References

ALLPRESS, J. G. (1965). *J. Inorg. Nucl. Chem.* **27**, 1521.

BACHMANN, H. G. & ZEMANN, J. (1961). *Acta Cryst.* **14**, 474.

BYSTRÖM, A. & WESTGREN, A. (1943). *Ark. Kemi Min. Geol.* **16B**, no. 14.

CROMER, D. T., LARSON, A. C. & ROOF, R. B. (1964). *Acta Cryst.* **17**, 272.

CRUICKSHANK, D. W. J. (1960). *Acta Cryst.* **13**, 774.

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.

FRONDEL, C. & BARNES, I. (1958). *Acta Cryst.* **11**, 562.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 206, 212. Birmingham: Kynoch Press.

KAY, M. I. (1961). *Acta Cryst.* **14**, 80.

KLUG, H. P. & ALEXANDER, L. E. (1954). *X-ray Diffraction Procedures*, p. 376. New York: John Wiley.

KOVBA, L. M., POLUNINA, G. P., SIMANOV, YU. P. & IPPOLITOVA, B. A. (1961). *Issledovania v Oblasti Khimii Urana*, p. 15. Moscow Univ. Press.

LECIEJEWICZ, J. (1961). *Acta Cryst.* **14**, 66.

LIPSON, H. & WOOLFSON, M. M. (1952). *Acta Cryst.* **5**, 680.

MILLS, O. S. & ROLLETT, J. S. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 117. Oxford: Pergamon Press.

RIETVELD, H. M. (1966). *Acta Cryst.* **20**, 508.

ROOF, R. B. (1961). *Acta Cryst.* **14**, 934.

ROOF, R. B., CROMER, D. T. & LARSON, A. C. (1964). *Acta Cryst.* **17**, 701.

RÜDORFF, W. & PFITZER, F. (1954). *Z. Naturforsch.* **9b**, 568.

SAMSON, S. & SILLÉN, L. G. (1947). *Ark. Kemi Min. Geol.* **25A**, no. 21.

SLEIGHT, A. W. & WARD, R. (1962). *Inorg. Chem.* **1**, 790.

ZACHARIASEN, W. H. (1954). *Acta Cryst.* **7**, 795.

The Crystal and Molecular Structure of *meso*-3,3'-Di-(*p*-bromophenyl)bi-3-phthalidyl

BY V. KALYANI, H. MANOHAR* AND N. V. MANI†

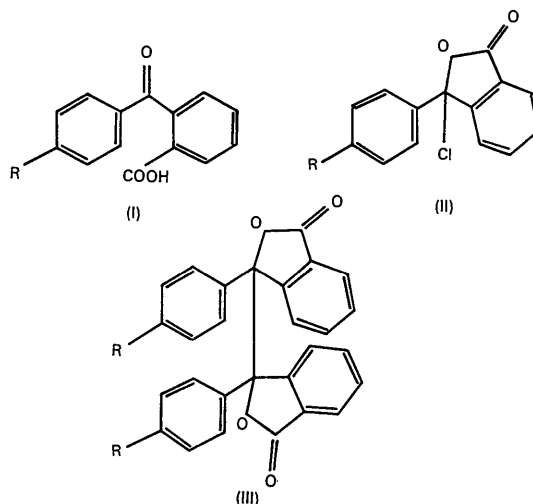*Department of Physics, Indian Institute of Science, Bangalore 12, India*

The crystal structure of the title compound has been determined by the heavy-atom method and Fourier techniques using visually estimated photographic data. It crystallizes in the space group $P\bar{1}$ with cell dimensions $a = 7.98$, $b = 8.08$, $c = 9.66$ Å, $\alpha = 85°23'$, $\beta = 98°24'$ and $\gamma = 104°41'$. The parameters have been refined by three-dimensional least-squares procedures with anisotropic thermal vibrations for all the atoms. The final R index for 932 observed reflexions is 0.096. It has been established that the stereoisomer taken up for investigation is the *meso* form existing in a staggered configuration. Two characteristics of the lactone group, *viz.*, the inequality of the C–O bonds and the planarity of the group are also confirmed in the present study.

Introduction

A variety of reducing agents convert *o*-benzoylbenzoic acids (I) and their acid chlorides (II) to 3,3'-diarylbiphthalidyls (III). Two isomers, *viz.* the racemic (DL) [IV and V, one being the *dextro* (D) and the other the *laevo* (L) form] and the *meso* form (VI) having structure (III) are theoretically possible. However, no attempt has so far been made to define their stereochemistry. This information would be of considerable value in understanding the steric factors involved in their formation, particularly because the two stereoisomers are formed in unequal proportions. In view of this, the more

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(IV)

(V)

(VI)
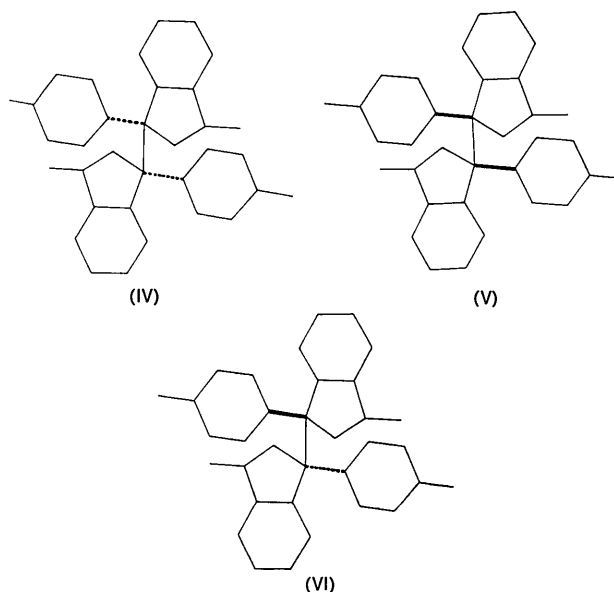
abundant isomer of the bromo derivative (III, 4'R = Br) was taken up for X-ray analysis, the results of which are reported below.

Crystal data

The halo derivatives and the unsubstituted diphenyl-biphthalidyl (III, 4'R = Br, Cl and H) were prepared by the reaction of o-benzoylbenzoyl chlorides (II, 4'R = Br, Cl and H) with a solution of sodium iodide in acetone. The stereoisomers, *meso* and racemic, were separated by fractional crystallization. The more abundant fractions of the three compounds were kindly made available to us by Prof. M.V. Bhat of the Organic Chemistry Department. The crystals were transparent and most of the specimens were tabular or needle-shaped. The crystal data for all the three compounds are summarized in Table 1. The cell dimensions were determined from rotation and zero-level Weissenberg

photographs taken with Cu $K\alpha$ radiation for crystals rotating about the three crystallographic axes. Density determinations were made by flotation in aqueous potassium iodide solution.

