The Crystal Structure of *p*-Nitroperoxybenzoic Acid

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The crystal structure of *p*-nitroperoxybenzoic acid, $C_7H_5NO_5$, is orthorhombic, $P2_12_12_1$, a=5.81 (2), b=5.05 (2), and c=26.34 (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.

$a = 5.81 (2) \text{ Å at } -15^{\circ}\text{C}$	$D_m = 1.586 \text{ g.cm}^{-3}$
b = 5.05(2)	$D_x = 1.576 \text{ g.cm}^{-3}$
c = 26.34(5)	Z = 4
$V = 772 \cdot 8 \text{ Å}^3$	$\mu_{\rm Cu} K_{\alpha} = 6.07 \ {\rm cm}^{-1}$

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:

Η	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 fullmatrix refinement on an IBM 7090 (Shiono, 1966). The weighting scheme was $\omega^{-1} = 1.0 + 0.1 |F_{obs}| +$ $0.002|F_{obs}|^2$. 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 $\left[-\left(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl\right)\right]$.

	x	У	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)	<i>−</i> 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)	<i>−</i> 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)	<i>−</i> 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)	<i>−</i> 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)	<i>−</i> 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.

	H= 0 K= 0 39 21 21- 83 57 57 271 217 217-	0 9 0 10 0 11	82 96 96 57 67 0 189 177 177 578 559 0	- 0 14 67- 15 - 0 16 559 17	187 169 101- 140 144 93 186 181 78 112 103 77-	135 10 110- 11 163 12 67- 13	212 183 178 100 87 6- 95 96 87 142 147 15-	87- 10 41- 11 146 12	120 116 104 154 139 74- 29* 41 34-	51- 21 118 24 1	399 42 42 399 47 29	7- 2 37-
10	314 319 319 140 114 114 98 96 96 186 180 180	0 12	90 68 68 69 54 0 138 305 305	- 0 18 54 19 - 0 21 74- 22	58 45 42 19* 33 11 18* 17 17- 10* 9 1	$ \begin{array}{r} 17 & 14 \\ 31- & 15 \\ 2 & 16 \\ 9- & 17 \end{array} $	110 100 99 131 117 114- 109 108 96 214 22 19	10 13 28- 14 48- 15 11 16	123 190 127- 83 89 62- 65 72 49- 86 81 74	27 2 65- 3 53- 4 33- 5	95 110 55 79 75 14 56 69 67 79 66 41	- 74- 14- - 52-
20 28 30	65 72 72 111 105 105 158 194 194	0 16 0 17 0 18	377 272 272 84 74 0 23* 26 26	0 24 74- 0 0	75 39 29- H= 1 K• 4 160 151 0	27 18 19 151 21	96 89 81 41• 42 16 59 71 27-	35- 19 39 20 66	109 112 109- 43* 48 47- . H* 3 K* 2	26 6 10- 7 8	98 85 56 70 58 53 172 138 98	63- - 24- 98
13	He 0 Ke 1 101 72 0 120 3 0	72- 20 3- 22	186 165 0 113 96 96 26* 36 36	165- 1 0 2 0 3	131 111 105 29* 25 6 29* 51 19 29* 62 41-	37- 24- 1 47- 2 10- 3	18• 21 21 26• 40 40 52 55 34	1 1 3- 2 43- 3	56 60 5- 91 85 49 96 83 83	60- 10 69 11 4 12	101 95 70 128 88 88 124 86 40	- 64 0 - 76-
5	683 759 0 882 1005 0 155 160 0	759- 25 1005- 26 160- 27	149 147 0 25* 36 36 55* 64 0	147 5 0 6 64 7	29* 21 20 30* 39 15- 30* 26 25	5 4 36 5 7 6	90 88 87 73 91 76 123 112 31-	6 4 50- 5 107 6	82 74 7 148 134 5 215 217 185	73 13 134- 14 113 15	59 50 47 18* 11 7 83 71 32	- 18 - 8- - 63
