The Crystal and Molecular Structure of 3-(*p*-Bromophenyl)phthalide

By V. Kalyani and M. Vijayan*

Department of Physics, Indian Institute of Science, Bangalore-12, *India*

The structure of 3-(*p*-bromophenyl)phthalide, $C_{14}H_9O_2Br$, has been solved by the heavy-atom and trial-and-error methods. The compound crystallizes in the orthorhombic space group *Pbca* with eight molecules in an elementary cell of dimensions $a = 6·17$, $b = 26·95$ and $c = 14·48$ Å. The positional and thermal parameters were refined by the least-squares method to an *R* value of 0·066 for 549 observed reflexions. The plane of the phenyl ring is inclined at an angle of 97° 30′ to the plane of the fused-ring system. This conformation of the molecule is substantially different from that in the corresponding *meso* compound. The lactone group in the molecule exhibits the expected structural characteristics. The molecular coordination number in this structure is 10 and the packing coefficient 0·66.

Introduction

3,3′-Diphenyl-bi-3-phthalidyl can exist in two isomeric forms, *viz.* the *meso* and the racemic forms. The isomers are formed in unequal proportions, the more abundant one being the *meso* form (Manohar, Kalyani, Bhat & Kamath, 1966). Detailed X-ray analyses of the bromo and chloro derivatives of the more abundant isomer have already been carried out in this laboratory (Kalyani, Manohar & Mani, 1967; Kalyani & Vijayan, 1969). 3-Phenylphthalide (II) is obtained by replacing one half of the molecule of the unsubstituted isomer (I) by a hydrogen atom. In other words, structurally, 3-phenylphthalide constitutes just one half of *meso*-3,3′-diphenyl-bi-3-phthalidyl. The X-ray structure analysis of the bromo derivative of the former was undertaken in order to study the changes brought about in the molecular geometry as a result of the joining together of the two halves in the *meso* form.

(I)   (II)

Experimental

3-Phenylphthalide was prepared by the reaction of an aqueous alcoholic solution of sodium borohydride

---

* Present address: Chemical Crystallography Laboratory, South Parks Road, Oxford, England.

with *o*-benzoylbenzoic acid. The bromo and the chloro derivatives were prepared in a similar manner, using *o*-(*p*-bromobenzoyl)benzoic acid and *o*-(*p*-chlorobenzoyl)benzoic acid respectively instead of *o*-benzoylbenzoic acid. The crystals of the three compounds were kindly supplied by Dr K. M. Kamath and Professor M. V. Bhat of the Organic Chemistry Department of this Institute. The unsubstituted compound crystallized as transparent tabular plates and the two derivatives grew as thin, cylindrical, transparent needles. The space group and the unit-cell dimensions of the three compounds were determined from oscillation and Weissenberg photographs. The densities of the samples were measured by flotation in aqueous potassium iodide solutions. The crystal data for these compounds are given in Table 1. The closeness of the unit-cell dimensions of the bromo and the chloro derivatives indicated that they were isomorphous.

Intensity data for 3-(*p*-bromophenyl)phthalide were collected using Cu *Kα* radiation from a needle-like specimen of mean radius 0·0053 cm. The reciprocal levels *Hkl* for $H = 0$ through 4 were recorded by the multiple-film equi-inclination Weissenberg method. An interesting feature observed in these photographs was the reduction in the intensities of reflexion spots with increasing Bragg angle. For $\sin^2 \theta > 0·5$ only 22 reflexions were in the observable range in the entire three dimensional data. The diminution of intensity was more pronounced in layers with increasing *h* index. The 4*kl* level contained only 37 observable reflexions although the total number of possible reflexions in that level was 379. The 5*kl* level was blank even after 40 hours of exposure and hence no attempt was made to record data from levels with $h > 4$. Out of a total of 1983 possible independent reflexions recorded in the zero and four higher level photographs, only 549 were in the measurable range, the rest being too weak to be observed. The intensities were measured by visual comparison with time-exposure calibrated strips. They were corrected for the Lorentz–polarization factor and for the variation in spot shape in the upper level Weissenberg photographs (Phillips, 1954) using a program

devised by Nambudiri (Kannan, Vijayan & Nambudiri, 1966). On account of the inappreciable value of μr ($\mu = 50\cdot21$ cm^{-1}, $r = 0\cdot0053$ cm, $\mu r = 0\cdot27$), absorption corrections were not considered necessary.

As the crystals were fine thin needles, it was not possible to cut them along the b or c axis to collect intensity data.

These procedures were repeated for recording, estimating and processing the intensities of the $0kl$ reflexions from the isomorphous chloro derivative by use of a needle-like specimen of mean radius 0·013 cm. The rapid fall-off of intensities with high Bragg angle was observed in this case also, despite the fact that the radius of the crystal was more than twice that used to collect data from the bromo derivative.

Structure analysis

An examination of the tentative wire models of the structure and the distribution of symmetry elements in the unit cell suggested that efficient packing of molecules could be achieved only if the bromine atom, the phenyl ring and the five membered part of the fused ring system lay parallel to the b axis. The very high intensity of the low order reflexion 004 strengthened the above opinion.

As a first attempt at the solution of the structure a Patterson projection was computed with the $0kl$ intensity data. The most striking feature of this map was the concentration of vector density in regions parallel to the b axis around $z = 0$ and $z = \frac{1}{4}$. This feature could be explained on the basis of the anticipated molecular orientation described above. However, the position of the heavy atom could not be identified unambiguously from this synthesis. Hence, a bromine-sharpened Patterson map was computed and the y and z coordinates of the bromine atom were derived from it. The coordinates were further confirmed by a '$(\varDelta F)^2$' synthesis

(Frueh, 1953), constructed with the squares of the differences in the absolute values of the $0kl$ structure factors from the bromo and the chloro derivatives.

For 41 out of 106 observed reflexions in the $0kl$ zone, the contributions from the bromine atom were greater than half of the corresponding F_0 values. An electron density projection was synthesized with these 41 coefficients. A trial model was proposed on the basis of the considerations mentioned earlier, which explained the features of the bromine-phased Fourier synthesis satisfactorily. The first set of structure factor calculations for this model yielded a residual index of 0·510. The y and z coordinates and the individual isotropic temperature factors were refined by iterative difference-Fourier syntheses to $R = 0\cdot302$ for zonal data. It must, however, be mentioned that on account of the systematic absence of reflexions with odd values of k, the zonal data were simultaneously compatible with coordinate y,z and $\frac{1}{4} - y,z$.