The good agreement in axial dimensions and inter-axial angles (Table 1) for the triclinic crystals of bromo and chloro compounds as well as similarity in their crystal habits suggested a high degree of isomorphism between the two compounds. Statistical tests (Wilson, 1949; Howells, Phillips & Rogers, 1950) carried out with corrected intensities in $h0l$ and $0kl$ zones to distinguish between the space groups $P1$ and $P\bar{1}$ were ambiguous. This is probably due to the presence of heavy atoms and also to the inadequate number of observations used to draw the $N(z)$ distribution curves.

The bromine substituted title compound (III, 4'R = Br) was first taken up for X-ray analysis and the heavy atom method was employed for the solution of the structure.

Data collection

The three zero-levels were recorded with Cu $K\alpha$ radiation by the multiple-film Weissenberg technique. Higher level integrated intensities of the general hkL reflexions, for L from 1 through 8, were collected by the equi-inclination method. Of the 2720 possible independent reflexions accessible in the effective copper sphere, 1913 were recorded, out of which 932 were in the measurable range. The intensities were estimated visually by means of a time-exposure calibrated strip prepared with the same specimen and corrected for Lorentz and polarization factors. The physical corrections for absorption for cylindrical specimens of mean radii 0·20, 0·22 and 0·32 mm were applied to the $0kl$, $h0l$ and hkl data respectively (Bond, 1959). Wilson's (1942) procedures were used to derive the absolute scale for all the three zero-level data and comparison of common reflexions yielded the scale factors to be used for the conversion of the higher level data.

Table 1. *Crystal data for diphenylbiphthalidyl and its halo derivatives*

		Unsubstituted, $C_{28}H_{18}O_4$	Bromo derivative, $C_{28}H_{16}O_4Br_2$	Chloro derivative, $C_{28}H_{16}O_4Cl_2$
Formula weight		418·42	576·24	487·32
Cell parameters	a	7·72	7·98	7·89
	b	14·38 ± 0.02 Å	8·08 ± 0.02 Å	8·06 ± 0.02 Å
	c	9·93	9·66	9·65
	α	—	85·4	88·7
	β	98·5 $\pm 0.9°$	98·4 $\pm 0.9°$	99·5 $\pm 0.9°$
	γ	—	104·7	104·4
Unit cell volume,	U	1090·4 Å³	595·2 Å³	585·8 Å³
Space group		$P2_1/c$ (no.14)	$P\bar{1}$ (no.2)	$P\bar{1}$ (no.2)
Density	D_m	1·288 g.cm⁻³	1·619 g.cm⁻³	1·371 g.cm⁻³
	D_c	1·274	1·607	1·381
Molecules per unit cell,	Z	2	1	1
	$F(000)$	436 e	286 e	250 e
Linear absorption coefficient for X-rays ($\lambda = 1.542$ Å)		6·98 cm⁻¹	49·99 cm⁻¹	26·96 cm⁻¹

Structure determination

The analysis of the structure was commenced assuming the centrosymmetric space group. With one formula unit in the full cell, the space group requirement will be fulfilled only if the molecule has a centre of inversion as its symmetry element. The easy convergence of the refinement of the structure in this space group to a final R value of 0·096 confirmed the validity of our assumption and also definitely established that the substance under investigation was indeed a *meso* isomer. Further support is received from the fact that the abundant fraction of the free diphenylbiphthalidyl crystallizes in the uniquely derivable space group $P2_1/c$. With only two formula units of this compound in the monoclinic cell and a fourfold multiplicity of a general position, considerations of space group symmetry again require that the molecule should possess a centre of symmetry. Therefore the assumption of the same molecular symmetry for the abundant isomer of the bromo compound was amply justified.

The bromine positions were easily found by interpretation of (010) and (001) Patterson projections made using 84 and 75 observed reflexions respectively. The Fourier syntheses based on the bromine phases constructed subsequently with 78 and 71 amplitudes from $h0l$ and $hk0$ zones confirmed the heavy atom positions. The first set of structure factor calculations yielded the R values 0·24 and 0·31 for the two respective zones, when 16 and 13 lighter atoms, placed on the peaks, were included in the calculations.

Successive approximations to the electron densities in these projections initiated with phases given by the bromine and refined by continually adding lighter atoms to the trial model gave a reasonably accurate picture of the molecular structure. The trial structure at this stage included all the atoms other than hydrogen atoms and the atomic parameters were refined by an iteration process of residual electron density projections down the b and c axes. The refinement using zonal data was terminated when the R values did not drop below 0·22 and 0·19.

For the foregoing calculations, the atom form factors were derived with the use of an analytical expression involving five constants for each atom (Forsyth & Wells, 1959) and a uniform isotropic B value of 3·5 Å^2 was applied to all atoms. The above mentioned Fourier summations at 6° intervals were done on the Ferranti SIRIUS computer at N.A.L., Bangalore, with programs devised in this laboratory (Kannan, Vijayan & Nambudiri, 1966).

Three-dimensional refinement of the structure by the least-squares method was then attempted with all 932 observed reflexions. The initial stage of the refinement, which involved the diagonal approximation and use of individual isotropic thermal parameters, was done on the CDC-3600 computer system at Bombay with a program prepared by Kannan *et al.* (1966). The atom form factors were now modified by use of a nine-

parameter analytical expression evolved by Cromer & Waber (1965). Three separate sets, each consisting of three cycles of structure-factor least-squares (SFLS) calculations, lowered the overall R value from 0·30 to 0·185. The unusual feature in these calculations was the consistently low values ranging from 1·5 to 2·5 Å^2 of the isotropic B values indicated for all atoms. These were increased at the end of every cycle to values between 3·0 and 4·5 Å^2 and the various zones were individually scaled up before another run was made. The low values of the thermal parameters encountered here may be attributed to appreciable variations in absorption factors from the mean due to the large absorption coefficient of 50 cm^{-1} ($\lambda = 1·542$ Å) and consequently, the final temperature factors reported are probably lower than the true ones. Bond distances and valency angles computed for the first time at this stage revealed considerable distortions in the phenyl ring with C–C lengths varying from 1·2 to 1·6 Å and internal angles from 108 to 130°. Atomic positions of the carbons C(1) to C(6) (Fig. 1) were then adjusted by trial to bring the distances in the phenyl ring to normal values.

