Laboratory of the University of Pittsburgh.

SHIONO, R. (1968). Unpublished work.