A three-dimensional Patterson function was then synthesized. This diagram also consisted of elongated regions of vector density parallel to the a and b axes at $z = 0$, $\frac{1}{4}$ and $\frac{1}{2}$. Another striking feature of this diagram was a pseudo mirror plane at $y = \frac{1}{4}$. An examination of the observed peaks on the basis of the expected bromine–bromine vectors revealed that they were compatible with two alternative positions of the bromine atom at 0·250, 0·083, 0·133 and 0·250, 0·167, 0·133. The persistence of this ambiguity between positions y and $\frac{1}{4} - y$ in three dimensions and the pseudo mirror plane in the Patterson diagram were consequences of the x coordinate of the bromine atom being $\frac{1}{4}$. Also, this value of the x coordinate implied that the bromine-phased three-dimensional Fourier synthesis would have a false mirror symmetry at $x = \frac{1}{4}$ over and above the ambiguity in the y coordinates.

However, a bromine-phased three-dimensional Fourier synthesis was computed using 227 out of 549 ob-

Table 1. *Crystal data for 3-phenylphthalide and its halo derivatives*

		Unsubstituted, $C_{14}H_{10}O_2$	Bromo derivative, $C_{14}H_9O_2Br$	Chloro derivative, $C_{14}H_9O_2Cl$
Formula weight		210·22	289·13	244·67
Unit-cell dimensions	a	6·08 ± 0·02 Å	6·17 ± 0·02 Å	6·06 ± 0·02 Å
	b	7·58	26·95	26·48
	c	23·40	14·48	14·47
	α	—	—	—
	β	92°20′ ± 1°	—	—
	γ	—	—	—
Unit-cell volume U		1077·6 Å^3	2407·5 Å^3	2322·0 Å^3
Space group		$P2_1/c$	$Pbca$	$Pbca$
Number of molecules per unit cell		4	8	8
Calculated density D_c		1·296 g.cm^{-3}	1·595 g.cm^{-3}	1·400 g.cm^{-3}
Measured density D_m		1·277	1·596	1·397
Linear absorption coefficient for Cu $K\alpha$ radiation		7·06 cm^{-1}	50·21 cm^{-1}	28·07 cm^{-1}
Total number of electrons per unit cell		440	1152	1008
Melting point		115°C	134°C	125–6°C

served reflexions. Because of the ambiguity and false symmetry mentioned earlier, it was found that four different models (which may be referred to as A, B, C and D) explained the features of the electron density map more or less satisfactorily. The already known orientation of the molecule in the $0kl$ projection (with an ambiguity in the y coordinates) was helpful in proposing these models. It may be mentioned that among these models, C and D were obtained by substituting $\frac{1}{4} - y$ for y in models A and B respectively.

None of these models could be eliminated on the basis of packing considerations or the disagreements between the observed and calculated structure factors. However, models A and B gave almost the same set of signs whereas models C and D gave another set of signs. Hence, two Fourier syntheses were computed by use of these two sets of signs. The map computed with the signs given by models C and D had peaks of expected heights at geometrically feasible positions. The other map, though explainable on the basis of a molecular model, was much poorer in quality compared to the previous one. Hence, a trial model was proposed on the basis of the former and this model gave an R index of 0·397 for all the observed reflexions. In eight cycles of isotropic structure factor least-squares calculations this index was reduced to 0·156. It may be mentioned that in the course of this refinement the orientation of the phenyl ring with respect to the phthalide ring changed substantially. At this stage anisotropic temperature factors were introduced for the bromine atom only, and in two more cycles of structure factor least-squares calculations the R index was reduced to 0·121. The foregoing calculations were done on the Elliott-803B computer at the Hindustan Aeronautics Limited, Bangalore, using a general block-diagonal s.f.l.s. program devised by Dr G. A. Mair of the Royal Institution, London.

Further refinement of the structure was carried out on the CDC-3600 computer installed at the Tata Institute of Fundamental Research, Bombay, using a full-matrix least-squares program written by Busing, Martion & Levy (1962), modified by W. C. Hamilton, J. A. Ibers & C. K. Johnson and adapted for the CDC-3600 computer by S. Srikanta. In these calculations all the atoms were treated with anisotropic temperature factors and all the reflexions were given unit weights. The anisotropic temperature factors were of the form

$$\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)] .$$

The form factors used were those given by Cromer & Waber (1965). In six anisotropic cycles the discrepancy index was reduced to 0·091.

At this stage, it was found that 125 out of the 397 unobservable reflexions in the $\sin^2 \theta$ range of 0 to 0·5 had F_c's greater than 0·6 of the corresponding minimum observable values. Hence, these reflexions were also included in further least-squares analysis. Their F_o values were assumed to be equal to 0·6 of the corresponding minimum observable values. The refinement

was terminated after four more s.f.l.s. cycles. The final R index for 549 observable reflexions was 0·066. In the final cycle, the average and maximum shifts in positional parameters were 0·61σ and 1·33σ respectively. Comparable shifts to standard deviation ratios were also observed for thermal parameters. However, it may be mentioned that one thermal parameter, viz b_{13} of C(11), tended to increase unduly and hence it had to be fixed arbitrarily at 0·01015 to retain the thermal vibration-ellipsoid of C(11) as real.

Results

The final positional parameters of the atoms are given in Table 2. Components of the temperature factor tensors and the average B values defined as $(B_1 + B_2 + B_3)/3$, where B_1, B_2, B_3 correspond to principal axes of thermal vibration ellipsoids, are listed in Table 3. A list of observed and calculated structure factors is presented in Table 4. The unobservable reflexions used in the least-squares refinement are also included in this list. Fig. 1 shows superimposed sections of the final three-dimensional electron-density map computed with the phases given by the final s.f. cycle.