The last set of structure factor calculations showed some consistent discrepancies between F_o and F_c values which suggested introduction of anisotropic (ellipsoidal) thermal parameters for some of the atoms. Indeed difference electron density diagrams constructed with $h0l$ and $hk0$ data earlier clearly indicated an anisotropic vibrational pattern for the bromine atom. The final cycles of SFLS refinement were performed on the National Elliott 803-B computer at Hindustan Aeronautics Ltd, Bangalore, with a generalized program devised by Dr G. A. Mair of the Royal Institution, London. This program minimizes the function $\Sigma w|kF_o - F_c|^2$, where w is the weight assigned to the observed structure factors and k is a refinable scale correction. This program uses the block-diagonal approximation with a 3×3 matrix for the positional parameters and a 6×6 or 1×1 matrix for the anisotropic or isotropic thermal parameters of each atom. The scale factor for the F_o's and the overall isotropic B

Table 2. *Fractional atomic coordinates*
e.s.d.'s $\times 10^3$ Å in parenthesis

	x	y	z
Br	0·5373 (2)	0·2429 (2)	0·5666 (2)
O(1)	−0·3576 (11)	0·2592 (11)	−0·0204 (12)
O(2)	−0·1562 (10)	0·1097 (10)	0·0542 (10)
C(1)	0·3739 (18)	0·1847 (17)	0·4046 (16)
C(2)	0·4429 (17)	0·1971 (16)	0·2750 (14)
C(3)	0·3242 (15)	0·1712 (15)	0·1539 (16)
C(4)	0·1425 (14)	0·1270 (15)	0·1584 (14)
C(5)	0·0753 (17)	0·1161 (15)	0·2883 (15)
C(6)	0·1970 (18)	0·1451 (17)	0·4126 (16)
C(7)	0·0132 (13)	0·0939 (14)	0·0232 (14)
C(8)	0·0531 (14)	0·2311 (14)	−0·0952 (13)
C(9)	0·2005 (16)	0·2747 (16)	−0·1720 (14)
C(10)	0·1992 (18)	0·4068 (16)	−0·2747 (16)
C(11)	0·0626 (17)	0·4901 (16)	−0·3026 (15)
C(12)	−0·0817 (18)	0·4450 (16)	−0·2251 (15)
C(13)	−0·0827 (14)	0·3100 (15)	−0·1235 (13)
C(14)	−0·2150 (18)	0·2328 (17)	−0·0271 (16)

Table 3. *Observed and calculated structure factors* (× 50)

Column 1

h	k	F_{obs}	F_{calc}
		$\ell = 0$	
1	0	270	-321
1	1	836	-575
1	2	2962	2758
1	3	934	-938
1	4	1303	-1216
1	5	415	-341
1	6	437	307
1	-2	4410	4881
1	-3	912	992
1	-4	3114	-2976
1	-5	2359	-2098
1	-6	607	498
1	-7	441	530
2	0	2098	2402
2	1	1392	-1175
2	2	1349	-1205
2	3	1015	714
2	4	973	989
2	5	604	-587
2	6	-437	-381
2	-1	1451	1361
2	-2	1675	-1659
2	-3	1828	-1606
2	-4	1997	1963
2	-5	800	852
2	-6	916	-847
2	-7	1238	-1243
2	-9	515	600
3	0	1751	-1851
3	1	932	946
3	3	392	-475
3	5	441	480
3	-1	1699	-1605
3	-2	2667	2459
3	-3	1196	1226
3	-4	651	-653
3	-5	909	-956
3	-6	1056	870
3	-8	696	-601
4	1	1252	-1181
4	2	1383	-1274
4	3	840	830
4	4	622	705
4	6	392	-481
4	-1	967	1081
4	-2	568	335
4	-3	864	-916
4	-4	798	766
4	-5	1120	1100
4	-7	1014	-969
5	1	876	880
5	3	440	-527
5	-1	633	-594
5	-2	669	407
5	-3	958	994
5	-5	392	-438
6	5	396	-260
6	-1	1424	1450
6	-3	751	-783
7	1	522	490
7	-3	535	440
7	-4	527	-447
7	-5	515	-501
8	2	396	244
8	-1	630	627
8	-3	563	-435
8	-5	441	354
0	1	1301	1213
0	2	4462	-4724
0	3	2667	-2538
0	4	1403	1401
0	5	345	-163
0	6	1016	-1102
0	7	282	7
0	8	477	451
0	9	201	240
		$\ell = 1$	
0	1	1499	1557
0	2	1883	-1916
0	3	739	-834
0	4	1064	-1152
0	5	503	580
0	-1	113	-94
0	-2	3643	3895
0	-3	1766	1691

Column 2

h	k	F_{obs}	F_{calc}
0	-4	1194	-1129
0	-5	2158	-2088
1	0	2663	3098
1	1	527	440
1	2	2249	-2384
1	3	857	909
1	4	976	784
1	6	1081	-1038
1	-1	995	-694
1	-2	1372	-1472
1	-4	1748	1844
1	-6	1196	-1088
1	-7	829	-833
2	0	1452	-1483
2	1	1499	1588
2	2	1763	1695
2	3	490	-544
2	4	695	-809
2	5	412	440
2	-1	1663	-1598
2	-3	736	697
2	-4	711	-703
2	-6	770	711
3	1	1806	-1706
3	2	696	-735
3	3	1221	1184
3	4	1129	1137
3	5	595	-551
3	-1	2025	1941
3	-2	1053	-1059
4	0	1027	-971
4	1	1531	1480
4	3	1261	-1219
4	5	601	587
4	7	550	-459
4	-1	1578	-1567
4	-2	760	668
5	1	1248	1274
5	3	685	570
5	5	712	-515
5	-1	1775	1737
5	-2	502	350
6	0	966	898
6	1	946	923
6	3	805	-844
6	-1	677	-735
7	1	656	-725
7	2	490	506
7	-1	1095	1125
-1	0	4810	5136
-1	1	1086	996
-1	2	4574	-4919
-1	3	1570	-1463
-1	4	548	448
-1	6	529	-365
-1	-1	2720	2672
-1	-2	1614	-1527
-1	-3	839	-841
-1	-5	1323	1255
-1	-6	685	-737
-1	-7	665	-641
-2	0	2960	-3150
-2	2	2806	3063
-2	4	2597	-2629
-2	5	657	-493
-2	6	1114	902
-2	7	685	590
-2	8	505	-404
-2	-1	511	316
-2	-2	2714	2894
-2	-3	1035	1093
-2	-4	1495	-1462
-2	-5	654	-707
-3	0	5091	3348
-3	1	554	530
-3	2	1555	-1991
-3	3	563	-501
-3	4	1088	1125
-3	5	714	777
-3	6	892	-930
-3	-2	2448	-2553
-3	-4	764	823
-3	-6	411	-502
-4	0	1157	-1266
-4	2	2624	2755
-4	3	1546	1641
-4	4	1764	-1811
-4	5	870	-904
-4	6	420	450

