courante. La position des atomes d'hydrogène confirme l'existence de telles liaisons. Ces positions sont systématiquement à l'extérieur de la droite reliant les deux atomes d'oxygène ou d'azote liés par liaison hydrogène. Les angles (O,H,O) ou (O,H,N) constatés pour les quatre liaisons sont compris entre 145 et 171 ° (*A*, 158 °; *D*, 171 °; *C*, 145 °; *B*, 146 °). Les interactions *A* et *D* d'une part ainsi que *B* et *C* d'autre part sont pratiquement coplanaires ainsi que l'illustre la Fig. 1(*d*).

Les atomes de chlore et les groupes phényle étant respectivement éloignés les uns des autres, les autres interactions, qui s'établissent pour assurer la stabilité du cristal, ne sont que des interactions faibles.

Les programmes utilisés pour l'affinement par moindres carrés des paramètres atomiques lors de cette étude sont: le programme d'affinement de blocs moléculaires rigides de Vallino (1969) et le programme *ORFLS* de Busing, Martin & Levy (1962).

L'auteur remercie vivement M.A. Resplandy, sous directeur au Muséum d'Histoire Naturelle, de lui avoir aimablement offert l'étude de différents acides *N*-arylphtalamiques et d'avoir animé d'interessantes discussions.

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The Crystal and Molecular Structures of (*a*) 2,2'-Diiodo- (*b*) 2,2'-Dibromo- (*c*) 2,2'-Dichloro- (*d*) 2-Iodo-2'-bromo- and (*e*) 2-Iodo-2'-chloro-dibenzoyl Peroxides

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Monoclinic crystals of (*a*) 2,2'-diiodo- (*b*) 2,2'-dibromo (*d*) 2-iodo-2'-bromo- and (*e*) 2-iodo-2'-chloro-dibenzoyl peroxide are isostructural with two molecules per unit cell of average dimensions $a=12\cdot98$, $b=4\cdot11$, $c=15\cdot37$ Å, and $\beta=121\cdot21°$. Although the $P2_1/c$ space group symmetry apparently favored for molecular close-packing is satisfied approximately by all halogen and carbon atoms, the actual space group is Pc with an asymmetric arrangement of oxygen atoms. 2,2'-Dichlorodibenzoyl peroxide (*c*) necessarily has C_2 molecular symmetry in the orthorhombic space group $P2_12_12$, with two molecules per cell ($a=13\cdot33$, $b=12\cdot94$, $c=3\cdot84$ Å). The geometries of the peroxide linkage in (*a*), (*b*), and (*c*) are similar, with an average oxygen–oxygen distance of 1·45 Å and an average peroxide dihedral angle of 109°. Single crystals of peroxides (*a*), (*d*), and (*e*) undergo solid state transformations to single crystals of isomeric products.

Introduction

Our completed studies† of the solid state decomposition of 2,2'-diiododibenzoyl peroxide‡ (I*a*) have shown that *single crystals* of (I*a*) are slowly, continuously, and completely transformed to *single crystals* of an isomer, 1,3-dihydro-1-(*o*-iodoiodobenzoyloxy)-3-oxo-1,2-benziodoxole (II*a*) during storage at room temperature for several weeks. While continuous exposure of the peroxide crystals to X-radiation at room temperature accelerates the transformation, which, under these conditions, is essentially complete after about one week, the molecular and crystal structure of the resulting solid is identical with that formed during normal storage.

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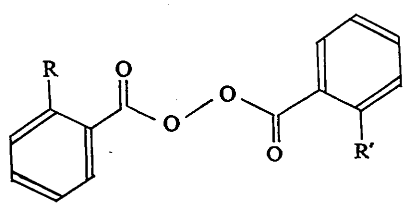
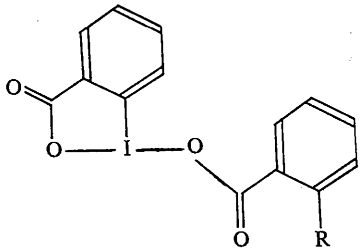
† Manuscript in preparation.

‡ Kinetic studies of the decomposition of (I*a*) in various *solvents* have been reported by Leffler, Faulkner & Petropoulos (1958) who also first observed that (II*a*) is formed during the decomposition of solid peroxide.



a $R=R'=I$
b $R=R'=Br$
c $R=R'=Cl$
d $R=I, R'=Br$
e $R=I, R'=Cl$
f $R=I, R'=F$
g $R=I, R'=H$

(I)



a $R=I$
b $R=Br$
c $R=Cl$

(II)

This topotactic* phase transformation is a rare example† of a solid state organic chemical reaction which, although necessitating extensive migrations of polyatomic moieties, does not disrupt the long-range order of the single-crystal matrix. Although the crystals become opaque during the transformation, their external form is unchanged. We have determined the crystal structure of the reactant (I*a*) and product (II*a*) in order to investigate the mechanism of the solid state transformation. A detailed discussion of the crystallographic transformation, atomic migrations, and solid state chemical reaction mechanism will be presented in a separate publication.

We report here the crystal and molecular structure of the reactant peroxide as well as the analogous bis-*o*-bromobenzoyl and bis-*o*-chlorobenzoyl peroxides [(I*a*), (I*b*), and (I*c*), respectively]. The latter two structures were determined in order to study the variations in molecular packing between consecutive members of the halogenated peroxide series. The results of these studies have proved useful in the design of other 2-iododibenzoyl peroxide derivatives which could be expected to undergo analogous transformations. Thus, crystals of 2-iodo-2′-bromodibenzoyl peroxide (I*d*) and 2-iodo-2′-chlorodibenzoyl peroxide (I*e*) are isostructural with both (I*a*) and (I*b*) and, accordingly, undergo similar single-crystal transformations. 2-Iodo-2′-fluorodibenzoyl peroxide (I*f*) and 2-iododibenzoyl peroxide (I*g*) also undergo single-crystal transformations although they are not isostructural with any of the other peroxides. These additional examples of single-crystal transformations are presently under investigation.

Experimental

The symmetrical peroxides (I*a*–I*c*) were obtained from the reaction of the corresponding *o*-halobenzoyl chlorides with sodium peroxide according to the procedure of Leffler *et al.* (1958). The hitherto unreported unsymmetrical peroxides (I*d*) and (I*e*) were obtained from the reactions of *o*-iodobenzoyl chloride and the sodium salt of the corresponding peracid. Single crystals of the peroxides suitable for diffraction studies were obtained by slow crystallization from dichloromethane–methanol solvent mixtures at -10 to -40 °C. Small specimens, approximately $0{\cdot}05\times0{\cdot}10\times0{\cdot}05$ mm were cut from the long needles in order to minimize absorption errors. Since single crystals of all four peroxides decompose at room temperature in the X-ray beam, a different, freshly crystallized specimen was used to obtain the intensities from each reciprocal lattice layer. In the case of (I*a*), optimum exposure times (approximately 48 hr) for each layer were estimated by noting the period required for the appearance of reflections from the product lattice.

The lattice parameters for the five peroxides (Table 1) were obtained from least-squares analysis of calibrated Weissenberg photographs. Approximate determinations of the crystal densities by flotation methods indicated the presence of two molecules per unit cell. In each analysis, the multifilm, equi-inclination Weissenberg method (Cu $K\alpha$; $\lambda=1{\cdot}542$ Å) was used to record the intensities from the first three reciprocal lattice layers perpendicular to the short lattice repeat. All three layers from all peroxides exhibit discrete high-angle reflections out to $2\theta_{\max}=150°$. Alternative diagonal settings were examined in order to correlate these intensities which were estimated visually, corrected for the Lorentz and polarization factors and placed on the absolute scale using the method of Wilson (1942).

1. 2,2′-Dichlorodibenzoyl peroxide (I*c*)

The colorless acicular orthorhombic crystals are elongated along [001] and have systematically absent spectra for the classes $h00$ ($h=2n+1$) and $0k0$ ($k=2n+1$). The presence of only two molecules per unit cell and these absences are consistent with space group $P2_12_12$ and C_2 molecular symmetry, in the absence of disorder. This

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* Topotaxy denotes a process in which three-dimensional crystallographic correspondence exists between the initial and final stages of a transformed crystal. For a review of topotactic transformations see Glasser, Glasser & Taylor (1962).

† An extensive single-crystal study of the topotactic transformation of anthracene photo-oxide to anthrone and anthraquinone has been reported by Lonsdale, Nave & Stephens (1966). The radiation-initiated polymerization in single crystals of vinyl stearate is another recent example of a topotactic transformation (Morosoff, Morawetz & Post, 1965).

symmetry imposes no restriction on the peroxide C–O–O–C dihedral angle.*

The approximate molecular orientation in [001] projection was estimated from a study of two-dimensional space-filling models which were constructed assuming a peroxide dihedral angle of 90°, phenyl rings parallel to (001) and C_2 molecular symmetry. Rotation of the cardboard models about the molecular twofold axis indicated minimum intermolecular overlaps when the angle φ between the line joining the chlorine atoms in each molecule and the crystallographic *a* axis scanned the range 20–30°. A more refined computer study in which the three-dimensional intermolecular overlaps were examined as a function of both φ and the molecular displacement along **c** (defined by the chlorine fractional *z* coordinate) was completed by Miss Barbara Kaski of this department. The predicted parameters, $\varphi=28°$, $z_{\text{Cl}}=0{\cdot}036$, were in good agreement with the values $\varphi=26°$, $z_{\text{Cl}}=0{\cdot}038$ computed from the final refined atomic coordinates. Least-squares refinements* of all coordinates, isotropic temperature factors for carbon and oxygen atoms, and anisotropic temperature factors for the chlorine atom (45 variables in total) converged to $R=0{\cdot}11$ for the 516 independent reflections (Table 2) when parameters changed by less than about one-third the estimated errors. (Although refinements assuming a completely anisotropic model produced

Table 1. *Crystal data*

Compound	*a*	*b*	*c*	*β*	*V*	ϱ_{calc}	*Z*	$\mu_{\text{Cu}}\ K\alpha$	Space group
(I*a*)	13·05 ± 0·01 Å	4·214 ± 0·003 Å	15·47 ± 0·01 Å	121·1 ± 0·1°	728 Å^3	2·25 g.cm^{-3}	2	350 cm^{-1}	*Pc*
(I*b*)	12·93 ± 0·01	3·998 ± 0·003	15·27 ± 0·01	121·1 ± 0·1	676	1·96	2	89	*Pc*
(I*c*)	13·33 ± 0·01	12·94 ± 0·01	3·841 ± 0·003	—	663	1·58	2	50	$P2_12_12$
(I*d*)	12·96 ± 0·01	4·12 ± 0·01	15·38 ± 0·01	121·2 ± 0·1	700	2·13	2	267	*Pc*
(I*e*)	13·00 ± 0·01	4·077 ± 0·003	15·38 ± 0·01	120·9 ± 0·1	700	1·91	2	202	*Pc*

Table 2. *Observed and calculated structure factors for* (I*c*)

The scale for FO and FC is 5 × the absolute scale.