Table 2. *Final positional coordinates in fractional units*

Standard deviations ($\times 10^5$) are given in parentheses.

|	x	y	z
Br	0·28038 (38)	0·16532 (6)	0·14559 (13)
O(1)	0·93097 (210)	0·44832 (37)	0·12697 (75)
O(2)	0·63774 (184)	0·40464 (34)	0·16059 (66)
C(1)	0·31847 (298)	0·23570 (46)	0·13196 (79)
C(2)	0·15670 (268)	0·26745 (52)	0·16462 (95)
C(3)	0·19656 (246)	0·31805 (51)	0·15945 (84)
C(4)	0·39891 (271)	0·33535 (50)	0·12257 (85)
C(5)	0·56863 (249)	0·30287 (55)	0·09466 (98)
C(6)	0·52208 (256)	0·25187 (60)	0·09683 (92)
C(7)	0·42455 (246)	0·39278 (54)	0·12186 (107)
C(8)	0·44627 (353)	0·41202 (58)	0·02092 (108)
C(9)	0·30003 (271)	0·41277 (50)	−0·05058 (131)
C(10)	0·37384 (307)	0·43901 (55)	−0·12608 (99)
C(11)	0·57906 (349)	0·46339 (48)	−0·13330 (112)
C(12)	0·72262 (319)	0·46121 (54)	−0·05802 (128)
C(13)	0·63573 (352)	0·43790 (58)	0·01585 (116)
C(14)	0·75427 (320)	0·43203 (53)	0·10085 (146)

The bond lengths and bond angles, their standard deviations and the principal axes of thermal vibration ellipsoids were calculated using a function and error program devised by Busing, Martin & Levy (1964), modified by C. K. Johnson and adapted for the CDC-3600 computer by S. Srikanta.

Discussion

The dimensions of the molecule are given in Fig. 2. Fig. 3 shows a perspective view of the molecule as seen normal to the plane of the fused ring system. The corresponding view of the *meso* compound is also shown in the same Figure for comparison.

Table 3. *Anisotropic thermal parameters and the equivalent isotropic temperature factors* $b_{ij} \times 10^5$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	B (Å²)
Br	5785	220	885	−351	−60	18	7·54
O(1)	2891	185	855	42	170	−15	5·65
O(2)	1832	193	705	−273	88	90	4·77
C(1)	5326	124	104	−244	−71	−26	4·20
C(2)	3974	133	492	−28	−57	−160	4·68
C(3)	2148	174	354	10	−324	69	3·76
C(4)	2583	155	373	−423	−220	112	3·85
C(5)	1826	170	624	333	−140	−23	4·32
C(6)	3238	168	406	−100	202	145	4·40
C(7)	682	234	763	−259	−52	48	4·75
C(8)	2019	137	616	289	232	57	4·07
C(9)	2249	131	804	300	250	30	4·66
C(10)	4499	127	388	676	55	−63	4·60
C(11)	4914	116	585	−165	1015	79	5·25
C(12)	5550	173	510	881	−201	−77	5·92
C(13)	2829	166	412	149	224	74	4·20
C(14)	745	160	1156	−248	155	−86	5·16
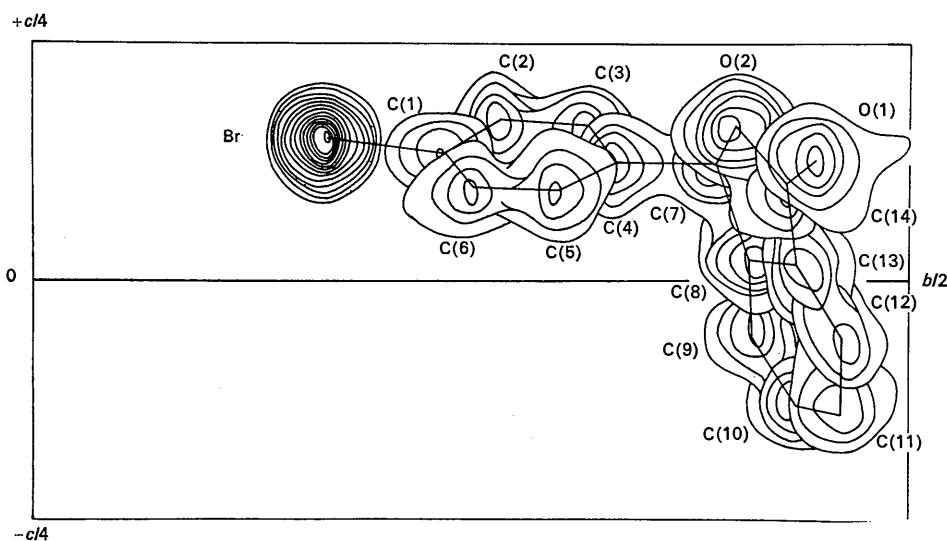
Fig. 1. Final three-dimensional electron-density projection along the a axis. Contours are at intervals $1,2,3,\ldots$e.Å⁻³ for C and O and $1,3,5,\ldots$e.Å⁻³ for Br.
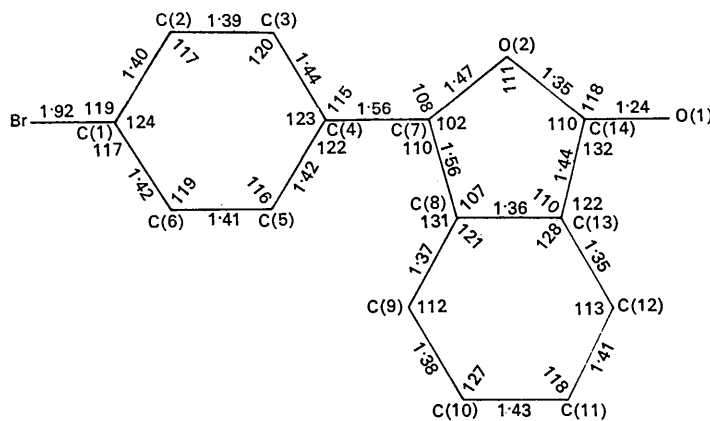
Fig. 2. Bond lengths (Å) and bond angles (°) in 3-(p-bromophenyl)phthalide. The average standard deviation in bond lengths is 0·025 Å and in bond angles 1·4°.