Column 3

h	k	F_{obs}	F_{calc}
-4	8	550	-545
-4	-3	330	-310
-5	0	781	862
-5	1	1555	1611
-5	3	550	-727
-5	4	756	711
-5	5	593	694
-5	6	920	-806
-5	7	905	-994
-5	-1	1035	-964
-5	-2	670	-817
-5	-3	542	586
-5	-5	490	-593
-6	1	556	-633
-6	2	415	522
-6	3	699	689
-6	5	767	-916
-6	-1	1203	1291
-7	1	594	810
-7	3	885	-1062
-7	-1	473	125
		$\ell = 2$	
0	0	1597	1739
0	1	1254	983
0	2	3645	-3459
0	3	270	361
0	4	1215	1347
0	5	548	-630
0	6	795	-854
0	-1	2093	2311
0	-2	2107	-2227
0	-3	240	61
0	-4	927	862
0	-5	256	308
0	-6	721	-690
0	-7	682	-665
1	0	1663	-1666
1	1	5564	5821
1	3	2172	-2219
1	4	1032	-1059
1	5	1259	1102
1	7	714	-736
1	-1	2838	-2700
1	-2	513	482
1	-3	2374	2553
1	-4	995	-4026
1	-5	1362	-1302
2	1	1571	-1629
2	2	279	-291
2	3	2460	2377
2	5	1122	-1024
2	6	639	-626
2	-1	2943	2721
2	-3	2551	-2263
2	-4	314	-192
2	-5	1476	1536
3	1	2274	2149
3	3	1237	-1125
3	5	787	824
3	7	368	-524
3	-1	2176	-2137
3	-2	1641	-1453
4	3	1182	-980
4	1	1761	-1673
4	2	697	697
4	3	1015	1045
4	5	622	-582
4	-5	2393	2146
4	-2	456	525
5	0	1039	1086
5	1	1309	1346
5	3	1296	-1254
5	-1	604	-662
5	-2	993	-1052
6	1	643	-973
6	-1	1421	1349
6	-2	1020	1106
7	0	446	594
-1	0	2546	-2861
-1	1	986	902
-1	2	1352	1290
-1	3	1112	-1161
-1	4	1885	-1662
-1	5	484	603
-1	6	942	969
-1	8	411	-466
-1	-2	2492	2690

Column 4

h	k	F_{obs}	F_{calc}
-1	-3	1533	1527
-1	-4	1251	-1125
-2	0	1486	1585
-2	1	1336	-1101
-2	2	2409	-2133
-2	3	702	574
-2	4	956	1054
-2	6	514	-595
-2	-2	817	-831
-2	-3	437	413
-2	-4	942	994
-3	0	1054	-1183
-3	1	443	-372
-3	2	1212	1299
-3	3	1080	860
-3	4	1506	-1250
-3	6	865	837
-3	8	587	-563
-3	-1	1118	-947
-3	-3	1615	-1463
-3	-3	580	608
-3	-4	479	-430
-3	-5	644	-741
-4	0	2098	2077
-4	1	902	891
-4	2	955	-946
-4	4	531	694
-4	6	368	-442
-4	-1	554	-492
-4	-2	958	-1087
-5	1	579	360
-5	2	1918	1844
-5	4	1074	-1102
-5	5	662	-840
-5	-2	363	586
-6	0	880	863
-6	4	368	344
-7	1	981	-963
-7	2	742	720
-7	4	632	-703
-7	5	433	-529
-7	6	329	427
-7	-1	786	804
-7	-2	383	834
-8	3	481	-624
		$\ell = 3$	
0	0	225	95
0	1	2591	2723
0	2	834	884
0	3	3375	-3474
0	5	978	1133
0	7	726	-765
0	9	186	263
0	-1	2075	-2341
0	-2	1074	1135
0	-3	2661	2664
0	-4	455	-414
0	-5	1096	-1255
0	-6	397	-555
1	0	574	-521
1	1	619	-744
1	2	1681	1484
1	3	400	468
1	5	1444	-1406
1	-1	1717	1753
1	-2	1005	742
1	-3	924	-988
1	-4	934	-303
1	-5	475	514
1	-7	393	-500
2	0	1486	1311
2	1	3613	3500
2	2	734	675
2	3	2124	-2051
2	5	405	399
2	7	500	-579
2	-1	2220	-2083
2	-4	362	461
2	-5	782	-990
3	1	1861	-1696
3	2	443	431
3	3	1364	1380
3	5	808	-877
3	-1	2271	2074
3	-2	666	691
4	0	1283	1160
4	1	1220	1202

Column 5

h	k	F_{obs}	F_{calc}
4	2	338	-322
4	3	1182	-1109
4	5	538	480
4	-1	1278	-1187
4	-2	1027	-948
5	1	1237	-1226
5	4	463	-389
5	-1	1822	1731
5	-2	1067	1037
6	0	457	492
6	2	757	-847
7	0	529	-569
8	0	613	595
-1	0	2011	2012
-1	1	3260	-3208
-1	2	1847	-1775
-1	3	999	1136
-1	4	850	869
-1	5	996	-1002
-1	7	400	508
-1	8	256	325
-1	9	337	-394
-1	-1	3713	3230
-1	-2	194	259
-1	-3	1799	-1729
-1	-5	831	943
-1	-7	376	-547
-2	0	1560	-1580
-2	1	2842	2526
-2	2	2037	1775
-2	3	349	-1168
-2	4	1661	-1528
-2	6	1145	1073
-2	-1	2665	-2462
-2	-2	1516	1355
-2	-3	988	1136
-2	-4	271	-412
-2	-5	402	-624
-2	-6	487	-427
-3	0	1180	1264
-3	2	1551	-1412
-3	3	1663	1549
-3	4	1847	1777
-3	5	1123	-1028
-3	6	874	-1021
-3	8	256	371
-3	-1	318	-216
-3	-2	1055	-1074
-3	-4	564	620
-3	-5	283	-285
-4	0	1183	-1200
-4	1	1214	1015
-4	2	2033	2014
-4	4	1285	-1245
-4	6	535	644
-4	8	557	-696
-4	-1	438	-564
-4	-2	756	756
-4	-4	573	-722
-4	-5	276	-491
-4	-6	415	593
-5	0	1123	1185
-5	1	456	453
-5	4	370	404
-5	6	755	-851
-5	8	233	171
-5	-2	401	-560
-6	1	692	-705
-6	2	383	525
-6	3	532	678
-6	4	701	-738
-6	-1	542	639
-6	-2	286	505
		$\ell = 4$	
0	1	2158	-2260
0	2	483	385
0	3	1045	1119
0	4	247	-304
0	5	1084	-1124
0	7	424	537
0	-1	1262	1531
0	-2	1168	1028
0	-3	743	-967
0	-4	380	310
0	-5	705	724
0	-6	503	-526
0	-7	407	-482
1	0	1557	1328