H	K	FO	FC
L = 0			
2	0	127	119
4	0	50	33
6	0	180	160
8	0	64	54
10	0	114	116
12	0	82	76
14	0	19	0
1	1	151	174
2	1	232	218
3	1	162	149
4	1	215	233
5	1	142	132
6	1	35	21
7	1	155	159
8	1	16	18
9	1	70	59
10	1	100	106
11	1	20	12
12	1	47	48
13	1	40	40
14	1	38	41
15	1	25	26
16	1	21	23
0	2	140	119
1	2	179	207
2	2	176	171
3	2	44	40
4	2	151	142
5	2	70	57
6	2	77	69
7	2	60	55
8	2	132	106
9	2	143	132
10	2	38	41
11	2	106	109
12	2	71	70
13	2	30	24
14	2	19	17
15	2	19	22
16	2	13	5
1	3	283	292
2	3	59	53
3	3	221	220
4	3	108	101
5	3	268	254
6	3	149	121
7	3	54	51
8	3	35	37
9	3	32	29
10	3	19	18
11	3	20	21
12	3	20	13
13	3	26	23
14	3	32	32
15	3	28	33
16	3	13	4
0	4	109	87
1	4	146	120
2	4	133	123
3	4	95	84
4	4	17	3
5	4	166	127
6	4	15	12
7	4	43	44
8	4	92	95
9	4	75	72
10	4	69	56
11	4	41	44
12	4	20	14
13	4	23	26
14	4	18	3
15	4	27	32
16	4	27	28
1	5	145	107
2	5	172	138
3	5	137	149
4	5	145	131
5	5	39	32
6	5	167	143
7	5	90	69
8	5	18	13
9	5	19	8
10	5	20	8
11	5	41	40
12	5	92	92
13	5	19	9
14	5	23	20
15	5	14	8
16	5	27	36
0	6	161	165
1	6	62	62
2	6	192	193
3	6	151	126
4	6	69	57
5	6	16	16
6	6	32	31
7	6	18	5
8	6	66	71
9	6	52	54
10	6	20	17
11	6	20	10
12	6	34	37
13	6	18	6
14	6	16	8
15	6	13	14
1	7	180	159
2	7	20	15
3	7	16	9
4	7	75	69
5	7	158	141
6	7	48	43
7	7	114	112
8	7	20	20
9	7	47	48
10	7	36	35
11	7	46	46
12	7	19	8
13	7	40	42
14	7	20	20
0	8	16	6
1	8	67	59
2	8	67	61
3	8	26	22
4	8	41	33
5	8	73	83
6	8	44	42
7	8	52	51
8	8	53	53
9	8	24	22
10	8	53	54
11	8	22	22
12	8	24	28
13	8	16	16
1	9	18	10
2	9	42	40
3	9	112	118
4	9	66	62
5	9	78	83
6	9	20	26
7	9	81	83
8	9	71	64
9	9	31	24
10	9	19	11
11	9	18	19
12	9	29	27
13	9	21	23
0	10	101	99
1	10	19	6
2	10	29	29
3	10	62	63
4	10	105	112
5	10	41	34
6	10	20	23
7	10	31	23
8	10	61	59
9	10	19	12
10	10	56	52
11	10	17	1
12	10	19	19
1	11	20	12
2	11	20	20
3	11	54	54
4	11	82	84
5	11	41	47
6	11	20	3
7	11	73	4
8	11	19	6
9	11	18	18
10	11	22	23
0	12	62	68
1	12	54	50
2	12	27	30
3	12	31	39
4	12	20	21
5	12	20	2
6	12	19	1
0	14	18	30
1	15	21	24
2	15	10	14
3	15	17	18
L = 1			
1	0	359	362
2	0	196	185
3	0	140	138
4	0	189	185
5	0	41	27
6	0	106	105
7	0	17	4
8	0	97	91
9	0	80	77
10	0	171	174
11	0	44	48
12	0	22	8
13	0	22	14
14	0	20	2
15	0	18	15
16	0	28	32
0	1	151	175
1	1	281	343
2	1	209	210
3	1	251	251
4	1	146	142
5	1	42	47
6	1	141	137
7	1	78	74
8	1	19	15
9	1	27	23
10	1	49	44
11	1	59	58
12	1	45	41
13	1	38	41
14	1	35	49
0	2	14	16
1	2	278	290
2	2	273	252
3	2	68	60
4	2	176	168
5	2	75	63
6	2	95	90
7	2	183	153
8	2	66	62
9	2	82	87
10	2	22	22
11	2	78	72
12	2	22	27
13	2	22	26
0	3	82	72
1	3	32	26
2	3	68	66
3	3	99	104
4	3	126	115
5	3	208	209
6	3	16	11
7	3	82	80
8	3	45	44
9	3	31	40
10	3	58	60
11	3	78	81
12	3	22	23
13	3	49	54
14	3	26	37
0	4	146	128
1	4	129	131
2	4	118	114
3	4	95	90
4	4	15	2
5	4	84	77
6	4	79	71
7	4	57	53
8	4	61	56
9	4	85	86
10	4	58	62
11	4	22	20
12	4	22	27
13	4	32	27
14	4	23	20
0	5	145	127
1	5	111	90
2	5	152	139
3	5	69	70
4	5	147	141
5	5	17	21
6	5	168	152
7	5	52	51
8	5	36	29
9	5	22	9
10	5	22	21
11	5	22	6
12	5	44	55
13	5	20	10
14	5	31	39
0	6	62	53
1	6	82	88
2	6	169	161
3	6	44	43
4	6	30	31
5	6	49	43
6	6	34	32
7	6	31	32
8	6	75	81
9	6	34	31
10	6	45	49
11	6	34	38
12	6	26	31
13	6	24	27
14	6	17	23
0	7	69	53
1	7	84	76
2	7	41	37
3	7	96	95
4	7	86	80
5	7	119	118
6	7	62	62
7	7	37	40
8	7	44	38
9	7	39	39
10	7	45	48
11	7	33	43
12	7	20	14
13	7	18	21
0	8	114	107
1	8	87	75
2	8	88	87
3	8	20	16
4	8	40	29
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6	8	75	83
7	8	77	77
8	8	52	50
9	8	68	69
10	8	22	14
11	8	41	48
12	8	19	14
0	9	20	24
1	9	54	49
2	9	72	69
3	9	111	103
4	9	57	50
5	9	44	32
6	9	59	54
7	9	79	80
8	9	22	15
9	9	22	14
10	9	21	18
11	9	19	14
12	9	17	22
0	10	114	106
1	10	22	10
2	10	50	52
3	10	67	64
4	10	39	43
5	10	22	12
6	10	90	81
7	10	27	28
8	10	22	1
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10	10	45	48
11	10	17	5
0	11	22	3
1	11	45	44
2	11	39	34
3	11	34	28
4	11	59	58
5	11	22	26
6	11	58	58
7	11	21	22
8	11	20	17
9	11	19	14
0	12	22	13
1	12	45	52
2	12	39	38
3	12	22	14
4	12	22	9
5	12	21	13
0	13	32	38
1	13	21	20
2	13	21	22
3	13	42	35
4	13	20	6
5	13	30	25
6	13	19	14
0	14	19	9
1	14	19	17
2	14	19	15
3	14	18	14
L = 2			
1	0	129	145
2	0	44	33
3	0	113	110
4	0	132	123
5	0	29	32
6	0	140	134
7	0	21	30
8	0	89	91
9	0	71	73
10	0	24	38
11	0	24	16
12	0	23	21
13	0	29	37
14	0	19	3
0	1	81	83
1	1	65	67
2	1	138	162
3	1	170	186
4	1	167	174
5	1	45	49
6	1	101	87
7	1	83	75
8	1	136	116
9	1	95	88
10	1	42	38
11	1	42	33
12	1	62	46
13	1	33	42
0	2	36	38
1	2	109	122
2	2	33	37
3	2	236	199
4	2	113	98
5	2	35	29
6	2	45	42
7	2	129	108
8	2	79	73
9	2	63	60
10	2	37	26
11	2	48	50
12	2	40	45
13	2	21	23
0	3	174	172
1	3	127	126
2	3	66	69
3	3	72	68
4	3	45	48
5	3	99	102
6	3	61	61
7	3	57	46
8	3	70	63
9	3	24	24
10	3	32	37
11	3	42	40
12	3	23	17
13	3	83	72
0	4	123	119
1	4	82	83
2	4	98	99
3	4	121	102
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5	4	52	52
6	4	48	40
7	4	51	53
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9	4	84	82
10	4	32	44
11	4	24	30
12	4	39	36
13	4	20	16
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1	5	46	47
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2	7	49	51
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4	7	45	47
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7	7	24	19
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7	10	52	52
8	10	21	23
0	11	32	48
1	11	36	42
2	11	36	44
3	11	24	21
4	11	35	41
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6	11	22	20
7	11	36	46
8	11	27	33
0	12	23	10
0	13	21	12

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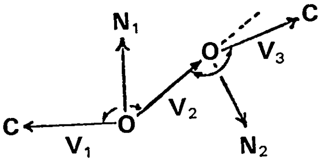
* We define the peroxide dihedral angle as the angle less than 180° between the axial vectors $\bar{N}_1=\bar{V}_2\times\bar{V}_1$ and $\bar{N}_2=\bar{V}_2\times\bar{V}_3$. (Note that a planar *trans* arrangement defines a dihedral angle of 180, not 0°.)



* In all least-squares refinements described in this paper, weights were assigned according to $\omega=1/\sigma^2(F_o^2)=(3{\cdot}5/F_o)^4$ for $F_o>3{\cdot}5F_{\min}$ and $\omega=1/F_{\min}^4$ for $F_o\le 3{\cdot}5F_{\min}$. The quantity minimized was $\sum\omega(F_o^2-F_c^2)^2$. Form factors were taken from *International Tables for X-ray Crystallography* (1962).

slightly lower R values [90 variables], we attribute no physical significance to the resulting thermal parameters, since they had uniformly large estimated errors and in some cases were not positive definite.) In each determination described in this paper, the unobserved reflections were included in every computation at one half the local minimum observable value. Final coordinates and thermal parameters in accord with a molecular C_2 axis at $x=\frac{1}{2}$, $y=0$ are given in Tables 3 and 4.