The average C–C distance and the mean C–C–C angle in the phenyl ring are 1·412 Å and 119·9° respectively. The corresponding distance and angle in the six membered part of the phthalide ring are 1·384 Å and 119·6°. The root mean square displacements of the atoms in these two rings from the respective mean planes are 0·019 and 0·025 Å respectively. The bromine atom lies 0·136 Å away from the plane of the phenyl ring and the observed aromatic C–Br distance of 1·921 Å is slightly greater than the normally accepted value of 1·85 Å (*International Tables for X-ray Crystallography*, 1962).

The lactone group in the molecule is constituted by the atoms C(7), C(13), C(14), O(1) and O(2). The group is nearly planar. The root mean square displacement of the atoms from this plane is 0·031 Å. Also, the lactone group exhibits the important expected characteristics. The lengths of the asymmetric C–O bonds are 1·465 and 1·345 Å, the shorter one being adjacent to the carbonyl group (Przybylska & Ahmed, 1958; Gabe, 1962; Karle & Karle, 1966). Again, the exocyclic angles around C(14) are asymmetric and both of them are greater than the internal angle. Of the two exocyclic angles, the one nearer to O(2) is less than the

Table 4. *Observed and calculated structure factors* (× 100)

Calculations are for the contents of the unit cell.

k	l	F_{obs}	F_{calc}
		h = 0	
0	2	5717	5621
0	4	45893	-47411
0	6	16739	16663
0	8	14770	14709
0	10	9847	- 9336
0	14	2144	2768
2	2	12971	12323
2	4	14562	13381
2	5	6247	6661
2	6	4011	- 4414
2	7	2327	- 2040
2	9	5283	- 5074
2	10	1901	2157
2	11	4455	4720
2	12	2254	- 2117
2	13	3776	4600
4	0	9906	-10416
4	1	11956	12499
4	3	2973	2681
4	4	4078	3874
4	5	15600	-14565
4	6	9228	- 8539
4	7	2671	2418
4	8	2847	- 2695
4	9	7972	8170
4	10	3425	3920
6	0	1782	- 1505
6	2	13942	-12871
6	4	12233	-12156
6	6	5770	6649
6	8	2948	2661
6	9	1888	- 1712
6	10	6681	- 6479
6	14	2119	2529
8	0	23856	-23970
8	1	20565	-20863
8	2	3425	- 3611
8	3	8675	- 8993
8	4	8774	8763
8	5	16277	15563
8	6	5552	- 5168
8	7	3651	- 3749
8	8	4539	- 4406
8	9	6072	- 6586
8	10	3070	2914
8	11	3651	3919
8	15	1834	- 2133
10	0	16764	-17091
10	1	5392	6232
10	2	2210	1534
10	4	13062	13210
10	5	9847	- 9136
10	6	3215	- 2905
10	8	7117	- 6407
10	9	3400	3344
10	10	2144	2553
10	11	2596	- 2972
10	12	2321	2493
12	0	21636	20822
12	1	4194	3927
12	2	2662	- 2835
12	3	1694	1298
12	4	10391	-10418
12	5	5283	- 5055
12	6	8977	9253
12	8	3343	3481
12	9	1999	1745
12	10	3853	- 3842
14	0	11991	-11999
14	1	8188	- 8663
14	2	2730	3015
14	3	7267	- 7385
14	4	8800	9224
14	5	5636	6039
14	6	2905	- 2908
14	9	3626	- 3957
14	10	2639	2856
16	0	6597	- 6527
16	1	4998	4855
16	2	1751	1815
16	3	2726	3025
16	4	3157	2423
16	5	3249	- 4032
16	6	4354	- 4973
16	9	3710	3146
16	10	4817	4828
18	0	9320	9105
18	2	3986	- 3990
18	4	8977	- 8971
18	6	5184	5950
18	7	1776	1618
18	8	4781	5111
20	1	4327	- 4545
20	5	6313	6345
20	6	1842	- 2058
20	7	1825	- 1937
22	0	2119	- 2017
22	1	5392	5175
22	3	2119	2929
22	4	3040	3340
22	5	2662	- 3247
24	0	3735	4067
24	1	1554	1609
24	4	2177	- 2081
26	1	2144	- 2288
30	0	2905	3167
		h = 1	
0	2	22487	-23414
0	4	14782	14490
0	6	13174	12225
0	8	12109	-11364
0	10	1943	- 1912
0	12	5211	6357
1	1	12240	11853
1	2	12689	12455
1	3	2019	1917
1	4	4078	3923
1	6	4309	- 4934
1	7	2164	2328
1	10	2343	2062
2	1	13814	-13411
2	2	21976	22615
2	3	16453	16890
2	4	10382	-10197
2	5	2345	2217
2	6	10195	- 9784
2	7	10088	-10025
2	8	8700	8137
2	9	1999	2435
2	10	2130	2471
2	11	2489	2590
2	12	2856	- 2346
2	13	3091	- 2705
3	2	6238	- 5883
3	3	2528	- 1806
3	4	5453	- 5002
3	5	4438	4163
3	6	6431	5881
3	7	2810	2889
3	8	5324	5158
3	9	2603	- 2756
4	1	3740	3588
4	2	3229	3689
4	3	9945	- 9566
4	4	3917	- 3297
4	5	2499	- 2504
4	6	5604	- 5638
4	7	7452	6961
4	11	3593	- 4113
5	1	6943	- 6797
5	2	12878	-12266
5	3	2562	1890
5	4	4622	4207
5	5	4597	- 4651
5	6	8094	7943
5	7	5020	- 4518
5	8	2643	- 2524
5	9	1960	1901
5	10	2527	- 2377
5	12	2404	2230
6	1	8180	- 7281
6	2	26588	-27992
6	3	4960	- 4618
6	4	7019	6587
6	5	3376	2818
6	6	9426	9652
6	7	1812	1865
6	8	9243	- 9190