Column 6

h	k	F_{obs}	F_{calc}
1	1	3020	2926
1	2	1258	1108
1	3	3263	-3186
1	4	1138	-1045
1	5	1079	988
1	7	450	-322
1	9	285	320
1	-1	2455	-2325
1	-2	486	344
1	-3	1284	1261
1	-5	843	-894
1	-6	311	-388
2	1	2134	-1970
2	2	1279	1176
2	3	555	600
2	4	718	-669
2	5	827	-828
2	-1	2636	2597
3	0	1729	1552
3	1	1234	1231
3	2	930	-860
3	3	1053	-986
3	4	592	506
3	5	431	342
3	-1	1504	-1481
3	-2	849	-1103
4	0	996	-921
4	1	1047	-942
4	2	535	583
4	3	382	415
4	4	564	-554
4	-1	506	601
4	-2	1216	1374
5	0	1090	1097
5	2	1076	-1113
5	4	552	584
5	-1	437	-290
5	-2	877	-884
6	0	825	-836
6	2	600	612
6	4	442	-453
6	-1	437	-407
7	0	639	662
7	2	461	-523
-1	0	1128	-1060
-1	1	614	800
-1	2	352	-200
-1	3	1475	-1420
-1	5	898	942
-1	6	311	390
-1	9	479	-485
-1	-1	975	-944
-1	-2	1518	1278
-1	-3	1507	1483
-1	-5	658	-618
-1	-6	437	-525
-2	1	1283	-1162
-2	2	1555	-1457
-2	3	818	720
-2	4	1149	990
-2	5	889	-783
-2	7	572	530
-2	9	298	-352
-2	-1	2134	1953
-2	-3	557	-548
-2	-4	301	-383
-3	0	1207	-1139
-3	1	2879	2525
-3	2	1398	1344
-3	3	1287	-1199
-3	4	1006	-1032
-3	6	414	356
-3	-1	1207	-1176
-3	-2	583	321
-3	-3	1140	1314
-3	-5	971	-870
-3	-5	534	-620
-4	0	892	871
-4	2	377	-468
-4	3	984	931
-4	5	962	-905
-4	6	882	-977
-4	-1	1466	1366
-4	-2	365	-326
-4	-3	535	-659
-4	-4	773	-897
-5	1	1514	1442
-5	2	898	901
-5	3	447	-279

Table 3 (*cont.*)

Column group 1:

h	k	F_{obs}	F_{calc}
-5	4	1499	-1543
-5	-4	522	-565
-6	0	693	691
-6	2	843	-911
-6	3	1023	-968
-6	4	383	435
-6	5	724	-721
-6	6	134	-795
-6	8	419	435
-6	-1	444	511
-7	1	377	-324
-7	3	485	409
-7	8	247	-304
-7	-1	293	336

ℓ = 5

h	k	F_{obs}	F_{calc}
0	0	1027	1017
0	1	1840	1844
0	2	1395	-1390
0	3	1597	-1590
0	5	1005	1109
0	-1	936	-973
0	-2	675	-780
0	-3	897	992
0	-4	929	1033
0	-5	397	-582
0	-6	349	-498
1	0	1822	-1716
1	1	1258	-1152
1	2	1232	1098
1	3	1067	1053
1	4	1899	-1823
1	5	389	-356
1	6	539	512
1	7	573	435
1	-1	1777	1754
1	-2	2051	2192
1	-3	997	-797
1	-4	1135	-1021
2	0	1343	1281
2	1	872	795
2	2	974	-963
2	3	453	-400
2	5	613	555
2	6	555	-488
2	-9	436	-348
3	0	1456	-1360
3	2	1378	1226
3	3	548	528
3	4	953	-968
4	0	1422	1241
4	1	379	319
4	2	1306	-1279
4	4	697	702
4	6	289	-264
4	-2	615	-1474
5	0	1037	-1007
5	2	532	564
5	4	450	-431
6	0	790	801
6	2	629	-661
6	4	264	293
7	1	285	252
7	2	305	390
7	3	238	-252
8	0	573	547
-1	0	1312	-1089
-1	1	1716	-2133
-1	2	346	352
-1	3	1679	1587
-1	5	1029	-985
-1	7	710	729
-1	-1	1644	1618

Column group 2:

h	k	F_{obs}	F_{calc}
-1	-2	298	309
-1	-3	663	-708
-1	-4	377	241
-1	-5	781	814
-2	0	1373	-1184
-2	1	905	949
-2	2	710	649
-2	3	1565	-1382
-2	4	340	308
-2	5	1250	1152
-2	7	348	-442
-2	-1	1527	-1470
-2	-2	862	692
-2	-3	1386	1321
-2	-4	465	-389
-3	1	1337	-1201
-3	3	845	741
-3	4	494	423
-3	5	675	-663
-3	6	456	-389
-3	7	559	480
-3	9	284	-303
-3	-1	901	874
-3	-5	651	643
-4	1	752	690
-4	2	950	854
-4	3	793	-786
-4	4	985	-870
-4	6	410	352
-4	-2	1129	1077
-4	-3	389	407
-4	-4	617	-561
-4	-5	245	-360
-4	-6	200	-338
-5	0	1359	1386
-5	2	1173	-1233
-5	4	434	433
-5	5	675	-777
-5	6	415	476
-5	-1	1285	1331
-5	-3	468	-561
-5	-4	249	-402
-6	0	619	572
-6	1	731	659
-6	3	646	-649
-6	4	389	-532
-6	5	569	-637
-7	1	268	-302
-7	3	461	297
-7	4	389	464
-7	5	643	-519
-7	6	433	-458
-7	8	660	316
-8	7	260	-262
-9	3	215	277

ℓ = 6

h	k	F_{obs}	F_{calc}
0	0	1267	-1240
0	1	1040	-828
0	2	1489	1115
0	3	795	808
0	4	901	-916
0	5	795	-813
0	6	274	432
0	7	343	395
0	-1	808	763
0	-2	763	797
1	0	1396	1338
1	1	901	891
1	2	1329	-1326
1	3	844	-670
1	-1	355	358
1	-2	1090	-1040