Table 3. *Fractional atomic coordinates for* (I*c*)

	x	y	z
Cl(1)	0·1944 (2)	0·1533 (2)	0·038 (10)
C(2)	0·2911 (6)	0·2262 (6)	0·197 (30)
C(3)	0·2776 (6)	0·3311 (7)	0·247 (40)
C(4)	0·3543 (8)	0·3919 (7)	0·378 (40)
C(5)	0·4484 (7)	0·3515 (7)	0·430 (40)
C(6)	0·4670 (6)	0·2439 (8)	0·378 (40)
C(7)	0·3860 (6)	0·1837 (6)	0·254 (40)
C(8)	0·4036 (6)	0·0694 (6)	0·236 (40)
O(9)	0·3536 (5)	0·0044 (5)	0·355 (30)
O(10)	0·4886 (4)	0·0546 (4)	0·025 (30)

Discussion of structure

Individual bond distances and angles are shown in Fig. 1. Errors are estimated to be 0·02 Å and 1·5° from internal comparisons of similar bond types and angles. The maximum deviation from the least-squares plane through the six benzene carbon atoms (plane P_1, Table 5) is 0·02 Å while the chlorine and carboxyl carbon atoms lie on opposite sides of this plane at distances of 0·03 and 0·16 Å respectively. The dihedral angle between the two phenyl planes in each molecule is 142°. The carboxyl group is rotated about the C–C single bond relative to the aromatic ring through a relatively large angle (52°) in contrast to dibenzoyl peroxide itself (3°42′, 9°30′) (hereafter DBP) (Sax & McMullan, 1967) and 4,4′-dichlorodibenzoyl peroxide (both are ~0°) (hereafter DCBP) (Caticha-Ellis & Abrahams, 1968) which have no bulky *ortho* substituent.

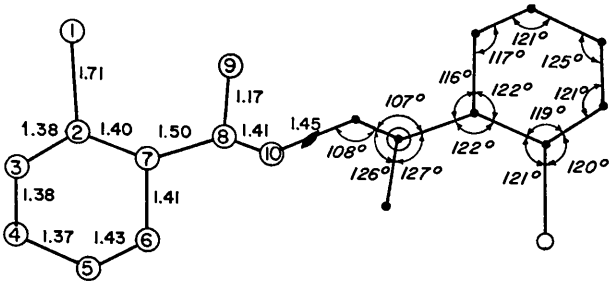


Fig. 1. Bond distances and valence angles for (I*c*).

Table 4. *Thermal parameters*

(E.s.d.'s × 10^4 are given in parentheses)

(*a*) Anisotropic thermal parameters for the halogen atoms*

Structure		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I*c*	Cl(1)	0·0046 (1)	0·0081 (1)	0·022 (20)	−0·0003 (3)	−0·0026 (3)	−0·0013 (4)
I*b*	Br(1)	0·0120 (2)	0·058 (30)	0·0069 (3)	0·0033 (5)	0·0023 (2)	0·0018 (6)
I*b*	Br(2)	0·0104 (2)	0·508 (40)	0·0066 (2)	0·0005 (4)	0·0018 (4)	0·0021 (7)

(*b*) Isotropic thermal parameters for the light atoms†

	B(I*b*)	B(I*c*)
C(2)	3·3 (0·9)	2·7 (0·2)
C(3)	3·4 (0·7)	3·9 (0·2)
C(4)	4·7 (1·0)	5·3 (0·2)
C(5)	3·2 (0·7)	3·3 (0·2)
C(6)	4·9 (1·0)	4·4 (0·2)
C(7)	2·2 (0·7)	4·2 (0·2)
C(8)	2·5 (0·7)	3·0 (0·2)
O(9)	4·6 (0·4)	4·1 (0·1)
O(10)	4·8 (0·5)	3·3 (0·1)
C(12)	3·3 (0·8)	–
C(13)	2·3 (0·6)	–
C(14)	2·2 (0·6)	–
C(15)	3·6 (0·8)	–
C(16)	1·7 (0·5)	–
C(17)	4·2 (1·0)	–
C(18)	4·7 (1·0)	–
O(19)	8·2 (0·6)	–
O(20)	4·8 (0·5)	–

* Of the form $\exp(-\sum\sum h_ih_j\beta_{ij})$.

† Of the form $\exp(-B\sin^2\theta/\lambda^2)$.

Table 5. *Least-squares planes*†

Plane P_1 (I*c*)

$-0{\cdot}264x-0{\cdot}197y+0{\cdot}944z=-0{\cdot}90$

	Deviation		Deviation
Cl(1)	−0·03 Å	C(5)‡	−0·01 Å
C(2)‡	0·01	C(6)‡	0·00
C(3)‡	−0·02	C(7)‡	0·00
C(4)‡	0·02	C(8)	0·16

Plane P_2 (I*c*)

$0{\cdot}569x+0{\cdot}033y+0{\cdot}822z=3{\cdot}81$

C(7)‡	0·00	O(9)‡	−0·01
C(8)‡	0·02	O(10)‡	−0·01

Plane P_3 (I*b*)

$0{\cdot}286x+0{\cdot}911y+0{\cdot}298z=2{\cdot}15$

C(12)‡	0·02	C(15)‡	−0·05
C(13)‡	−0·05	C(16)‡	0·01
C(14)‡	0·07	C(17)‡	0·00

Table 5 (*cont.*)

Plane P_4 (I*b*)

$0{\cdot}251x+0{\cdot}891y+0{\cdot}378z=3{\cdot}43$

C(2)‡	0·04	C(5)‡	−0·08
C(3)‡	−0·12	C(6)‡	0·01
C(4)‡	0·14	C(7)‡	0·01

† Planes are defined in terms of the orthonormal axes *x*,*y*,*z*, which are directed along the crystallographic axes *a*, *b* and *c** respectively.

‡ These atoms were used to calculate the plane.

The oxygen–oxygen distance of 1·45 ± 0·02 Å in (I*c*) also has been observed in the bromoperoxide (I*b*) through the independent structure analysis described below (1·48 ± 0·02 Å in DCBP and 1·46 ± 0·015 Å in DBP). The peroxide dihedral angle of 106 ± 3° differs from the virtually orthogonal value (91 ± 2°) in DBP

Table 6. *Observed and calculated structure factors for* (I*b*)

The scale for FO and FC is 10 × the absolute scale.