6	9	2059	- 2177
6	12	3047	3773
7	1	7079	- 6898
7	2	9547	- 8838
7	3	2514	- 2665
7	5	1973	- 1920
7	6	3756	4035
8	1	14732	-14152
8	3	8335	8179
8	4	5807	- 5896
8	5	2043	1722
8	7	6423	- 6377
8	8	4016	4216
8	9	3349	3403
8	11	2003	3841
8	12	2684	- 2628
9	2	3142	- 2555
9	3	5107	- 4412
9	8	1871	- 1698
10	1	5566	5256
10	2	11210	11596
10	3	10171	-10327
10	4	3627	- 4039
10	6	3688	- 3174
10	7	6733	6711
10	8	4181	4819
10	12	3074	- 3119
11	1	5686	5254
11	2	1543	- 1655
11	3	2043	- 1979
12	1	3567	3468
12	2	12359	-12209
12	4	8716	8647
12	6	8309	8997
12	8	6171	- 5758
12	10	2377	- 2274
13	1	1679	- 1959
13	2	7939	8631
13	3	5151	4974
13	5	3589	2593
13	6	4475	- 4740
13	10	2092	1844
14	1	2915	- 2741
14	2	10473	10064
14	3	12170	12028
14	6	2623	- 3163
14	7	6916	- 7473
14	8	2546	2520
15	2	2415	3242
15	4	2714	- 2655
15	8	2951	3125
16	1	5497	6087
16	2	8369	8030
16	3	5592	- 5320
16	5	1600	- 1219
16	6	4607	- 4749
16	7	5318	4856
17	1	2009	- 2234
17	3	1864	1619
17	4	2443	2347
18	2	8204	- 7902
18	3	3384	- 3581
18	4	2830	3424
18	6	2901	3806
18	8	3074	- 3328
20	1	4483	- 3752
20	2	4569	4160
20	3	2925	3197
20	4	2138	- 2272
20	7	3074	- 3033
21	2	2961	2781
22	3	3047	- 3698
23	2	2234	- 2409
24	2	4865	- 4347
24	6	3003	2202
		h = 2	
0	2	4857	4844
0	4	10231	10034
0	6	8904	- 9276
0	10	8276	8492
1	0	4160	4312
1	1	2737	3270
1	4	5265	- 5311
1	5	2692	- 2125
1	7	4139	4253
1	8	5227	5429
1	10	1569	- 1399
1	12	3365	- 3840
2	0	7052	7297
2	1	12876	12859
2	2	7217	- 7263
2	3	10001	9576
2	4	7273	- 7357
2	5	8038	- 7567
2	6	10655	10620
2	8	5419	4788
2	9	6424	6121
2	10	4812	- 4910
3	0	6709	6082
3	1	8803	- 8843
3	3	3181	- 3678
3	4	4904	- 4578
3	5	7078	6844
3	6	2986	- 2409
3	9	1903	- 1937
3	11	2709	2744
4	0	8664	9137
4	1	9871	-10057
4	2	2128	- 2192
4	3	4028	- 4399
4	4	7669	- 7554
4	5	10923	11264
4	6	2480	1810
4	7	2997	2921
4	9	3402	- 3185
4	10	1758	- 1556
5	0	7834	- 7963
5	1	2157	1757
5	3	2184	2007
5	4	2649	2036
5	6	3483	- 4046
5	7	1605	- 1349
6	0	14331	-14631
6	2	2997	3370
6	3	1455	1460
6	4	6840	9342
6	5	2072	1695
6	6	7650	- 7789
6	8	3695	- 3663
6	10	4036	3882
7	0	2148	2807
7	1	2388	- 2061
7	2	5457	- 5565
7	3	2148	- 1720
7	4	5301	- 5667
7	6	3217	3223
7	10	1618	- 1427
8	0	8074	8652
8	1	7641	8561
8	3	2737	2740
8	4	5014	- 5041
8	5	9189	- 8910
8	6	1916	1362
8	9	2784	2869
8	11	3438	- 2857
9	0	2628	2726
9	2	2737	- 2755
9	4	2662	- 2374
9	6	1955	2280
10	0	5234	6216
10	1	7354	- 7097
10	3	2258	- 2349
10	4	1525	- [illegible]
10	5	7290	7122
10	6	2008	2479
10	7	2128	- 2061
10	8	1598	1523
10	9	4624	- 4703
11	0	8840	- 8908
11	1	[illegible]	2749
11	2	1732	2117
11	3	1728	1395
11	5	9658	[illegible]
11	8	3521	- [illegible]
11	10	2550	2412
12	0	12876	-13879
12	2	4821	4730
10	3	1263	[illegible]
12	4	10867	[illegible]
12	5	3494	[illegible]
12	6	6332	- [illegible]
12	8	4000	- 3710
12	9	2106	- [illegible]
12	10	4220	4341
13	0	1894	[illegible]
13	1	6460	[illegible]
13	2	4195	[illegible]
13	3	3483	[illegible]
13	4	2425	2642
13	5	5198	- [illegible]
13	9	2949	2364
14	0	2729	2676
14	1	6332	[illegible]
14	3	4396	[illegible]
14	5	5254	- 4905
14	6	3863	3828
14	9	4212	4471
14	10	2452	- [illegible]
15	0	3121	3654
15	1	2013	- 2289
15	2	2172	1961
15	3	1222	[illegible]
15	5	2935	[illegible]
15	7	[illegible]	- [illegible]
16	0	4772	4539
16	1	5586	- 5651
16	3	3033	- 3320
16	4	3835	- 3059
16	5	6055	5815
16	7	1734	1578
17	0	4801	- 4489
17	4	3935	- 3334
17	8	2452	- 2359
18	0	7309	- 6503
18	3	1811	- 1792
18	4	4036	4007
18	6	3391	- 3235
19	0	[illegible]	3274
19	4	[illegible]	- [illegible]
20	0	5762	[illegible]
20	1	4433	2611
20	4	4184	- 3901
20	5	6482	- 6041
21	0	2405	2806
21	2	2174	- [illegible]
21	4	4220	- 4217
22	0	2433	1628
22	1	3438	- [illegible]
23	0	2452	- 2296
23	1	1993	- 1707
23	3	2024	- 1793
24	0	2433	- 1638
26	1	3318	2058
28	1	2166	- 1503
30	0	2645	- 2439
		h = 3	
0	2	10800	11032
0	4	6102	- 5742
0	6	5921	- 5668
0	8	5193	4771
0	12	2526	- 2759
1	1	2498	- 2117
1	2	3096	- 2612
1	3	2554	- 2376
1	4	3616	3559
1	6	3376	3631
1	8	2246	- 2774
1	10	2441	- 2229
2	1	6405	6282
2	2	6162	- 5898
2	3	6667	- 6324
2	5	3124	- 2515
2	6	3085	2944