Column group 3:

h	k	F_{obs}	F_{calc}
1	-3	358	151
1	-4	759	661
1	-5	428	-426
1-	-6	357	-300
2	0	1659	-1567
2	2	1350	1327
2	3	719	704
2	4	1389	-1465
2	5	638	-736
2	6	512	572
2	-5	1028	946
3	0	1741	1591
3	1	372	347
3	2	1237	-1261
3	4	371	446
3	-1	260	218
4	0	1147	-1193
4	2	661	770
4	4	332	-460
4	6	250	283
4	-1	383	-325
5	0	681	689
5	1	250	-285
5	2	689	-750
5	4	428	537
6	0	652	-587
6	1	445	594
6	2	201	385
6	3	340	-350
6	4	216	-453
7	0	443	331
-1	0	1024	968
-1	1	287	382
-1	2	675	-732
-1	3	874	-819
-1	4	870	817
-1	5	890	899
-1	6	535	-521
-1	7	480	-532
-1	-1	816	-701
-1	-2	830	-693
-1	-4	542	605
-2	0	1082	-1021
-2	1	1414	-1384
-2	2	1558	1433
-2	3	1290	1256
-2	4	499	-479
-2	5	572	-589
-2	7	301	298
-2	-1	299	356
-2	-2	968	1108
-2	-3	1054	-1017
-2	-5	490	534
-3	1	680	703
-3	2	227	312
-3	3	559	-665
-3	5	469	580
-3	7	456	-555
-3	9	187	128
-3	-1	819	-812
-3	-2	410	261
-4	1	700	-817
-4	3	633	695
-4	5	902	-959
-4	7	263	397
-4	-1	622	676
-4	-3	542	-688
-4	-4	358	313
-5	3	971	-1007
-5	-2	711	600
-5	-3	507	600
-5	-5	315	-392
-6	0	903	875

Column group 4:

h	k	F_{obs}	F_{calc}
-6	1	469	-526
-6	2	915	-1040
-6	3	427	-369
-6	4	531	551
-6	7	282	409
-6	8	182	233
-6	-1	525	596
-7	3	258	-348
-7	4	361	-393
-9	1	202	250

ℓ = 7

h	k	F_{obs}	F_{calc}
0	0	1894	2120
0	1	532	552
0	2	1549	-1534
0	3	1114	-1144
0	4	357	521
0	5	277	330
0	8	255	287
0	-2	900	-1142
0	-4	435	524
1	0	1287	-1123
1	1	772	-806
1	2	910	961
1	4	772	-809
1	6	563	724
1	7	180	218
1	-1	815	748
1	-2	1643	1786
1-	3	536	602
1	-4	947	-1081
1	-5	521	-661
2	0	1359	1306
2	1	635	-652
2	2	1082	-1035
2	4	503	648
2	5	419	-566
2	7	140	211
2	-1	796	703
3	0	858	-816
3	2	722	763
3	3	324	-414
3	4	387	-446
3	6	276	441
3	-1	471	-510
4	0	606	568
4	1	535	-637
4	2	408	-392
4	3	291	368
4	4	389	530
4	5	231	-262
5	0	412	-325
5	1	542	673
5	2	441	524
5	3	388	-543
5	4	187	-291
5	-1	980	-1023
6	1	327	-421
-1	0	1118	-1095
-1	1	579	-636
-1	2	1149	1299
-1	3	980	1056
-1	4	1016	-1102
-1	5	721	-830
-1	6	257	223
-1	7	269	264
-1	-1	540	581
-1	-2	849	807
-1	-3	600	-471
-2	1	642	664
-2	2	563	-498
-2	4	376	-360

Column group 5:

h	k	F_{obs}	F_{calc}
-2	5	405	458
-2	6	570	-548
-2	7	598	-692
-2	8	176	169
-2	-1	230	63
-2	-2	366	-497
-2	-3	395	-496
-3	1	397	-445
-3	2	677	597
-3	3	1028	1104
-3	4	605	-569
-3	5	772	-786
-3	7	226	265
-3	-1	960	1004
-3	-3	668	-720
-4	0	498	458
-4	1	689	710
-4	3	505	-594
-4	6	358	-440
-5	7	201	334
-6	2	443	-463
-6	3	352	-467
-6	5	481	610
-6	-2	229	241

ℓ = 8

h	k	F_{obs}	F_{calc}
0	1	434	-402
0	4	390	-432
0	5	259	354
0	6	498	542
0	-2	1097	1240
0	-3	556	689
0	-4	378	-572
1	1	906	-785
1	2	855	-888
1	3	415	385
1	4	586	622
1	6	250	-388
1	7	226	300
1	-3	571	515
2	0	525	-442
2	1	285	248
2	2	606	530
2	3	413	-416
2	4	446	-464
2	6	242	276
2	-1	531	-508
3	0	652	464
3	1	727	-800
3	2	431	-477
3	3	520	612
3	4	393	501
3	5	389	-461
3	6	244	-407
3	-1	667	676
4	1	713	870
4	2	421	474
4	3	416	-538
4	4	262	-364
4	-5	802	-868
5	1	357	-531
5	3	293	330
-1	0	1040	1064
-1	2	1254	-1322
-1	3	389	-326
-1	4	414	373
-1	5	76	110
-1	8	139	193
-1	-1	604	693
-1	-2	916	-888
-1	-4	387	-443
-2	0	751	-714

Column group 6:

h	k	F_{obs}	F_{calc}
-2	1	285	-547
-2	2	865	769
-2	3	629	613
-2	4	778	-813
-2	5	705	-768
-2	6	306	257
-2	7	238	231
-2	-1	1038	1033
-2	-3	172	-178
-2	-4	324	-451
-3	0	871	1038
-3	1	575	524
-3	2	653	-651
-3	3	370	-390
-3	4	336	234
-3	6	496	-472
-3	7	175	-264
-3	8	206	236
-3	-1	444	404
-3	-2	756	-951
-4	2	403	386
-4	3	202	277
-4	4	707	-648
-4	5	338	-440
-4	7	168	179
-4	-1	427	435
-5	1	448	533
-5	2	347	-331
-5	3	496	-655
-5	5	457	555
-5	6	269	-191
-5	7	308	-422
-6	2	277	-182
-6	-7	236	384
-3	2	154	197

ℓ = 9

h	k	F_{obs}	F_{calc}
0	1	554	-592
0	2	627	-592
0	3	415	518
0	4	617	743
0	-4	403	481
1	0	573	-538
2	0	495	411
-1	0	369	-293
-2	0	877	983
-4	0	603	664

ℓ = 10

h	k	F_{obs}	F_{calc}
0	0	250	-136
0	1	357	524
0	2	247	322
0	3	403	-547
0	5	248	288
0	6	232	177
0	-1	519	-635
-1	0	722	796

ℓ = 11

h	k	F_{obs}	F_{calc}
0	1	290	-264
0	3	253	383

ℓ = 12

h	k	F_{obs}	F_{calc}
0	1	374	484

are refined in a 2×2 matrix. The anisotropic temperature exponent T has the form

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

and the weighting scheme used, due to Mills & Rollett (1961), has the form

$$\sqrt{w} = \left[1 / \left\{1 + \left(\frac{k|F_o| - b}{a}\right)^2\right\}\right]^{\pm}$$

The constants a and b set by the users have the values 32 and 20 respectively for $k = 0.5$.*

Anisotropic thermal factors were first applied to bromine atom and O(1) of the lactone ring, which had high B values, then progressively to atoms of the phenyl

* Dr G. A. Mair states in the program description that this weighting scheme works satisfactorily for photographic data with $a = 8F_{min}$ and $b = 5F_{min}$ and we have used these values for $F_{min} = 4$.

ring and finally extended to all atoms. Following seven cycles of SFLS calculations, the refinement was terminated when the R value dropped to 0·096 from an initial value of 0·185 for all the observed reflexions. Table 3 lists the F_o and F_c values based on the final atomic positions given in Table 2. Structure factors have been computed for about 980 unobserved reflexions (not given), of which only 60 are slightly above the threshold amplitudes.