H	L	FO	FC
K = 0			
0	2	727	729
0	4	923	886
0	6	334	314
0	8	648	621
0	10	73	69
0	12	314	290
0	14	83	46
0	16	86	89
1	2	87	70
-1	2	585	630
1	4	782	807
-1	4	1307	1229
-1	6	748	679
1	6	749	699
1	8	351	317
-1	8	666	594
1	10	244	239
-1	10	370	357
1	12	157	128
-1	12	208	210
1	14	76	44
-1	14	174	168
1	16	82	114
-1	16	133	130
2	0	119	96
2	2	902	969
-2	2	1002	1013
-2	4	146	109
2	4	578	521
2	6	615	589
-2	6	829	757
-2	8	153	153
2	8	324	318
2	10	312	301
-2	10	591	639
-2	12	77	66
2	12	174	187
2	14	135	167
-2	14	307	290
-2	16	63	54
-2	18	51	66
3	0	135	99
3	2	792	753
-3	2	1201	1332
3	4	63	69
-3	4	200	184
3	6	582	559
-3	6	626	631
3	8	75	57
-3	8	224	235
3	10	273	268
-3	10	436	443
3	12	70	51
-3	12	76	54
3	14	82	106
-3	14	181	197
-3	16	67	73
-3	18	61	123
4	0	927	948
4	2	799	732
-4	2	1071	1032
4	4	625	642
-4	4	847	756
4	6	370	363
-4	6	850	830
4	8	207	203
-4	8	629	653
4	10	154	171
-4	10	375	325
4	12	109	128
-4	12	227	250
-4	14	78	75
-4	16	163	157
-4	18	47	76
5	0	748	782
5	2	67	112
-5	2	186	175
5	4	453	420
-5	4	941	960
5	6	87	36
-5	6	453	368
5	8	238	262
-5	8	391	426
5	10	71	14
-5	10	153	133
5	12	103	126
-5	12	741	698
5	14	210	149
-5	16	192	194
-5	18	79	49
6	0	229	222
6	2	130	114
-6	2	624	572
-6	4	409	389
6	4	566	620
6	6	208	232
-6	6	963	793
6	8	203	224
-6	8	616	612
6	10	63	21
-6	10	308	265
-6	12	226	218
-6	14	182	143
-6	16	196	182
-6	18	97	58
7	0	442	446
7	2	424	398
-7	2	611	531
7	4	117	116
-7	4	396	378
7	6	91	80
-7	6	459	437
7	8	163	164
-7	8	190	193
7	10	116	112
-7	10	475	464
-7	12	175	146
-7	14	241	224
-7	16	73	22
-7	18	100	104
8	0	71	77
8	2	348	367
-8	2	450	487
-8	4	74	58
8	4	104	121
8	6	227	222
-8	6	658	631
8	8	60	44
-8	8	88	52
-8	10	285	307
-8	12	116	109
-8	14	240	201
-8	16	73	66
-8	18	115	93
9	0	264	257
9	2	238	257
-9	2	288	285
9	4	134	118
-9	4	278	287
9	6	152	172
-9	6	361	383
-9	8	245	193
-9	10	340	295
-9	12	270	288
10	0	241	269
-10	2	89	65
10	2	89	69
10	4	121	126
-10	4	341	350
10	6	61	40
-10	6	86	131
-10	8	343	385
-10	10	77	59
-10	12	273	255
-10	14	77	75
-10	16	141	134
-10	18	110	58
11	0	178	183
11	2	82	31
-11	2	91	45
11	4	76	76
-11	4	208	196
-11	6	180	187
-11	8	465	480
-11	10	78	33
-11	12	119	126
-11	14	152	152
-11	16	67	80
12	0	75	26
12	2	89	94
-12	2	176	222
-12	4	208	203
-12	6	91	59
-12	8	78	64
-12	10	78	130
-12	12	102	106
-12	14	127	130
-12	16	63	68
13	0	58	87
-13	2	119	142
-13	4	85	69
-13	6	202	193
-13	8	76	69
-13	10	175	167
-13	12	73	20
-13	14	67	107
-13	16	57	6
-14	2	43	68
-14	4	74	54
-14	6	79	90
-14	8	70	107
-14	10	140	130
-14	12	66	82
K = 1			
0	0	85	59
0	1	485	523
0	2	914	1000
0	3	286	314
0	4	292	295
0	5	508	477
0	6	754	700
0	7	181	155
0	8	75	74
0	9	187	178
0	10	399	373
0	11	90	111
0	12	90	57
0	13	87	72
0	14	158	170
1	0	802	871
-1	1	78	104
1	1	1024	1116
1	2	317	391
-1	2	846	945
1	3	140	110
-1	3	402	428
1	4	310	359
-1	4	477	495
-1	5	89	50
1	5	418	352
-1	6	583	605
1	6	614	543
-1	7	149	175
1	7	293	251
1	8	210	199
-1	8	329	358
-1	9	78	87
1	9	225	226
1	10	311	291
-1	10	336	325
1	11	91	96
-1	11	177	163
1	12	89	44
-1	12	91	107
-1	13	89	50
1	13	143	141
-1	14	84	114
1	14	125	134
2	0	1063	1205
-2	1	153	166
2	1	568	661
-2	2	420	430
2	2	432	456
2	3	257	223
-2	3	704	741
2	4	627	696
-2	4	704	776
2	5	199	193
-2	5	230	219
-2	6	129	136
2	6	287	295
2	7	156	158
-2	7	380	369
2	8	336	310
-2	8	555	590
-2	9	75	111
2	9	203	137
-2	10	81	91
2	10	120	131
2	11	89	89
-2	11	150	165
2	12	128	139
-2	12	274	270
2	13	75	52
-2	13	90	57
-2	14	87	44
-2	15	121	62
3	0	745	771
3	1	49	80
-3	1	513	607
-3	2	95	130
3	2	143	178
-3	3	197	209
3	3	384	378
3	4	697	641
-3	4	737	765
3	5	218	203
-3	5	540	443
3	6	155	158
-3	6	195	203
3	7	253	244
-3	7	375	355
3	8	352	316
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3	9	90	45
-3	9	339	312
3	10	90	51
-3	10	183	186
-3	11	86	40
3	11	113	116
3	12	134	157
-3	12	311	289
3	13	66	35
-3	13	276	236
-3	14	89	129
-3	15	144	51
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4	1	57	85
4	2	392	474
-4	2	643	708
-4	3	195	199
4	3	268	225
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4	4	507	474
4	5	78	86
-4	5	214	225
4	6	291	305
-4	6	533	502
4	7	88	125
-4	7	108	89
-4	8	236	254
4	8	275	237
-4	9	223	212
4	10	86	99
-4	10	479	487
4	11	79	89
-4	11	84	41
4	12	117	113
-4	12	268	252
-4	13	275	248
-4	14	136	131
-4	15	86	47
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5	1	239	235
-5	1	245	278
5	2	440	401
-5	2	742	828
-5	3	255	239
5	3	298	277
5	4	159	146
-5	4	56	34
5	5	84	111
-5	5	201	188
5	6	267	261
-5	6	742	719
5	7	181	200
-5	7	451	404
5	8	90	91
-5	8	182	189
5	9	86	54
-5	9	225	235
5	10	137	138
-5	10	384	406
5	11	68	50
-5	11	84	61
-5	12	88	71
-5	13	90	99
-5	14	208	196
-5	15	87	62
6	0	209	184
-6	1	349	330
6	1	385	356
6	2	488	472
-6	2	512	530
6	3	81	8
-6	3	330	340
6	4	226	221
-6	4	286	286
6	5	89	68
-6	5	384	357
6	6	157	213
-6	6	602	565
6	7	90	31
-6	7	118	141
6	8	86	35
-6	8	287	270
6	9	79	96
-6	9	131	119
6	10	118	140
-6	10	279	294
-6	11	295	280
-6	12	233	231
-6	13	90	78
-6	14	137	145
-6	15	88	103
7	0	354	292
7	1	80	126
-7	1	170	189
-7	2	217	236
7	2	293	323
7	3	87	105
-7	3	243	236
7	4	313	277
-7	4	482	395
-7	5	183	168
7	5	276	255
7	6	89	95
-7	6	282	263
7	7	129	143
-7	7	290	296
7	8	78	103
-7	8	301	296
-7	9	78	73
-7	10	82	122
-7	11	171	170
-7	12	355	372
-7	13	90	41
-7	14	90	108
-7	15	152	121
8	0	386	346
8	1	99	97
-8	1	215	234
-8	2	79	57
8	2	89	37
-8	3	77	67
8	3	90	78
8	4	239	213
-8	4	425	410
8	5	88	103
-8	5	264	231
8	6	83	60
-8	6	201	173
8	7	75	5
-8	7	117	115
-8	8	420	405
-8	9	188	176
-8	10	84	99
-8	11	87	113
-8	12	237	241
-8	13	91	155
-8	14	90	19
-8	15	87	82
9	0	311	235
9	1	90	24
-9	1	175	152
9	2	103	131
-9	2	226	204
-9	3	84	48
9	3	89	84
9	4	149	107
-9	4	332	279
9	5	80	60
-9	5	189	158
9	6	72	16
-9	6	286	277
-9	7	165	153
-9	8	336	344
-9	9	226	218
-9	10	231	199
-9	11	89	68
-9	12	181	171
10	0	91	74
10	1	90	50
-10	1	90	102
10	2	201	157
-10	2	238	224
-10	3	89	73
10	3	94	72
10	4	76	21
-10	4	88	58
-10	5	231	218
-10	6	304	318
-10	7	87	64
-10	8	133	143
-10	9	177	160
-10	10	90	140
-10	11	90	67
-10	12	91	27
-10	13	90	80
-10	14	175	184
11	0	87	73
11	1	83	105
-11	1	89	35
11	2	156	140
-11	2	239	219
-11	3	137	165
-11	4	91	25
-11	5	90	64
-11	6	90	144
-11	7	90	77
-11	8	157	132
-11	9	90	73
-11	10	209	206
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-11	12	90	93
12	0	77	92
-12	1	82	61
-12	2	85	86
-12	3	87	55
-12	4	154	134
-12	5	90	119
-12	6	90	68
-12	7	238	226
-12	8	207	192
-12	9	90	41
-12	10	[illegible]	122
-12	11	88	89
-12	12	87	106
13	0	62	69
-13	1	69	56
-13	2	75	14
-13	4	164	153
-13	7	86	41
-13	8	172	180
-13	9	86	70
-13	10	85	15
-13	11	83	49
-13	12	81	117
K = 2			
0	0	294	314
0	1	308	415
0	2	86	122
0	3	512	536
0	4	303	297
0	5	382	320
0	6	45	64
0	7	304	288
0	8	286	244
0	9	263	221
0	10	58	52
0	11	154	127
0	12	64	83
0	13	78	83
0	14	44	66
0	15	66	85
1	0	335	450
1	1	350	386
-1	1	487	628
1	2	261	232
-1	2	279	312
1	3	808	818
-1	3	32	40
-1	4	204	212
1	4	433	465
1	5	88	111
-1	5	636	568
1	6	83	78
-1	6	183	178
-1	7	109	138
1	7	357	350
-1	8	180	145
1	8	274	244
-1	9	426	366
1	9	58	62
-1	10	133	115
1	10	59	17
-1	11	59	22
1	11	231	222
-1	12	66	45
1	12	[illegible]	136
1	13	47	20
-1	13	217	206
-1	14	128	129
-1	15	40	23
2	0	338	391
2	1	215	210
-2	1	359	438
2	2	303	327
-2	2	243	286
-2	3	235	240
2	3	347	334
-2	4	66	68
2	4	174	157
2	5	221	200
-2	5	618	550
2	6	240	193
-2	6	448	424
-2	7	139	142
2	7	392	319
-2	8	50	48
2	8	152	128
2	9	117	123
-2	9	329	282
2	10	115	110
-2	10	302	282
-2	11	154	121
2	11	166	181
2	12	49	60
-2	12	117	102
2	13	40	51
-2	13	259	218
-2	14	51	33
-2	15	44	37
3	0	404	419
3	1	703	678
-3	1	220	235
3	2	140	124
-3	2	515	573
3	3	270	242
-3	3	576	576
3	4	110	126
-3	4	34	35
-3	5	231	227
3	5	363	319
3	6	387	332
-3	6	388	387
3	7	266	245
-3	7	488	455
-3	8	85	75
3	8	59	32
3	9	153	165
-3	9	226	219
3	10	110	104
-3	10	226	191
-3	11	310	241
3	11	50	89
-3	12	205	163
3	12	42	15
3	13	53	62
-3	13	57	104
-3	14	107	96
-3	15	48	62
4	0	148	151
-4	1	[illegible]	140
4	1	529	491
-4	2	192	192
4	2	366	348
-4	3	601	615
4	3	49	12
-4	4	263	263
4	4	278	274
-4	5	105	95
4	5	256	238
-4	6	112	109
4	6	57	44
-4	7	493	496
4	7	59	44
4	8	88	13
-4	8	171	191
4	9	194	170
-4	9	52	66
4	10	117	115
-4	10	147	135
-4	11	231	199
4	11	44	32
-4	12	102	111
-4	13	58	64
-4	14	55	58
-4	15	132	188
5	0	274	271
-5	1	262	229
5	1	445	390
-5	2	72	94
5	2	115	113
-5	3	336	332
5	3	374	360
5	4	259	229
-5	4	354	323
-5	5	261	267
5	5	268	255
5	6	101	126
-5	6	44	29
5	7	176	167
-5	7	335	311
5	8	111	116
-5	8	266	222
5	9	154	135
-5	9	324	325
-5	10	84	121
5	10	44	54
-5	11	231	198
-5	12	77	113
-5	13	203	178
-5	14	56	47
-5	15	51	111
6	0	306	251
6	1	90	102
-6	1	451	420
-6	2	46	72
6	2	54	62
-6	3	105	94
6	3	263	200
6	4	134	154
-6	4	321	284
6	5	135	126
-6	5	381	352
-6	6	47	77
6	6	58	31
6	7	192	175
-6	7	49	81
6	8	101	89
-6	8	239	209
-6	9	379	343
6	9	44	14
-6	10	170	168
-6	11	202	177
-6	12	237	200
-6	13	203	208
-6	14	56	76
-6	15	52	48
7	0	54	97
7	1	196	178
-7	1	372	358
7	2	175	171
-7	2	206	208
-7	3	153	184
7	3	204	196
7	4	89	72
-7	4	115	128
-7	5	409	393
7	5	57	51
7	6	124	112
-7	6	271	252
7	7	172	109
-7	7	241	205
7	8	64	77
-7	8	53	90
-7	9	312	279
-7	10	199	178
-7	11	101	92
-7	12	89	88
-7	13	100	105
-7	14	56	63
-7	15	52	39
-7	16	123	5
8	0	58	44
8	1	178	159
-8	1	197	200
8	2	178	171
-8	2	194	204
8	3	176	153
-8	3	220	225
-8	4	82	80
8	4	56	40
8	5	139	110
-8	5	250	250
-8	6	332	301
8	6	47	51
-8	7	254	219
8	7	40	26
-8	8	128	106
-8	9	229	220
-8	10	58	57
-8	11	204	201
-8	12	155	142
-8	13	67	91
-8	14	146	141
-8	16	106	33
9	0	59	31
9	1	154	173
-9	1	59	31
-9	2	177	184
9	2	57	118
-9	3	307	263
9	3	54	42
9	4	50	59
-9	4	57	49
9	5	137	159
-9	5	57	21
9	6	37	21
-9	6	57	10
-9	7	200	199
-9	8	231	225
-9	9	58	60
-9	10	117	118
-9	11	205	183
-9	12	58	75
10	0	86	74
10	1	144	142
-10	1	58	116
-10	2	58	38
10	2	51	45
-10	3	205	185
10	3	47	47
-10	4	135	129
10	4	41	27
10	5	66	82
-10	5	[illegible]	97
-10	6	135	105
-10	7	178	[illegible]
-10	8	117	132
-10	9	205	203
-10	10	58	34
-10	11	233	215
-10	12	131	129
-10	13	55	56
-10	14	52	28
11	0	51	117
11	1	48	43
-11	1	93	106
11	2	43	26
-11	2	56	33
11	3	36	56
-11	3	57	22
-11	4	100	90
-11	5	233	224
-11	6	58	57
-11	7	77	103
-11	8	58	98
-11	9	100	118
-11	10	57	33
-11	11	56	46
12	0	42	58
-12	1	62	89
12	1	37	12
-12	2	50	54
-12	3	52	15
-12	4	81	105
-12	5	166	161
-12	6	73	110
-12	7	55	53
-12	8	96	80
-12	9	110	120
-12	10	54	84
-13	1	38	61
-13	3	44	54
-13	4	46	45
-13	5	48	48
-13	6	49	21
-13	7	50	64
-13	8	50	16
-13	9	50	46
-14	7	63	124