Table 4 (cont.)

k	l	F_{obs}	F_{calc}	k	l	F_{obs}	F_{calc}	k	l	F_{obs}	F_{calc}	k	l	F_{obs}	F_{calc}	k	l	F_{obs}	F_{calc}
	7	5481	4949	11	4	1641	-1908	3	1	5516	4814	9	7	1005	1397	3	8	855	-1047
3	11	2537	-147	11	6	2302	-745	3	5	5597	-4817	10	9	1155	-1697	3	8	860	-1956
3	1	6834	-6637	11	2	1275	1978	4	1	4716	4054	11	7	1055	1607	3	9	905	-766
3	2	3916	-3210	12	2	4596	4128	4	3	2801	3031	11	8	1115	-1436	3	11	960	1196
3	3	6083	656	12	3	1125	1813	4	5	3696	3768	12	3	890	1186	3	6	760	1359
3	4	5108	4197	12	4	6079	6005	5	0	4683	4172	12	7	1085	1661	4	9	940	1380
3	6	1540	1168	12	5	1740	1695	5	5	5576	3904	12	9	1190	1436	4	10	945	90
3	7	4718	-4560	12	6	4065	-3689	6	0	5165	5689	13	7	1110	-1960	6	4	685	-1754
3	10	569	243	12	2	3994	3511	6	2	2793	-2702	14	5	1045	1798	8	5	770	-579
4	1	4755	-4172	13	1	107	592	6	4	3350	-3101	14	3	1225	1458	9	5	795	-1145
4	3	9052	9132	13	2	3045	-2864	6	6	6196	5950	14	10	1250	1219	10	9	650	-1912
4	4	5230	5400	13	3	3777	-3576	9	1	3373	319	15	6	1175	-1151	11	9	955	951
4	7	7791	7357	13	4	2946	2301	9	5	3559	-3713	16	9	1150	-1744	13	8	950	-1246
4	8	3616	-2882	13	6	2387	2738	9	6	3639	-2785	17	8	1240	-1692	14	5	900	-1104
4	11	2096	2916	13	7	2472	2779	10	1	2617	2774	17	9	1055	1374	14	8	910	-1590
5	1	5492	5681	14	1	5416	5347	10	5	3374	-3432	18	1	1100	1005	16	4	970	1237
5	2	7049	7437	14	2	3592	-3706	11	0	4136	4058	20	5	1230	-1623	18	5	955	-1713
5	3	6700	-6387	14	3	4978	-4350	12	0	3739	3516	20	6	1245	-1730	19	1	945	-865
5	5	2881	-2687	14	4	4208	4217	12	1	2413	-2637	21	6	1555	-1250				
5	7	3430	2314	14	7	2260	-2994	12	3	2788	-2601	22	1	1330	1777			**h = 4**	
5	9	2415	-2251	15	1	3478	-3927	12	4	2824	-2673	22	4	1250	-1293				
6	1	2957	-2774	15	2	2331	3253	14	1	4586	-4506	24	1	1155	1657	0	4	1360	-1963
6	2	8224	8573	15	3	2368	2061	14	5	3710	3942					2	3	1970	-1762
6	3	2997	2262	15	6	2480	2021	15	0	4667	-4973			**h = 2**		2	6	1600	-1950
6	5	1500	1561	15	7	3562	-3660	15	1	4360	4747					2	7	1690	-1968
6	6	2545	-1831	16	1	3673	-3992	15	3	2896	2947	1	2	415	886	2	8	1770	-2343
6	7	2201	-2643	16	3	4122	4352	15	4	3256	3964	1	9	825	739	2	9	1215	-5560
6	8	4018	3900	16	5	1912	1410	16	1	2849	3102	3	7	770	-1009	3	3	1190	1470
6	9	1893	-2138	16	7	537	-2380					3	8	775	1109	3	9	1895	275
7	1	3692	-4137	17	2	6240	5787			**Unobserved reflections**		4	8	785	1339	3	8	1775	3031
7	2	3226	-3186	17	2	2433	-2363			**used in least**		4	11	950	1041	3	4	1400	-1634
7	3	2489	-2084	17	4	2184	1957			**squares analysis**		5	5	630	-1237	3	3	1790	1439
7	7	2238	2056	17	6	2537	-3058					5	12	940	-804	4	7	1710	-2416
8	1	4018	4582	18	2	2461	3041			**h = 0**		6	9	850	-977	4	5	1370	1930
8	2	6348	-6997	18	3	1996	-156					6	12	840	-1249	5	6	1645	2025
8	3	5556	-5656	18	4	1938	-2202	2	8	680	-1082	8	10	910	-1512	6	7	1745	-1988
8	4	2773	2749	18	8	2489	3136	4	11	860	-726	9	10	910	-1017	7	0	1365	-2154
8	6	3393	3267	19	4	2537	-2065	10	7	730	1415	10	11	940	-1402	7	2	1395	1117
8	7	2296	2054	20	1	556	3019	12	7	770	-1229	11	5	750	-1021	7	4	1535	1467
8	8	2378	2876	20	3	4735	-5446	14	7	915	1723	11	6	790	-1055	7	5	1615	2063
8	9	2424	2722	20	7	2461	3629	14	8	850	-975	12	1	680	-606	7	6	1690	-2300
9	2	2890	-2819	22	1	537	-2373	18	1	780	1152	14	2	755	-1314	8	1	1415	-1689
9	3	4232	4398	22	3	1938	1423	18	3	805	1048	14	7	885	1372	9	2	1450	1754
9	6	2201	1351	24	2	2433	1050	18	5	845	834	14	8	915	-1172	8	3	1610	-1866
9	7	2322	-1701					20	2	845	1250	15	4	825	587	8	4	1570	2178
9	8	2415	-1985			**h = 4**						17	1	835	575	9	8	1830	-1899
9	9	2682	2435							**h = 1**		17	5	890	-1000	10	0	1575	-2067
9	10	2094	-1966	1	0	3094	-2401					17	6	910	-998	10	4	1655	1934
10	1	4410	-4115	1	4	2274	2777	1	9	1045	1551	18	1	800	-1133	11	6	1790	1017
10	2	4512	-4812	1	3	4635	-4122	3	11	1195	-1335	18	2	870	1704	11	7	1830	-1958
10	3	5995	6172	1	5	3427	4127	4	8	985	-1521	18	5	910	-1348	13	0	1885	-1875
10	5	2144	2338	1	1	5981	6727	4	9	1065	-1154	19	2	890	-1539	13	1	1690	2089
10	6	1513	1625	1	9	4141	-3641	4	10	1135	1816	22	3	940	-1417	13	3	1735	2034
10	7	4065	-4605	2	0	3804	-3661	6	10	1155	-1540					14	0	1730	-2309
10	8	2433	-2171	2	1	4716	5302	7	7	960	-1054			**h = 3**		14	3	1770	-2172
10	10	1967	-2172	2	4	2385	2399	7	10	1170	-1671					17	1	1830	-1660
11	2	3319	3128	2	5	4967	4415	8	10	1180	-1679	1	7	795	1442				
11	3	2042	2184	3	0	4018	4196	9	5	880	-1336	2	4	625	787				