A disconcerting feature of the refinement procedures which persisted till the end concerns the large parametral shifts shown for some of the light atoms particularly those of the phenyl ring. Considerable fudging of the shifts had to be exercised in these cases for every

Fig. 1. Sections of the final three-dimensional electron density map projected on the (010) plane. As the molecule possesses an inversion centre, only one half is represented. Contours start at 1·0, 1·5 and 3·0 e.Å⁻² for C, O and Br respectively. Intervals are at 0·5 e.Å⁻³ for C and O and 2 e.Å⁻³ for Br.

cycle, as, otherwise, the indicated movements would have resulted in a highly distorted geometry of the phenyl ring. The reason for this is not quite clear, although it is believed to be partly due to the use of 'truncated' three-dimensional data and partially diagonalized matrix elements. A final three-dimensional difference map (not shown) was computed in an attempt to locate the hydrogen atoms; but it did not prove useful in indicating their positions. Hence the hydrogen atoms were located at a calculated distance of 1·08 Å from the appropriate carbons. Addition of all the hydrogen atoms to the model lowered R by only 0·1%. A temperature factor of 4·5 Å² was used for all the H atoms; neither this nor their positional parameters was refined. The mean parametral shift in the light atom position in the ultimate least-squares cycle was 0·021 Å ($\sim 1·4\sigma$), the only exceptions being the x coordinate of C(1) and the y coordinate of C(6) for which the shifts measured as much as 2·6σ. The shifts in the heavy atom position was 0·0006 Å ($\sim 0·3\sigma$). The e.s.d.'s (σ's) are the average values obtained from the inverse of the appropriate block-matrix A_{mm}^{-1} and from the relation

$$\sigma_{mm} = [A_{mm}^{-1} \Sigma \, w(|kF_o - F_c|)^2/(n-s)]^{\frac{1}{2}},$$

where the symbols have the usual meanings.

Results

The final atomic coordinates (in fractional units) that resulted from our analysis and the e.s.d.'s (in Å) (in parenthesis) are given in Table 2. The components b_{ij} of the anisotropic thermal parameters and the equivalent isotropic B values (Å²) as evaluated from Hamilton's (1959) formula

$$B = \tfrac{4}{3} \sum_i \sum_j b_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$$

are represented in Table 4. The magnitudes and direction cosines of the principal axes of thermal vibration

Table 4. *Anisotropic thermal parameters* ($\times 10^4$) *for th e expression*

$$T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{31}hl + b_{12}hk)]$$

and the equivalent isotropic thermal parameters (*Hamilton*, 1959)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}	B
Br	256	272	119	184	−79	−113	5·73 Å²
O(1)	120	219	163	159	101	51	4·61
O(2)	105	108	123	44	−1	122	3·08
C(1)	269	139	109	80	−19	−75	4·77
C(2)	178	181	64	118	−20	−33	3·66
C(3)	112	142	118	−19	−55	73	3·54
C(4)	105	126	69	54	28	14	2·73
C(5)	190	126	74	115	32	85	3·28
C(6)	207	185	97	49	−30	118	4·27
C(7)	67	127	73	73	20	43	2·38
C(8)	105	99	61	32	37	72	2·37
C(9)	169	174	56	12	38	137	3·45
C(10)	228	139	94	95	29	69	4·03
C(11)	192	173	72	73	−13	48	3·79
C(12)	245	131	77	71	−27	8	3·99
C(13)	119	142	52	18	−13	80	2·72
C(14)	190	180	117	−93	−59	70	4·68

ellipsoids, as derived from the parameters of Table 4, are listed in Table 5. Although serious attempts to interpret these values are not made in view of their limited accuracy mentioned earlier, the maximum motion appears to be in a direction normal to the 'phthal-idyl' ring. The final three-dimensional electron density map corresponding to the asymmetric half of the molecule is shown in Fig. 1 by means of superimposed contour sections drawn perpendicular to *b* axis. The atomic arrangement is also indicated.

Table 5. *Magnitudes and direction cosines, relative to the reciprocal crystallographic axes, of the principal axes of the thermal vibration ellipsoids*

Atom	Axis i	B_i (Å²)	g_{i1}	g_{i2}	g_{i3}
Br	1	2·98	0·7769	0·1593	0·7257
	2	8·56	−0·5984	0·1158	0·6459
	3	6·00	0·1977	0·9813	−0·2373
O(1)	1	7·49	0·7771	0·7630	0·2702
	2	2·22	−0·2310	0·5156	−0·8422
	3	4·32	−0·5856	0·3902	0·4679
O(2)	1	4·93	0·8690	0·3017	0·5879
	2	1·88	0·4454	0·3897	−0·8028
	3	2·36	−0·2148	0·8730	0·1001
C(1)	1	7·34	0·5686	0·4451	−0·7028
	2	3·21	0·5553	0·6556	0·6590
	3	3·36	−0·5925	0·6278	−0·2523
C(2)	1	1·95	−0·6740	0·2876	−0·6907
	2	5·52	−0·2121	0·8298	0·2538
	3	4·13	0·5613	0·5385	−0·6689
C(3)	1	4·80	−0·5318	0·6291	−0·4493
	2	2·26	0·6416	0·2795	−0·6751
	3	3·47	0·5536	0·7261	0·5855
C(4)	1	3·47	0·6971	0·8289	−0·1898
	2	1·85	−0·6909	0·5308	−0·1158
	3	2·46	0·1875	0·1781	0·9754
C(5)	1	4·43	0·5398	0·4128	0·8296
	2	2·42	−0·8329	−0·1631	0·4342
	3	2·89	−0·1255	0·8965	−0·3536
C(6)	1	1·72	0·8824	0·3942	−0·3282
	2	6·47	−0·4332	0·5462	−0·7025
	3	4·88	0·1832	0·7405	0·6312
C(7)	1	3·36	0·2780	0·8954	0·4050
	2	1·22	−0·1595	0·4400	−0·9050
	3	2·05	−0·9473	−0·0705	0·1335
C(8)	1	1·90	−0·8774	0·0584	0·2465
	2	3·15	0·4508	0·3131	0·9005
	3	2·70	0·1643	0·9484	−0·3596
C(9)	1	1·72	−0·8756	0·0223	0·2788
	2	4·33	0·4613	0·7744	0·5672
	3	3·70	−0·1454	0·6324	−0·7755
C(10)	1	2·56	−0·7994	0·0219	0·4293
	2	5·35	−0·4304	0·3149	−0·8733
	3	3·96	0·4197	0·9492	0·2324
C(11)	1	5·18	−0·0793	0·8357	−0·5397
	2	2·85	0·9854	0·3781	0·2136
	3	3·85	−0·1504	0·3996	0·8152
C(12)	1	5·86	−0·2027	0·0096	0·9352
	2	2·42	0·7575	0·8085	0·1640
	3	3·88	−0·6205	0·5889	−0·3146
C(13)	1	1·43	0·8402	0·3641	−0·4153
	2	3·66	−0·0039	0·9259	0·2143
	3	2·97	−0·5428	0·1046	−0·8846
C(14)	1	6·82	−0·4070	0·6329	−0·6205
	2	3·02	−0·1127	0·4726	0·7839
	3	3·81	0·9065	0·6137	−0·0367