10	315 307 0 135 89 0 87 89 0 162 157 0	307 28 89- 29 89- 30 157-	89 86 86 94 104 0 54 65 65 H= 1 K=	0 8 104- 9 - 0 10 1 11	30° 29 4- 68° 62 22 96 102 102- 68° 83 79	29- 1 59 8 4 9 25- 10	68 36 34 35• 28 7 134 123 94-	13- 8 27 9 79 10	90 81 72 77 72 58- 101 88 36	36 17 42- 18 80	17* 14 8 39* 35 17 H= 4 K*	12- 31
12	250 216 0 157 149 0 214 200 0	216 0 149 1 200- 2	85 65 0 263 320 320 331 404 31	65- 12 2 13 252- 14	96 81 48- 30* 33 9- 67* 55 55-	66 11 32- 12 7 13	142 133 131- 94 75 33 108 94 94	26 11 67 12 5 13	109 88 32 117 110 77- 61 57 48	82- 0 79 1 31- 3	58 55 55 94 111 82 83 68 59	- 75- 34-
16	140 127 0 182 188 0 21* 47 0 22* 6 0	188- 4	402 469 310 500 611 225 551 620 620 196 196 21	- 568- 15 - 568- 16 - 18-	94 88 88 66* 62 60 H* 2 K* 0 123 138 138-	15 15 16 0 17	131 123 63- 104 111 73 83 56 51-	106- 17 83- 18 24 19	97 134 134 76 94 5 83 82 42-	14 5 94 7 70 8	102 102 45 42* 58 54 42* 55 55	91 - 21 - 8-
20 21 22	22• 21 0 23• 22 0 23• 25 0	21 7 22 8 25- 9	218 220 5 383 347 7 132 119 108	- 220 1 340- 2 - 49 4	90 100 D 179 150 150- 567 494 494-	100- 18 0 19 0 20	19* 22 3 118 101 99 18* 28 20- 120 94 40-	21- 20 20 21 19- 72 0	52 44 37- 56 49 32- H= 3 K= 3	24 9 37- 135 2	59 67 62 H= 5 K= 21* 29 0 21* 29 29	26- 0 29
23 24 25	107 130 C 253 287 0 137 151 0 H= 0 K= 2	287 11 151- 12 13	151 112 42 156 136 94 261 238 238	221 104- 6 - 98 7 21 8	256 200 0 122 97 97- 269 287 0 260 204 204-	0 22 287- 23 0	5. 59 52- 47 42 29- H= 2 K= 4	27- 1 30- 2 3	106 109 91 33* 33 32 113 119 29-	59- 3 8 5 115- 6	21• 32 21• 43 21• 7	32 - 0
0	478 563 563 186 258 258- 150 144 144-	0 14 0 15 0 16	111 99 91 83 81 56 113 105 74	- 17 9 59- 10 74 11	86 64 0 16° 21 21 230 189 0	64- 0 0 1 159- 2	132 125 125- 26* 36 36 118 116 4- 103 96 69-	0 4 1 5 116- 6 67 7	90 70 36- 170 177 165 123 107 85- 104 125 39	60 8 65- 9 65- 10 118 11	121 123 C 142 117 117 141 96 C	123
, , , , , , , , , , , , , , , , , , , ,	212 209 205 141 120 120- 271 280 280-	0 18 0 19 0 20	72* 18 14 71 64 11 35* 34 2	- 12 13 - 63 14 21 15	19• 33 0 337 293 293 266 261 0	33 4 0 5 261- 6	26* 36 35 26* 43 14- 26* 21 19	10- 8 41- 9 9 10	112 100 5 46* 48 26- 70 63 49	100- 12 40 13 38 14	21* 32 32 68 58 0 20* 22 22	- 0 58- 0
7 8 9	219 230 230 380 399 399- 151 129 129 176 189 189-	0 21 0 23 0 24 0 25	138 116 11 62 62 30 37* 41 10 86 81 34	I- 35- 16 50- 17 I- 37- 18 I- 73 19	82 92 92 69 59 0 118 110 110- 23* 29 0	0 / 59- 8 0 9 29- 10	26° 42 41- 60° 70 61 71 94 19-	5 12 35- 13 92	96 94 59 420 44 30 H= 3 K= 4	73- 16 32- 17 18	46* 5* 54 63 69 0 122 102 102	- 0 69 0
11 12 13	123 105 106- 151 130 130- 44 44 44	0 26 C 27 0	59 87 40* 27 H= 1 K=	86- 20 27 21 2 22 21	24• 14 14- 91 109 0 38• 59 59-	0 11 109- 12 0 13 23 14	104 113 46- 59* 59 54 59* 59 24- 57* 58 20	103- 0 22 2 54 54- 0	135 156 0 135 116 116 H= 4 K= 0 149 134 134-	156- 6 0 1 0 2	H= 5 K= 43* 44 (61 77 65 75 85 48	1 - 44- - 42- 70
15	81 90 90- 51 55 55 31• 38 38	0 1 0 2 0 3	106 112 7 120 155 6 173 188 11	0- 88 24 141- 25 0- 153- 27	24* 19 19- 24* 20 0 109 118 0	0 20 0 118- 1	H= 2 K= 5 25* 33 33- 56* 47 23	0 2 41- 3	165 139 0 105 95 95 20• 36 0	139 3 0 4 34 5	107 107 87 43* 56 18 107 91 78	- 61- 53- 45