---

other by 14·1°. This also is a feature encountered in many γ-lactones (Fridrichsons & Mathieson, 1962; Jeffrey, Rosenstein & Vlasse, 1967; Kim, Jeffrey, Rosenstein & Corfield, 1967). The C–O distance in the carbonyl group is normal.

The bond lengths and bond angles in the structure are comparable to those in the corresponding *meso* compound (Kalyani, Manohar & Mani, 1967). The most important and significant difference between the molecular geometries of the two compounds pertains to the orientation of the phenyl ring with respect to the phthalide ring (see Fig. 3). In the present case, the plane of the phenyl ring is almost normal to that of the phthalide ring, the angle between the two planes
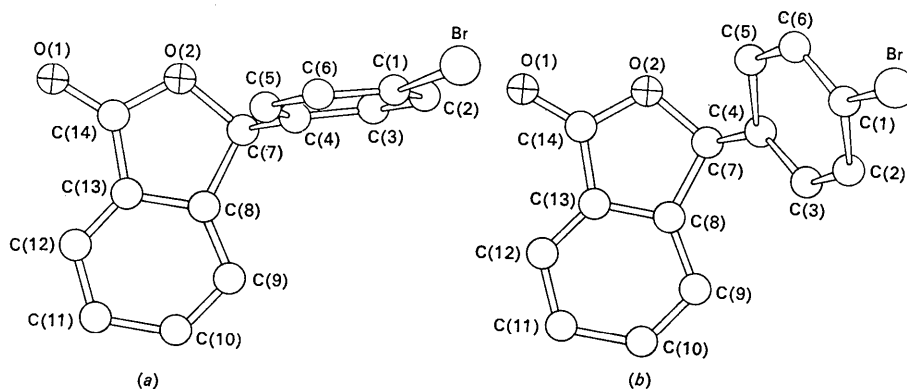

Fig. 3. (a) A perspective view of the molecule as seen normal to the plane of the phthalide ring. (b) The corresponding view in *meso*-3,3′-di-(p-bromophenyl)-bi-3-phthalidyl.

being 97°30'. This angle is less than that found in the *meso* compound by 26°40'. In the former, the phenyl ring is sterically more free to rotate about the C(4)–C(7) single bond and the only major factor that determines its orientation is the steric hindrance with the atoms in the phthalide ring. In the structure, the phenyl carbons C(3) and C(5) are in steric contact with O(2) and C(8) in the phthalide ring [C(3)–O(2)=3·586, C(3)–C(8)=3·579, C(5)–O(2)=2·935, C(5)–C(8)= 3·218 Å]. Any change in this orientation would clearly be sterically unfavourable. However, in the *meso* compound, the observed conformation of the phenyl ring was the one that satisfied the steric requirements arising from the interactions with the fused ring system of the same half of the molecule, on the one hand, and those arising from the interactions with the other half of the molecule on the other, to the greatest possible extent. Also, in the present case, the C(7)–Br vector makes an angle of 40·7° with the normal to the fused ring system. The corresponding angle in the *meso* compound is 33·7°. This again is a direct consequence of the steric interaction between the two halves of the molecule in the latter.

Molecular packing

Fig. 4 shows the arrangement of molecules in the structure viewed along the *a* axis. The intermolecular contacts correspond to normal van der Waal interactions and hence merit no special comment.

A survey of the intermolecular contact distances less than 4 Å showed that each molecule in the structure is in contact with 10 neighbouring molecules and has a molecular coordination number of 10. These neighbours include the molecules in the neighbouring unit cells and also the symmetry related molecules in the same cell. According to Kitaigorodskii (1955), a molecular coordination number of 10 provides adequate close packing, though in most organic structures this number is 12. The positions of the nine hydrogen atoms in the molecule were derived from geometrical considerations assuming a C–H distance of 1·08 Å. However, the inclusion of hydrogen atoms in the calculations did not reveal any new contact.