Table 7. *Observed and calculated structure factors for* (I*a*)

The scale for FO and FC is 10 × the absolute scale.

H	L	FO	FC
K = 0			
0	-2	547	644
0	-4	1294	1513
0	-6	371	371
0	-8	1000	973
0	-10	98	158
0	-12	691	519
0	-14	98	75
0	-16	118	165
-1	0	862	938
-1	2	1111	1046
-1	-2	253	306
-1	4	1631	1704
-1	-4	985	1305
-1	6	1043	1091
-1	-6	987	823
-1	8	1067	924
-1	-8	880	742
1	-10	696	588
-1	-10	286	307
1	-12	332	330
-1	-12	418	329
1	-14	255	263
-1	-14	91	25
1	-16	155	155
-1	-16	170	185
-1	16	155	155
-2	0	181	208
-2	-2	1513	1526
-2	2	1966	1662
-2	-4	876	858
-2	4	69	83
-2	6	2080	1311
-2	-6	1071	947
-2	-8	534	565
-2	8	192	182
-2	10	1140	1045
-2	-10	457	419
-2	12	103	23
-2	-12	322	322
-2	-14	204	213
-2	14	408	496
-2	16	87	22
-2	18	72	138
-3	0	178	156
-3	-2	1269	1406
-3	2	2097	1995
-3	-4	73	69
-3	4	432	368
-3	6	1097	1136
-3	-6	920	931
-3	8	435	430
-3	-8	100	67
-3	10	667	743
-3	-10	462	476
-3	12	102	148
-3	-12	96	72
-3	-14	170	147
-3	14	373	375
-3	16	146	145
-3	18	106	179
-4	0	1295	1234
-4	2	1579	1450
-4	-2	1025	1136
-4	4	1639	1165
-4	-4	856	872
-4	6	1423	1165
-4	-6	651	650
-4	8	1127	1086
-4	-8	339	346
-4	10	508	547
-4	-10	364	331
-4	12	457	504
-4	-12	242	179
-4	14	106	59
-4	16	340	265
-4	18	68	66
-5	0	1138	1235
-5	-2	172	226
-5	2	201	200
-5	4	1850	1456
-5	-4	857	778
-5	6	451	375
-5	-6	100	184
-5	8	766	832
-5	-8	404	437
-5	10	88	105
-5	-10	98	129
-5	12	992	977
-5	-12	182	149
-5	-14	271	88
-5	14	106	92
-5	16	369	326
-5	18	74	65
-6	0	726	698
-6	-2	192	178
-6	2	856	747
-6	-4	853	880
-6	4	936	916
-6	6	1218	1045
-6	-6	105	174
-6	8	1196	984
-6	-8	317	336
-6	10	583	538
-6	-10	87	64
-6	12	404	448
-6	-12	50	124
-6	-14	199	9
-6	14	333	315
-6	16	313	268
-6	18	217	159
-7	0	812	776
-7	-2	631	704
-7	2	949	805
-7	-4	229	249
-7	4	648	616
-7	6	780	785
-7	-6	167	167
-7	-8	241	255
-7	8	382	374
-7	10	861	795
-7	-10	170	163
-7	12	253	266
-7	14	374	416
-7	16	100	31
-7	18	232	215
-8	0	95	43
-8	-2	472	597
-8	2	878	855
-8	-4	106	62
-8	4	85	102
-8	6	1141	1030
-8	-6	318	401
-8	8	89	126
-8	-8	83	33
-8	10	551	563
-8	12	204	213
-8	14	370	374
-8	16	99	125
-8	18	112	153
-8	20	23	93
-9	0	364	393
-9	-2	413	444
-9	2	606	544
-9	-4	103	138
-9	4	568	463
-9	6	671	586
-9	-6	257	239
-9	8	515	431
-9	-8	64	61
-9	10	606	497
-9	12	455	466
-9	14	369	359
-9	16	173	207
-9	18	88	141
-9	20	20	123
-10	0	378	407
-10	-2	104	145
-10	2	230	235
-10	-4	237	190
-10	4	669	629
-10	6	99	95
-10	-6	74	48
-10	8	727	716
-10	10	103	98
-10	12	514	454
-10	14	105	91
-10	16	268	272
-10	18	76	53
-10	20	33	69
-11	0	330	296
-11	-2	96	71
-11	2	106	58
-11	-4	178	182
-11	4	442	391
-11	6	184	166
11	-6	106	166
-11	8	781	656
-11	10	105	108
-11	12	333	294
-11	14	203	204
-11	16	182	169
-11	18	159	138
-11	20	42	125
-12	0	213	156
-12	-2	129	113
-12	2	363	311
-12	4	372	339
-12	6	106	106
-12	8	106	131
-12	10	332	265
-12	12	231	215
-12	14	246	238
-12	16	86	94
-12	18	81	121
13	0	90	120
-13	2	261	279
-13	4	99	22
-13	6	498	364
-13	8	103	81
-13	10	406	303
-13	12	99	33
-13	14	182	191
-13	16	79	44
-13	18	68	163
-14	0	56	85
-14	2	214	136
-14	4	87	79
-14	6	261	184
-14	8	106	136
-14	10	375	265
-14	12	113	130
-14	14	206	158
-14	16	68	111
-16	2	62	16
-16	4	45	125
-16	6	76	97
-16	8	88	88
-16	10	64	58
-16	12	134	110
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0	3	812	841
0	4	365	291
0	5	829	781
0	6	1068	944
0	7	638	547
0	8	76	154
0	9	355	313
0	10	661	500
0	11	395	340
0	12	93	177
0	13	90	95
0	14	272	211
0	15	177	154
1	0	1072	1022
1	-1	142	210
1	1	1690	1812
1	-2	1056	1219
1	2	518	568
1	-3	1140	1080
1	3	232	228
1	-4	677	679
1	4	462	468
1	-5	52	61
1	5	784	772
1	6	758	695
1	7	535	454
1	-7	649	642
1	8	301	237
1	-8	624	552
1	9	490	463
1	-9	79	62
1	10	516	426
1	-10	484	412
1	11	263	222
1	-11	512	450
1	12	92	63
1	-12	303	241
1	13	281	243
1	-13	92	34
1	14	217	175
1	-14	164	171
1	-15	194	195
2	0	1646	1341
2	-1	127	168
2	1	1230	1212
2	-2	397	418
2	2	617	627
2	-3	1166	1288
2	3	359	337
2	-4	1008	1045
2	4	1017	906
2	-5	502	508
2	5	653	640
2	6	474	450
2	-6	214	201
2	7	258	216
2	-7	826	742
2	8	555	469
2	-8	911	841
2	9	511	421
2	-9	329	318
2	10	302	228
2	-10	155	126
2	11	92	132
2	-11	379	371
2	12	250	212
2	-12	522	415
2	13	80	131
2	-13	93	63
2	14	166	119
2	-14	90	36
2	-15	84	126
3	0	1025	1051
3	-1	961	1009
3	1	374	402
3	-2	42	89
3	2	55	177
3	-3	492	497
3	3	788	762
3	-4	1214	977
3	4	993	905
3	-5	878	929
3	5	487	499
3	6	193	131
3	-6	281	290
3	7	552	477
3	-7	538	524
3	8	584	454
3	-8	677	624
3	9	332	238
3	-9	735	705
3	10	93	43
3	-10	303	242
3	11	219	166
3	-11	86	102
3	12	267	209
3	-12	516	399
3	13	173	133
3	-13	528	438
3	-14	226	153
3	-15	87	59
4	0	611	619
4	-1	762	793
4	1	57	77
4	-2	841	925
4	2	707	648
4	-3	245	267
4	3	620	646
4	-4	768	748
4	4	671	588
4	-5	706	753
4	5	79	81
4	6	365	329
4	-6	651	707
4	7	385	387
4	-7	179	163
4	8	457	352
4	-8	370	400
4	9	174	96
4	-9	485	542
4	10	220	135
4	-10	600	651
4	11	235	163
4	-11	85	98
4	12	205	143
4	-12	255	249
4	-13	458	468
4	-14	262	254
4	-15	89	21
5	0	116	129
5	-1	669	734
5	1	442	408
5	-2	1115	1049
5	2	695	614
5	-3	514	550
5	3	590	596
5	-4	57	51
5	4	197	208
5	-5	537	596
5	5	210	192
5	6	464	411
5	-6	915	978
5	7	458	361
5	-7	741	776
5	8	93	128
5	-8	113	193
5	9	90	94
5	-9	490	513
5	10	83	190
5	-10	601	648
5	11	239	150
5	-11	181	271
5	12	125	68
5	-12	89	89
5	-13	92	47
5	-14	263	292
5	-15	221	201
5	-16	94	58
6	0	262	222
6	-1	576	496
6	1	729	694
6	-2	734	721
6	2	772	684
6	-3	720	679
6	3	203	160
6	-4	360	351
6	4	284	210
6	-5	419	466
6	5	295	285
6	6	400	341
6	-6	748	739
6	7	93	147
6	-7	451	489
6	8	89	44
6	-8	413	384
6	9	204	192
6	-9	163	161
6	-10	403	407
6	10	207	182
6	-11	560	548
6	-12	336	361
6	-13	92	97
6	-14	228	242
6	-15	257	234
6	-16	85	134
7	0	443	438
7	-1	244	268
7	1	463	448
7	-2	359	372
7	2	422	411
7	-3	610	655
7	3	89	61
7	-4	647	569
7	4	299	299
7	-5	303	279
7	5	525	467
7	6	225	197
7	-6	354	351
7	-7	678	645
7	7	88	95
7	8	153	149
7	-8	435	470
7	-9	196	214
7	-10	205	188
7	-11	376	387
7	-12	447	472
7	-13	93	163
7	-14	174	195
7	-15	257	243
7	-16	210	232
8	0	485	531
8	-1	408	424
8	1	331	323
8	-2	80	83
8	2	91	34
8	-3	255	316
8	3	174	203
8	-4	580	627
8	4	303	286
8	5	171	151
8	-5	438	481
8	6	87	53
8	-6	165	157
8	7	79	55
8	-7	257	283
8	-8	606	601
8	-9	473	474
8	-10	183	152
8	-11	252	267
8	-12	394	391
8	-13	303	315