18	158 169 169- 251 273 273 129 155 155- 100 100 100-	0 4	197 183 5 100 77 2 271 274 18	1- 176 3 73- 0 7- 200- 1 1- 97- 2	H= 2 K+ 1 105 139 139 105 108 107 201 247 231-	0 4 13 5 90	24* 23 18 78 49 39 H* 3 K* 0	15- 6 30 7 8	63 62 62- 111 106 0 255 218 218	106- 8 0 10	98 90 81 98 83 44 19* 26	6 2- 71 7 25-
22	41* 54 54- 41* 30 30- H= 0 K= 3	0 8 0 9 10	303 292 11 315 292 26 26C 252 15	3- 269- 3 9- 115 4 2- 201 5	115 137 73- 190 221 206- 204 204 137	116 1 79 2 152 3	84 62 0 71 75 75- 226 190 0	62- 9 0 10 190 11	168 146 0 94 92 92- 258 225 0	146 12 0 13 225 14	42* 67 52 42* 58 34 42* 74 10 40* 68 61	2 41 - 47- 5 73 4-
1	210 14 0 270 315 0 257 271 0 98 85 0	315- 12 271 13 80- 14	97 96 9 72 88 8 119 111 8	32- 7 3- 30 8 7- 70- 9	153 159 46 203 200 142- 204 195 188	152 5 141 6 52- 7	134 130 0 224 183 183 157 143 0	130- 14 0 15 143- 17	98 54 54- 121 111 0 21• 14 0	0 16	39• 43 4 38• 24 1 H= 5 K=	2 21
, , ,	122 162 0 82 79 0 81 73 0	102 - 15 79 - 16 73 17	21* 25 2 109 113 11 23* 39	1- 13 10 1 16- 11 6 39- 12	381 370 177- 94 93 82- 61 42 39- 194 160 10-	325 8 44 9 15- 10	17* 20 20 96 90 0 113 117 117 70 75 0	90-19 0 75 0	21* 23 23- 97 96 0 H* 4 K* 1 39* 57 57	96 1 2 0 3	118 115 83 65 5 41• 47 118 132 11	D- 43 B 46- 67
9 10 11	84 60 U 43 52 3 20+ 23 0	60- 19 52- 20 23 21	179 165 8 156 153 13 146 148 14	1- 144- 14 7 6? 16 5- 28 17	79 78 21- 120 126 75- 47* 57 26	75 13 100- 14 50 15	90 62 0 20• 16 16- 21• 22 0	62- 1 0 2 22- 3	17* 12 8- 7* 35 25 17* 30 1-	8 4 24 5 30- 6	18• 27 93 70 2- 18• 23 2	8 26 66 1- 9
12	84 87 0 115 121 0 90 90 0 36• 35 0	87 22 121 93- C 35 1	H= 1 K= 67 74 88 93	7 59-18 3 19 0 74-20 7 93 21	22* 35 25- 34* 39 32 175 174 40- 87 75 31-	25- 16 23 17 169- 19 68 20	22• 36 0 23• 44 0 24• 18 18-	36 5 44 6 0 7	115 118 80- 123 137 132 57 59 55	86 8 35- 9 23 10	18• 19 1 17• 21 80 74 4	8- 7 4 21 8- 56-
1	H# C K# 4 26* 18 18 59* 54 54	- 0 3	52 51 2 108 104 1 91 75 6	7 L4 27 0 103- 4- 40 0	107 91 89- H= 2 K+ 2 14* 12 12 183 185 49-	18- 22 24 178 0	23* 13 13- 113 96 96- H= 3 K* 1 350 419 0	0 8 0 9 10 419 11	104 97 4 83 75 74- 18* 17 8 104 99 52-	97- 11 11 15- 0 84 1	39* 29 2 Hb 6 K* 18* 30 3 57 69 3	- 15- 1 0 0 5 59-
•	- 117 122 127 84 86 88 H= 1 K# (. 354 337 0	0 6 337 8	97 91 5 111 102 5 78 \$6 3	0 77 2 2- 88- 3 0 47- 4	111 113 99 245 250 47- 225 224 179-	55- 1 246 2 135- 3	76 80 80 102 109 80- 138 147 120-	3 12 73 13 85- 14	105 71 25- 123 114 111- 186 187 152	66- 26- 0 109- 1	H# 6 K# 51 49 4 72 88 5	2 9- 0 9 65
	1 640 699 699 8 425 435 U 9 173 152 U 8 198 124 124	- 0 9 435-10 152-11	9 75 62 4 9 201 176 7 1 92 91 8 95 94 8	8- 40 7 159 6 7- 29- 1 4- 42 8	182 161 27 138 110 49- 138 137 126- 205 190 5-	159- 4 98- 5 53 6 190 7	78 69 68 24• 31 29- 94 92 71-	27 17 15- 16 12- 17 59 18	107 126 69 43* 40 38 47* 44 33-	106 14 30	16* 14 1 15* 25 2 34* 23 2	4- 1- 1 14- 0- 11-
	7 123 8: 0	81-1	9 VL 68 4	5 51 9	208 183 94	156 8	80 76 61	46- 19	42 59 42	42		