The space group *Pbca* does not correspond to the closest packed arrangement of asymmetric molecules. However, Kitaigorodskii lists this as a permissible space group for such molecules. The packing coefficient of the structure calculated from Kitaigorodskii's (1955) formula is 0·66 and is less than that (0·69) for the corresponding *meso* compound. This is understandable on the following grounds. The *meso* compound, with a molecular symmetry $\bar{1}$, crystallizes in the space group $P\bar{1}$. This space group corresponds to the closest packed arrangement of centrosymmetric molecules and hence the structure should have high packing efficiency. On the other hand, 3-(*p*-bromophenyl)phthalide crystallizes in a 'permissible' but not 'closest packed' space group and hence the packing coefficient of the structure is correspondingly low.
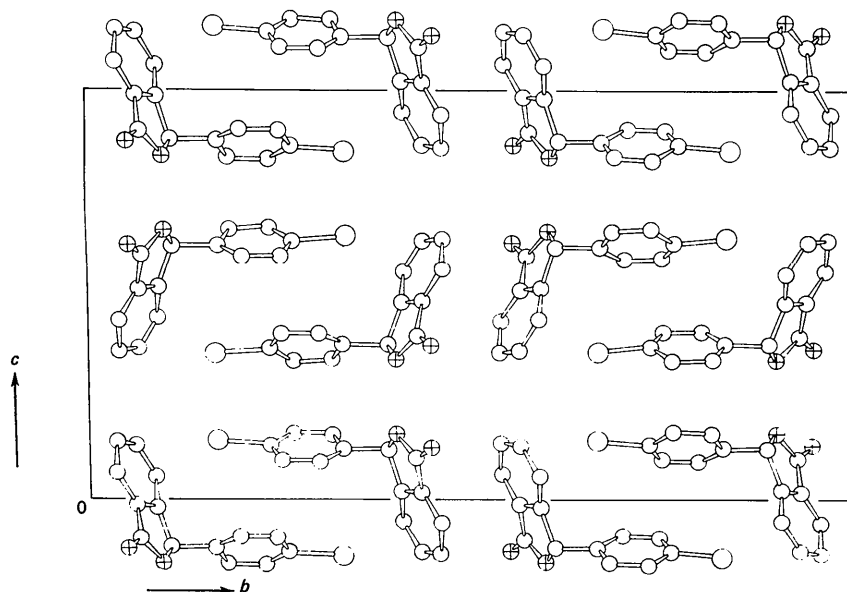
Fig. 4. The structure as seen along the *a* axis. The big open circles represent bromine atoms and the small open and crossed circles represent carbon and oxygen atoms respectively.

Bombay, for allowing them to the use CDC-3600 versions of the *ORFLS* and *ORFFE* programs and for many discussions on computation.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program.* USAEC Report ORNL–TM–305.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE, A Fortran Crystallographic Function and Error Program.* USAEC Report ORNL–TM–306.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.

FRIDRICHSONS, J. & MATHIESON, A. McL. (1962). *Acta Cryst.* **15**, 119.

FRUEH, A. J. (1953). *Acta Cryst.* **6**, 454.

GABE, E. J. (1962). *Acta Cryst.* **15**, 759.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JEFFREY, G. A., ROSENSTEIN, R. D. & VLASSE, M. (1967). *Acta Cryst.* **22**, 725.

KALYANI, V., MANOHAR, H. & MANI, N. V. (1967). *Acta Cryst.* **23**, 272.

KALYANI, V. & VIJAYAN, M. (1969). *Acta Cryst.* **B25**, 252.

KANNAN, K. K., VIJAYAN, M. & NAMBUDIRI, M. M. G. (1966). *A Unified Set of Crystallographic Programs.* Bangalore: Indian Institute of Science. Unpublished.

KARLE, I. & KARLE, J. (1966). *Acta Cryst.* **20**, 555.

KIM, S. H., JEFFREY, G. A., ROSENSTEIN, R. D. & CORFIELD, P. W. R. (1967). *Acta Cryst.* **22**, 733.

KITAIGORODSKII, A. I. (1955). *Organic Chemical Crystallography.* New York: Consultants Bureau.

MANOHAR, H., KALYANI, V., BHAT, M. V. & KAMATH, K. M. (1966). *Tetrahedron Letters*, **44**, 5413.

PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746.

PRZYBYLSKA, M. & AHMED, F. R. (1958). *Acta Cryst.* **11**, 718.

Effect of a Badly Misplaced Atom on the Residual

BY A.J.C. WILSON

School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332, *U.S.A.*
and Department of Physics, University of Birmingham, P. O. Box 363, *Birmingham* 15, *England**

The effect of an entirely misplaced atom in $P1$ (or two equivalent atoms in $P\bar{1}$) is to give residuals of approximately the following values:

	$P1$	$P\bar{1}$
$R = \langle \lvert \lvert F_{\text{wrong}} \rvert - \lvert F_{\text{right}} \rvert \rvert \rangle / \langle \lvert F \rvert \rangle$	$16f/\pi^{5/2} \Sigma^{1/2}$	$8\sqrt{2}f/\pi^{3/2} \Sigma^{1/2}$
$R_1 = \langle \lvert I_{\text{wrong}} - I_{\text{right}} \rvert \rangle / \langle I \rangle$	$8f/\pi^{3/2} \Sigma^{1/2}$	$32\sqrt{2}f/\pi^{5/2} \Sigma^{1/2}$
$R_2 = \langle (I_{\text{wrong}} - I_{\text{right}})^2 \rangle / \langle I^2 \rangle$	$2f^2/\Sigma$	$16f^2/3 \Sigma$

where f is the scattering factor of the misplaced atom and Σ is the sum of the squares of the scattering factors of all the atoms. These values seem too big to be overlooked unless the total number of atoms is very large.

1. Introduction

In connexion with the refinement of one of the structures of the apatite group, the question arose of the size of the residual to be expected if one atom were entirely misplaced, and the following calculations were therefore undertaken. Three disagreement indices or residuals are in common use, R based on the difference of the moduli of the structure factors, R_1 based on the difference of the squares of the moduli, and R_2 based on the square of the difference of the squares. The last, being effectively the variance of $\lvert F \rvert^2$, is considerably simpler to manipulate theoretically than are the other two, and the three residuals are, therefore, treated in reverse order below.

The calculations depend on averaging the difference between quantities calculated with the atom in the wrong place and similar quantities calculated with the atom in the right place. The vector difference between two atomic positions that can be regarded as a complete misplacement is, of course, a function of the Bragg angle, or more accurately of the scattering vector. If the 'right' position of the atom is r_0 and its assumed position is r, the difference in phase between their contributions to the reflexion with scattering vector S is $2\pi S \cdot (r_0 - r)$. For the calculations to proceed smoothly it is necessary for this phase difference to change by at least 2π as S takes on all orientations, so that an atom is entirely misplaced only if its distance from its correct position is larger than the reciprocal of the magnitude of the scattering vector. For the lowest-angle reflexions, therefore, the displacement

---

* Permanent address.