8	-14	93	40
8	-15	169	138
8	-16	180	169
9	0	453	359
9	-1	383	372
9	1	92	131
9	-2	247	283
9	2	153	152
9	-3	85	118
9	3	261	218
9	-4	417	406
9	4	219	203
9	5	84	32
9	-5	475	488
9	6	76	39
9	-6	360	365
9	7	214	110
9	-7	84	130
9	-8	559	497
9	-9	570	489
9	-10	253	261
9	-11	91	108
9	-12	262	256
9	-13	198	209
9	-14	226	216
9	-15	189	80
9	-16	84	123
10	0	228	148
10	-1	263	253
10	1	92	105
10	-2	344	322
10	2	256	195
10	-3	91	140
10	3	212	198
10	-4	90	137
10	4	80	88
10	5	72	13
10	-5	384	396
10	6	148	107
10	-6	383	428
10	7	42	136
10	-7	89	36
10	-8	90	164
10	-9	296	301
10	-10	263	277
10	-11	93	189
10	-12	93	24
10	-13	131	211
10	-14	222	246
10	-15	163	134
10	-16	81	6
11	0	90	77
11	-1	92	148
11	1	184	169
11	-2	303	307
11	2	201	174
11	-3	228	312
11	3	75	106
11	-4	93	31
11	4	65	9
11	5	112	82
11	-5	93	163
11	-6	262	255
11	-7	227	221
11	-8	149	134
11	-9	93	57
11	-10	303	309
11	-11	228	266
11	-12	92	151
11	-13	91	136
11	-14	216	208
12	-7	399	410
12	-8	227	253
12	-9	92	49
12	-10	196	198
12	-11	224	233
12	-12	191	138
12	-13	186	76
13	-9	218	220
K = 2			
0	-1	886	855
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0	-3	1044	935
0	-4	57	97
0	-5	760	691
0	-6	72	84
0	-7	518	487
0	-8	85	151
0	-9	519	535
0	-10	95	46
0	-11	179	217
0	-12	93	80
0	-13	184	220
0	-14	76	46
0	-15	61	99
1	0	148	163
1	-1	1237	1218
-1	-1	662	604
-1	-2	152	163
1	-2	68	121
1	-3	44	22
-1	-3	1745	1370
-1	-4	177	216
1	-4	53	117
1	-5	1361	1086
-1	-5	345	333
1	-6	68	150
-1	-6	77	146
1	-7	75	169
-1	-7	813	727
1	-8	82	64
-1	-8	89	119
1	-9	690	719
-1	-9	193	224
1	-10	93	54
-1	-10	96	46
1	-11	96	99
-1	-12	89	80
1	-12	95	44
1	-13	296	344
-1	-13	80	136
-1	-14	67	40
1	-14	82	69
1	-15	149	86
2	0	212	276
2	-1	1054	1019
-2	-1	319	332
2	-2	77	112
2	-3	488	521
-2	-3	1007	829
2	-4	52	152
-2	-4	69	63
2	-5	1324	1010
-2	-5	248	271
2	-6	216	182
-2	-6	82	81
2	-7	478	449
-2	-7	753	683
2	-8	80	71
-2	-8	93	18
2	-9	646	565
-2	-9	96	121
2	-10	91	124
-2	-10	95	72
2	-11	309	311
-2	-12	83	29
2	-12	96	94
2	-13	304	330
-2	-13	71	25
2	-14	87	78
2	-15	250	121
3	0	229	259
3	-1	609	578
-3	-1	1522	1116
3	-2	278	249
-3	-2	64	101
3	-3	1493	1086
-3	-3	531	555
3	-4	55	81
-3	-4	76	61
3	-5	481	480
-3	-5	539	580
3	-6	187	183
-3	-6	88	151
3	-7	1013	935
-3	-7	399	470
3	-8	78	106
-3	-8	95	97
3	-9	276	318
-3	-9	270	311
3	-10	90	48
-3	-10	92	82
3	-11	618	583
-3	-12	74	21
3	-12	95	112
3	-13	94	97
3	-14	90	57
3	-15	81	210
4	0	62	24
4	-1	84	145
-4	-1	1253	991
-4	-2	177	227
4	-2	58	47
4	-3	1243	1097
-4	-3	78	78
4	-4	59	51
-4	-4	83	116
4	-5	134	143
-4	-5	665	529
4	-6	68	23
-4	-6	93	157
4	-7	1024	913
-4	-7	95	76
4	-8	78	119
-4	-8	95	106
4	-9	84	11
-4	-9	262	326
-4	-10	85	41
4	-10	89	85
4	-11	462	483
-4	-12	61	41
4	-12	96	27
4	-13	95	116
4	-14	92	36
4	-15	84	292
5	0	71	140
5	-1	518	473
-5	-1	923	787
5	-2	66	125
-5	-2	80	79
5	-3	797	738
-5	-3	421	432
5	-4	162	141
-5	-4	89	121
5	-5	661	586
-5	-5	531	557
5	-6	71	87
-5	-6	96	103
5	-7	732	604
-5	-7	203	182
5	-8	80	54
-5	-8	92	48
5	-9	558	604
-5	-9	211	266
5	-10	74	52
5	-11	264	303
5	-12	95	84
5	-13	358	372
5	-14	92	39
5	-15	86	185
6	0	80	136
6	-1	937	813
-6	-1	273	293
6	-2	74	124
-6	-2	87	141
6	-3	238	279
-6	-3	393	433
6	-4	73	93
-6	-4	94	113
6	-5	903	775
-6	-5	203	277
6	-6	76	95
-6	-6	95	38
6	-7	168	171
-6	-7	260	311
6	-8	82	114
-6	-8	65	77
6	-9	763	729
-6	-9	75	108
6	-10	90	48
6	-11	175	205
6	-12	95	133
6	-13	358	418
6	-14	93	19
6	-15	87	41
7	0	87	58
7	-1	823	742
-7	-1	169	192
7	-2	82	107
-7	-2	93	56
7	-3	172	198
-7	-3	410	461
7	-4	80	63
-7	-4	96	73
7	-5	784	798
-7	-5	94	38
7	-6	81	93
-7	-6	90	57
7	-7	272	317
-7	-7	237	255
-7	-8	74	33
7	-8	86	67
7	-9	586	623
7	-10	92	46
7	-11	177	204
7	-12	96	66
7	-13	234	278
7	-14	92	15
7	-15	285	138
8	0	93	6
8	-1	452	416
-8	-1	269	290
8	-2	89	80
-8	-2	96	65
-8	-3	311	345
8	-4	87	57
-8	-4	93	17
8	-5	429	466
-8	-6	81	78
8	-6	87	133
8	-7	437	434
-8	-7	71	135
8	-8	90	95
8	-9	344	380
8	-10	94	61
8	-11	311	376
8	-12	96	100
8	-13	95	163
8	-14	92	54
8	-15	212	270
9	0	96	64
9	-1	95	81
-9	-1	311	332
9	-2	94	71
9	-3	530	535
-9	-3	222	72
-9	-4	85	28
9	-4	92	85
9	-5	92	104
-9	-5	189	212
-9	-6	66	46
9	-6	92	104
9	-7	458	466
9	-8	93	137
9	-9	94	134
9	-10	95	95
9	-11	359	401
9	-12	95	53
9	-13	94	27
9	-14	90	47
9	-15	84	246
10	0	94	131
-10	-1	258	295
-10	-2	87	12
10	-2	96	91
10	-3	359	357
-10	-3	80	79
-10	-4	72	36
10	-4	96	68
10	-5	95	188
-10	-5	60	154
-10	-6	39	67
10	-6	95	94
10	-7	311	391
10	-8	96	78
10	-9	235	290
10	-10	96	18
10	-11	357	389
10	-12	94	48
10	-13	91	159
10	-14	87	44
11	0	86	54
10	-1	95	146
11	-1	191	219
-11	-1	81	143
-11	-2	74	30
11	-2	92	28
11	-3	94	126
11	-4	95	72
11	-5	357	388
11	-6	95	8
11	-7	135	224
11	-8	95	58
11	-9	202	246
11	-10	94	62
11	-11	93	112
11	-12	91	72
11	-13	186	202
11	-14	83	22
12	-1	194	206
-12	-2	53	11
12	-3	87	36
12	-4	89	29
12	-5	257	277
12	-6	92	71
12	-7	92	18
12	-8	92	59
12	-9	224	233
12	-10	90	18
12	-12	85	25
12	-13	174	221
13	-1	62	133
13	-5	81	128
13	-6	83	58
13	-7	84	154
13	-8	84	17
13	-9	84	147
14	-7	175	204

in a sense opposite to that observed in DCBP (81·1 ± 3·4°). [A value of 112° was observed in (I*b*).]

It appears that the dihedral angle for peroxide groups not involved in hydrogen bonding will probably fall within a relatively narrow range of values as suggested by Sax & McMullan (1967). The average of the peroxide dihedral angles in DCBP, DBP, (I*b*) and (I*c*) suggests the range 97 ± 15°. [A value of 94° was predicted for the dicarboxylic peroxide moiety (Sax & McMullan, 1967)].

Most intermolecular contacts less than 3·85 Å occur parallel to the short lattice repeat. Fig. 2, which depicts the molecular packing in [001] projection, includes the intermolecular contacts within this limit which are approximately perpendicular to $\vec{c}$. No unusually close contacts are indicated even after an extension of the observed structure with reasonably placed hydrogen atoms.

2,2′-Dichlorodibenzoyl peroxide is another example in the group of chiral organic peroxy-compounds (Jeffrey, McMullan & Sax, 1964) which crystallize in space groups defined only by proper symmetry elements and thereby, either in small domains within the solid or throughout the entire crystal, exhibit the relatively rare phenomenon of spontaneous resolution.