C(4) NO(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	<i>p</i> -nitroperoxybenzoic
			acid		

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

Atoms in-	Atoms not	Distance	
cluded in	included	irom	a
plane	in plane	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
ŌÌÌ		0.000	B = 0.728
O(2)		0.000	C = 0.607
O(3)		0.000	D = 1.944
	C(1)	-0.019	
	$\tilde{C}(2)$	0.139	
	$\overline{C(3)}$	0.080	
	$\vec{C}(\vec{4})$	-0.104	
	C (5)	-0.258	
	ĊÓ	-0.218	

Table 3 (cont.)

Atoms in-	Atoms not	Distance	
cluded in	included	from	
plane	in plane	best plane	Constant
C(4)		-0.001	A = -0.363
N		0.002	B = 0.681
O(4)		-0.005	C = 0.636
O(5)		-0.005	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)	-0.568	

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 $O(3)H \cdots O(1)$, so as to form infinite spirals of percarboxyl groups. The constancy of the $O(H) \cdots O$ 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>i</i> C(1) C(2) C(3) C(4) C(5) C(6)	j C(2) C(3) C(4) C(5) C(6) C(1)	$\begin{array}{c} D_{ij} \\ 1.41 (2) \ \text{\AA} \\ 1.44 (2) \\ 1.37 (2) \\ 1.41 (2) \\ 1.41 (2) \\ 1.42 (2) \\ 1.40 (2) \end{array}$	<i>i</i> C(1) C(2) C(3) C(4) C(5) C(6)	j C(2) C(3) C(4) C(5) C(6) C(1)	k C(3) C(4) C(5) C(6) C(1) C(2)	$\angle (ijk)$ 120 (1)° 115 (1) 128 (2) 115 (2) 121 (1) 121 (1)
C(1) C(4) C(7) C(7) N	C(7) N O(1) O(2) O(4)	1·46 (2) 1·52 (2) 1·19 (2) 1·37 (2) 1·24 (2)	C(2) C(6) C(3) C(5)	C(1) C(1) C(4) C(4)	C(7) C(7) N N	114 (1) 125 (1) 118 (1) 113 (1)
N O(2)	O(5) O(3)	1·24 (2) 1·48 (2)	C(1) C(1) O(1) C(7) C(4) C(4)	C(7) C(7) C(7) O(2) N N	O(1) O(2) O(2) O(3) O(4) O(5)	130 (2) 107 (1) 123 (1) 107 (1) 117 (1) 118 (1)
		(0.007)	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).

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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 $O \cdots O$ and a $N \cdots O$ separation less than 3.2 Å.

Table	5.	Intermolecular	distances	less	than	3∙5 A	in
		p-nitropere	oxyb enz oic	acia	!		

i	j	Dij
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
Ν	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	
	Symmetr	y operation:	
i,	x	у	Z
j, a	x	-1+y	Z
Ь	x	1+y	z
с	1+x	1+y	Z
d	-x	$-\frac{1}{2}+y$	$\frac{1}{2} - z$
е	-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.

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