2. The isostructural peroxides (I*a*), (I*b*), (I*d*), and (I*e*)

The crystal structures of (I*a*) and (I*b*) at room temperature have been examined in detail while the crystal structures of (I*d*) and (I*e*) have been inferred from the isostructural relationship described below. Our qualitative observations on the rates of solid state peroxide decomposition support the solution kinetic studies of Leffler *et al.* (1958) which demonstrate the marked dependence of rate on the mass of the *ortho* substituent. At room temperature, crystals of (I*e*), (I*d*) and (I*a*) decompose at appreciably greater rates than crystals of (I*c*). Intensity data from these isostructural peroxides therefore are subject to considerable systematic errors which have resulted in relatively low-accuracy determinations. The more stable bromoperoxide (I*b*) is the more accurately defined representative of this isostructural group.

In each case, the acicular monoclinic crystals are elongated along [010] and have systematic absences for the $h0l$ spectra when $l=2n+1$. In addition, two classes of pseudo-extinctions were indicated for (I*a*) and (I*d*): (*a*) $0k0$ ($k=2n+1$) and (*b*) $h2l$ ($l=2n$). Of the $0k0$ spectra, only the 040 from (I*a*), the 020 from (I*d*), and the 020 and 010 reflections from (I*b*) were significantly above background level. The last low-intensity reflection has been observed from two different crystal set tings. The class (*b*) pseudoextinctions are particularly pronounced in (I*a*) where only ten even-order spectra* are of significant intensity. In the case of (I*b*), the $h2l$ intensities are more uniformly distributed between the even and odd orders of l.

Three space groups, Pc, $P2/c$, and $P2_1/c$ were considered initially for this group of structures. The last mentioned however, with only two centrosymmetric molecules per cell and a symmetry-fixed peroxide dihedral angle of 180° seemed less probable in view of the previously mentioned tendency toward an approximately orthogonal peroxide dihedral angle.

The three-dimensional Patterson syntheses, which were not consistent with $P2/c$, clearly revealed the essentially centrosymmetric molecular structures. However, attempted least-squares refinements assuming an exact molecular inversion center ($P2_1/c$) converged to the relatively high values $R=0{\cdot}20$ for (I*a*) and $R=0{\cdot}18$ for (I*b*) and resulted in an O–O distance of $\sim 1{\cdot}8$ Å and unacceptably large oxygen temperature factors. Difference Fourier syntheses at this stage suggested an acentric arrangement of oxygen atoms and indicated the correct space group to be Pc. A combination of Fourier and least-squares methods, similar to that described by Katz & Megaw (1967) for the refinement of the pseudosymmetric structure of potassium niobate, reduced the discrepancy index to the present value $R=0{\cdot}11$ for the 803 independent reflections of (I*b*) (Table 6) ($R_{h0l}=0{\cdot}09$). The R indices for (I*a*) computed with: (*a*) all 830 reflections (Table 7) and (*b*) omission of the $h2l$ unobserved reflections are $R_{h0l}=0{\cdot}14$, $R_{h1l}=0{\cdot}12$, $R^a_{h2l}=0{\cdot}20$, $R^b_{h2l}=0{\cdot}16$, $R^a_{\text{overall}}=0{\cdot}14$ and $R^b_{\text{overall}}=0{\cdot}13$. Further difference syntheses revealed four one-electron peaks corresponding to half of the hydrogen atoms; the other four were poorly defined by diffuse areas of positive electron density at the anticipated coordinates. None of the hydrogen atom coordinates was refined, although all eight atoms were introduced at reasonable positions (C–H = 1·08 Å) in order to facilitate the interpretation of intermolecular contacts.

Thermal parameters and fractional atomic coordinates for (I*b*) relative to a glide plane at $y=\frac{1}{4}$ are given in Tables 4 and 8 respectively. The independently determined atomic coordinates for (I*a*) are given in Table

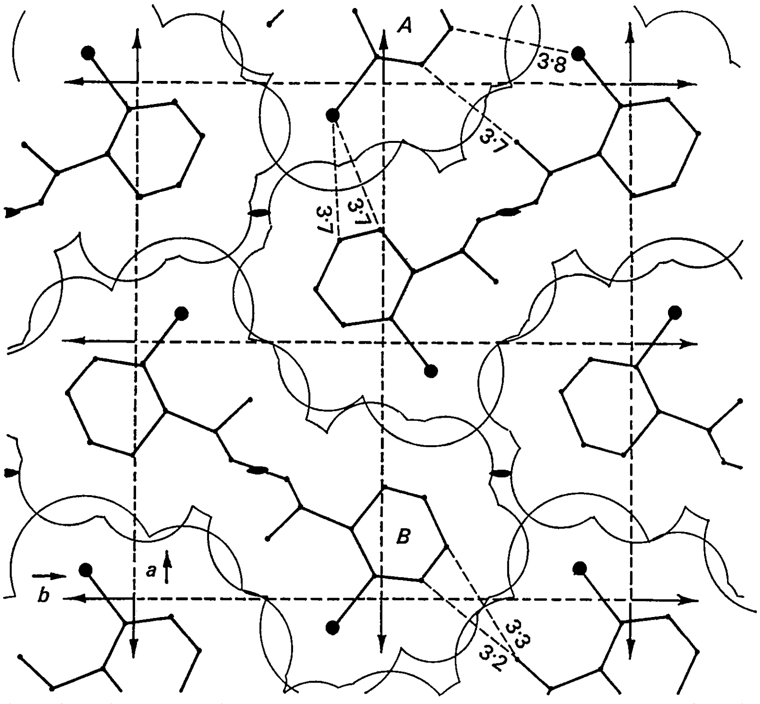

Fig. 2. The molecular packing of (I*c*) in [001] projection. Reasonably placed hydrogen atoms have been introduced as van der Waals spheres.

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* The even order spectra significantly above background are 120, 220, 320, $32\bar{2}$, $22\bar{6}$, $52\bar{4}$, 122, 422, 124 and $32\bar{6}$.

9. The pseudocentric arrangement of iodine atoms in (I*a*) with $y_I = 0{\cdot}379(\sim 3/8)$ provides an adequate explanation for the *h*2*l* spectra to which the otherwise intensity-dominating iodine atoms do not contribute when *l* is even.

Table 8. *Fractional atomic coordinates for* (I*b*)

(E.s.d.'s × 10^3 are given in parentheses)

	x	*y*	*z*
Br(2)	0·093 (1)	0·33 (10)	0·377 (1)
Br(1)	0·903 (1)	−0·33 (10)	0·631 (2)
C(2)	0·801 (3)	−0·17 (10)	0·504 (3)
C(3)	0·836 (3)	−0·18 (10)	0·419 (3)
C(4)	0·776 (4)	0·02 (10)	0·334 (3)
C(5)	0·659 (3)	0·09 (10)	0·303 (2)
C(6)	0·611 (3)	0·10 (10)	0·369 (3)
C(7)	0·682 (3)	−0·04 (10)	0·456 (2)
C(8)	0·638 (3)	−0·06 (10)	0·524 (2)
O(9)	0·676 (2)	0·05 (10)	0·615 (2)
O(10)	0·523 (2)	−0·21 (10)	0·479 (2)
C(12)	0·191 (3)	0·17 (10)	0·518 (3)
C(13)	0·138 (3)	0·18 (10)	0·567 (2)
C(14)	0·205 (2)	0·10 (10)	0·672 (2)
C(15)	0·309 (3)	−0·06 (10)	0·710 (2)
C(16)	0·371 (2)	−0·08 (10)	0·654 (2)
C(17)	0·301 (3)	0·04 (10)	0·537 (3)
C(18)	0·375 (3)	−0·02 (10)	0·486 (2)
O(19)	0·345 (2)	0·16 (10)	0·419 (2)
O(20)	0·462 (2)	−0·20 (10)	0·536 (2)

Table 9. *Fractional atomic coordinates for* (I*a*)

(E.s.d.'s × 10^3 are given in parentheses)

	x	*y*	*z*
I(2)	0·089 (1)	0·37 (10)	0·379 (1)
I(1)	0·903 (1)	−0·37 (10)	0·636 (1)
C(2)	0·803 (5)	−0·16 (30)	0·506 (4)
C(3)	0·816 (5)	−0·15 (30)	0·408 (5)
C(4)	0·760 (7)	0·05 (30)	0·316 (5)
C(5)	0·656 (6)	0·13 (30)	0·297 (5)
C(6)	0·587 (7)	0·09 (40)	0·357 (6)
C(7)	0·676 (5)	−0·04 (30)	0·457 (5)
C(8)	0·633 (8)	−0·08 (40)	0·527 (7)
O(9)	0·672 (4)	0·00 (10)	0·613 (3)
O(10)	0·517 (3)	−0·19 (20)	0·471 (3)
C(12)	0·210 (6)	0·13 (40)	0·533 (5)
C(13)	0·141 (5)	0·16 (30)	0·573 (4)
C(14)	0·216 (6)	0·07 (40)	0·677 (6)
C(15)	0·308 (9)	−0·05 (30)	0·702 (7)
C(16)	0·363 (4)	−0·10 (20)	0·644 (3)
C(17)	0·307 (8)	0·05 (40)	0·540 (7)
C(18)	0·367 (5)	0·00 (20)	0·428 (4)
O(19)	0·358 (5)	0·22 (20)	0·428 (4)
O(20)	0·466 (4)	−0·15 (20)	0·539 (3)

Discussion of structure

The independently determined crystal structures of (I*a*) and (I*b*) are very similar. With the exception of the four oxygen atoms, the molecular structures are three-dimensionally centrosymmetric within experimental error. The molecular asymmetry introduced by the diacyl peroxide group will be considered only in the case of the more precisely determined bromoperoxide (I*b*).

Pair-wise averages of aromatic bond distances and angles related through the molecular pseudocenter range from 1·34 to 1·44 Å and 115 to 123° with mean values of 1·40 Å and 119° respectively. The root-mean-square deviations from least-squares planes through

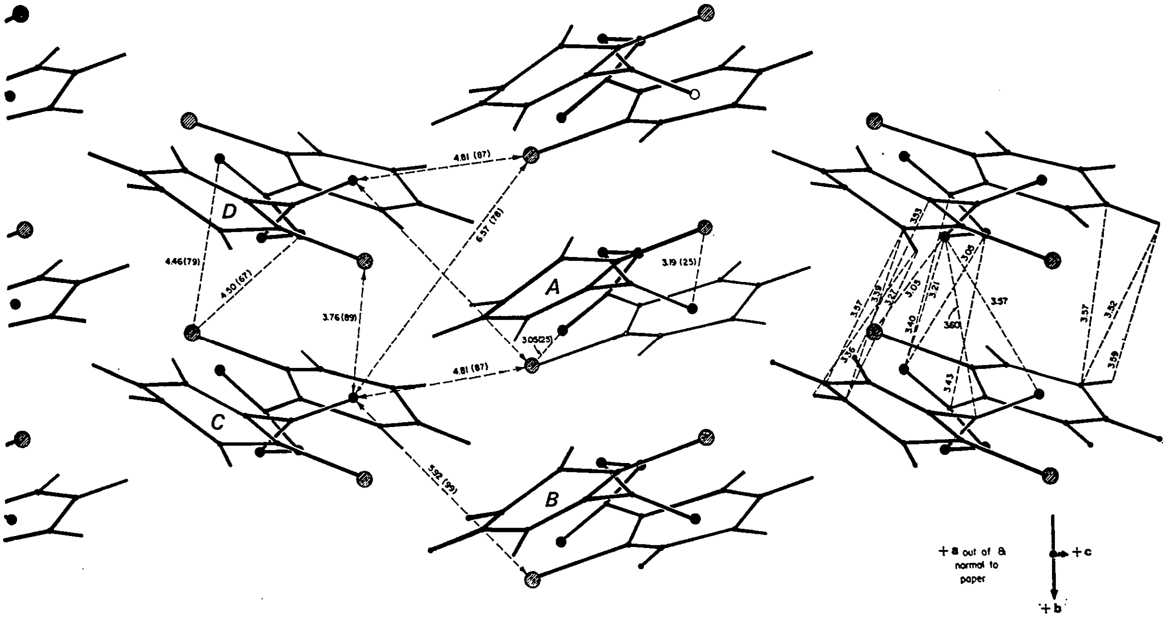

Fig. 3. A perspective drawing of the molecular packing in (I*b*) in projection along [100]. Selected bromine–oxygen distances in (I*b*) are shown completely. The corresponding iodine–oxygen distances in (I*a*) differ only in the last two decimal places which are shown in parentheses. The lettered molecules are related as: (*A*) *xyz*; (*B*) *x*, *y*+1, *z*; (*C*) *x*−1, $\frac{1}{2}-y$, $z-\frac{1}{2}$; (*D*) *x*−1, $-\frac{1}{2}-y$, $z-\frac{1}{2}$.

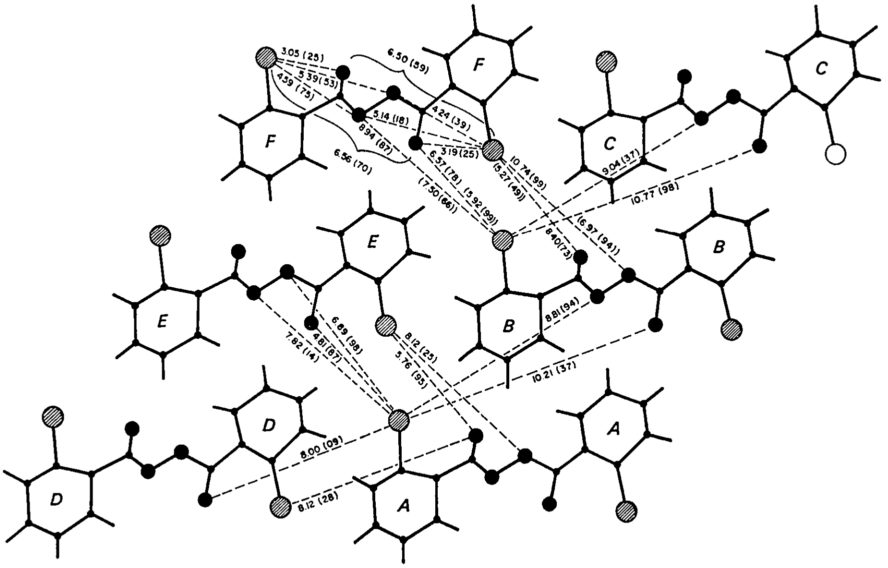

Fig. 4. The molecular packing of the isostructural peroxides in [010] projection. The bromine–oxygen distances in (I*b*) are shown completely. The corresponding iodine–oxygen distances in (I*a*) differ only in the last two decimal places which are shown in parentheses. The lettered molecules are related as: (*A*) *xyz*; (*B*) *x*, $\frac{1}{2}-y$, $z+\frac{1}{2}$; (*C*) *x*, $1+y$, $z+1$; (*D*) $x+1$, *y*, *z*; (*E*) $x+1$, $\frac{1}{2}-y$, $z+\frac{1}{2}$; (*F*) $x+1$, *y*, $z+1$. The entire values which occur in parentheses between molecules *B* and *F* correspond to contacts between a *B* molecule and an *F* type molecule at $x+1$, $1+y$, $z+1$. Intramolecular halogen–oxygen distances are shown in molecule *F*.

the individual benzene rings suggest an upper limit of 0·07 Å for the error in a C–C bond. The O–O distance in (I*b*) is 1·45 Å [1·5 in (I*a*) and 1·45 ± 0·02 Å in (I*c*)] while the average C–Br distance of 1·89 Å is in good agreement with the 1·885 ± 0·014 Å value reported for o-bromobenzoic acid. (Ferguson & Sim, 1962). The peroxide dihedral angle of 112° [111° in (I*a*)] is similar to that found in (I*c*).

The two least-squares planes through the benzene rings (planes P_3 and P_4, Table 5) are parallel with an approximate interplanar distance of 0·8 Å. Although each C–COO group also is planar within experimental error, the dihedral angles between the phenyl and carboxyl planes in each half, 18 and 55° respectively, are significantly different (the analogous dihedral angle in o-bromobenzoic acid is 18°). This unusual unsymmetrical arrangement of carboxyl groups appears to be the consequence of two mutually exclusive factors – the preferred geometry of the peroxide linkage, and molecular close-packing requirements which apparently favor the ubiquitous centrosymmetric $P2_1/c$ arrangement for the bulky halogen atoms and phenyl rings. Thus, *a peroxide dihedral angle different from* 180° *in an otherwise centrosymmetric molecular structure of this type necessarily defines two different orientations of the carboxyl groups relative to their respective phenyl rings.*

Intermolecular packing

The short lattice translation **b** corresponds to a van der Waals contact between two halogen atoms (2 × 2·1 Å). Fig. 3 depicts the molecular packing in projection along [100] and indicates the intermolecular distances less than 3·6 Å which result from the short translation. The average angle between the normals to the approximately parallel phenyl rings and [010] is 26° in both (I*a*) and (I*b*). The molecular packing in the close-packed layers parallel to (010) (Fig. 4) is particularly noteworthy since both the magnitude and direction of the lattice translational vectors **b** are strictly conserved throughout the single-crystal transformations of (I*a*), (I*d*) and (I*e*).

The chemical reaction which propagates the transformations results in the fission of every oxygen–oxygen bond with concomitant formation of two iodine–oxygen bonds. It is clear from the structure of the products [(II*a*), (II*b*) and (II*c*)] that only one of the latter bonds necessarily is formed *intra*molecularly. The unique distances between the iodine and oxygen atoms which could be imagined to interact in bond formation are shown in Figs. 3 and 4 along with the analogous, more precisely determined bromine–oxygen distances. The shortest *inter*molecular halogen–oxygen distance within the (010) layers is 4·8 Å.

The isostructural relationship

The independent analyses of (I*a*) and (I*b*) verify the strong isostructural relationship which was evident from a quantitative comparison of the corresponding *h*0*l* and *hll* spect a ($R_{h0l}^{a,b}=0·16$; $R_{hll}^{a,b}=0·22$). The unsymmetrical peroxides (I*d*) and (I*e*) also are isostructural with (I*a*) and (I*b*) even though (I*c*) is not. Since the *h*0*l* spectra of these four peroxides are very similar, the projected molecular arrangement is that shown in Fig. 4. Although ordered crystal structures with an alternating arrangement of iodine and bromine (chlorine) atoms along the lattice vector **c** are not consistent with the absence of *h*0*l* spectra with *l* odd, disordered structures in which the heavy atoms sites are randomly occupied by iodine and bromine (I*d*) or iodine and chlorline (I*e*) atoms can not be excluded. However, in no case have diffuse spectra or interlayer streaking been observed.

The near equivalence of these spectra is in striking contrast to the greatly different X-ray spectra which the respective peroxide crystals develop simply upon standing! Whereas single crystals of (I*a*), (I*d*) and (I*e*) are transformed to solids which exhibit clearly different single-crystal diffraction spectra, decomposed single crystals of (I*b*) exhibit only the diffuse scattering characteristic of amorphous solids.

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The Crystal Chemistry of the Rare Earth Orthoferrites

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The structural arrangements of the rare earth orthoferrites (from Pr to Lu) have been investigated by refining the respective crystal structures from X-ray diffraction data. It has been found that the distortion of the oxygen iron octahedra is small and almost constant when proceeding from $LuFeO_3$ to $SmFeO_3$. It begins to decrease at $NdFeO_3$, but even for $PrFeO_3$ it is of the same order of magnitude as in $LuFeO_3$. On the contrary, the oxygen polyhedra around the rare earth atoms are very distorted and their distortion varies appreciably across the series. The approximation that the coordination number of the rare earths is eight appears to be still valid. However, the data indicate that this is a good approximation only between $TbFeO_3$ and $NdFeO_3$. In fact, between $DyFeO_3$ and $LuFeO_3$ the seventh and eighth rare earth–oxygen distances increase while the radii of the rare-earths decrease. This indicates that for these compounds the seventh and eighth nearest oxygen atoms are becoming second-nearest neighbors. The ninth oxygen atom is a second-nearest neighbor throughout the series. Its distance from the rare earth decreases while the radii of the rare earths increase. At $PrFeO_3$ this distance begins to drop quite drastically so that at $LaFeO_3$ this oxygen atom cannot be considered to be a second-nearest neighbor. In this compound the difference between the eighth value, 2·805 Å, and the ninth, 3·041 Å, is 0·236 Å which is not large enough to assume that the coordination of the La^{3+} ions is eight. The arrangements of $InCrO_3$ and $InGaO_3$, which crystallize with the orthorhombic perovskite structure under high pressure, are discussed. In addition the possibility of synthesizing In_2O_3 with a perovskite-like arrangement under high pressure is proposed.

Introduction

The rare earth orthoferrites are known to crystallize with the orthorhombic distortion of the perovskite structure, which is a common arrangement for many ABO_3 compounds. For instance, the rare-earth orthochromites, orthovanadites, orthorhodites and orthoaluminates (from Sm to Lu) have been reported to be isostructural with $GdFeO_3$, which is considered the prototype of this series. In the cubic perovskite structure [see Fig. 1(*a*)] the *A* cations are surrounded by 12 equidistant oxygen ions, whereas the *B* cations are surrounded by an oxygen octahedron. In the orthorhombic distortion [see Fig. 1(*b*)] the *A* cations and the oxy-