Discussion

Interatomic bond lengths and valency angles in the molecule with the corresponding e.s.d.'s in parenthesis are indicated in Fig. 2. The mean value of the aromatic C–C bond is 1·406 Å, which is slightly above the normal value of 1·395 Å. However, since the standard deviation of this bond is 0·022 Å, by Cruickshank's significance criterion (Lipson & Cochran, 1957), the difference is not appreciable. None of the bond lengths between two sp^3 hybridized carbon atoms (1·571 Å), between sp^3 and sp^2 (1·538 Å) and between two sp^2 hybridized carbon atoms (1·494 Å) differ significantly from accepted values of 1·545, 1·525 (Sutton, 1958) and 1·477 Å (Dewar & Schmeising, 1959) respectively. The C(aromatic)–Br distance of 1·893 Å is normal and agrees well with the average of several recent accurate determinations.

The two nominally equivalent C–O bonds differ significantly in length. Similar differences were first encountered in the γ-lactone ring in himbacine hydrobromide (Fridrichsons & Mathieson, 1962) and have subsequently been authenticated from many other determinations (Karle & Karle, 1966; Gabe, 1962; Schoenborn & McConnell, 1962; Fridrichsons, Mathieson & Sutor, 1963; Kartha & Haas, 1964; Asher & Sim, 1965). The C(7)–O(2) bond length of 1·465 Å does not differ significantly from the C–O single bond distance of 1·43 Å (Sutton, 1958). On the other hand, the C(14)–O(2) bond adjacent to the C=O group is considerably shorter, being 1·353 Å. This shortening has been interpreted in two ways (McConnell, Mathieson & Schoenborn, 1964): either as due to the hybridization of O(2) which is assumed to be in a trigonal sp^2 state and its interaction with C(14); or, alternatively, as due to a partial double bond character of the C(14)–O(2) bond, with O(2) acquiring a positive charge and O(1) a negative charge. This accounts for the planarity of the atoms C(13), C(14), O(1), O(2) and C(7) of the lactone group, just as in the case of the ester group and carboxylic acids. These two characteristics, inequality of the two C–O bonds and planarity of the lactone group, have been confirmed in the present studies. The amount of double bond character of the C(14)–O(2) bond has been estimated from a plot of double bond character *versus* C–O bond lengths, as indicated by Curl (1959) and is found to be approximately 14%. In common with other structures, no evidence for the slight lengthening of the C(14)=O(1) double bond, as suggested by Curl, has been noticed, the bond distance of 1·221 Å ($\sigma = 0·021$ Å) agreeing well with the normal value of 1·23 Å (Sutton, 1958) within experimental limits.

The average value of the C–C–C angle in the two phenyl rings is 119·9°. The following points regarding the angles around the sp^2 hybridized carbon atom C(14) may be observed. Although the sum of the angles at C(14) is 360°, the two exocyclic angles are appreciably different from the internal angle of 107·5°. The internal angle in the lactone ring, *i.e.* not containing the double bond, is the smallest. Further O(1)–C(14)–O(2), the angle subtended by the two oxygen atoms, is smaller than O(1)–C(14)–C(13) by 8·6°. The latter interesting feature has been observed by us in several of the structures containing the γ-lactone ring system. A few examples of the differences between the two angles observed in various structures are as follows: (i) annotinine bromohydrin (Przybylska & Ahmed, 1958), 6°; (ii) himbacine hydrobromide (Fridrichsons & Mathieson, 1962), 7°; (iii) bromodilactone from jacobine (Mathieson & Taylor, 1963), 8° and 13°; (iv) *p*-bromobenzoate-glaucarubin (Kartha & Haas, 1964), 7°; (v) shellolic bromolactone hydrate (Gabe, 1962), 6° and (vi) anemonin (Karle & Karle, 1966), 5° and 8°. There are some significant differences between the tetrahedral angles at C(7). The widening of the angle C(4)–C(7)–C(8) is the result of steric hindrance between the hydrogen atoms attached to atoms C(3) and C(9), this close

contact being 2·22 Å. The decrease in the angle O(2)–C(7)–C(8) from 109·5° to 102·5° may be ascribed to the considerable strain in the γ-lactone ring as a result of the shortening of one C–O bond.

Since the bromine atom and the carbon atom C(1) to which it is attached have high temperature factors, it was felt that thermal motion might have considerable effect on the C–Br bond length. This distance was therefore corrected for thermal oscillations using the method of Busing & Levy (1964). The motions of C and Br cannot be described completely as either correlated or uncorrelated. However, the former description may be a better approximation to physical reality, as the C–Br bond is a strong covalent linkage. Therefore, the correction was applied assuming correlated or 'in phase' motion. It was however found that the corrected distance of 1·903 Å is not much different from the uncorrected value. The C(14)–O(1) distance was also corrected likewise, the corrected value being 1·225 Å. Here again the correction is not significant, being much smaller than the e.s.d. of the bond.

The equations for the mean planes through the phenyl ring, the fused ring system and the lactone group have been derived by Blow's method (Blow, 1960). The equations are referred to a set of orthogonal

C(8) – C(7) – C(7') = 107·1°
C(4) – C(7) – O(2) = 107·5°
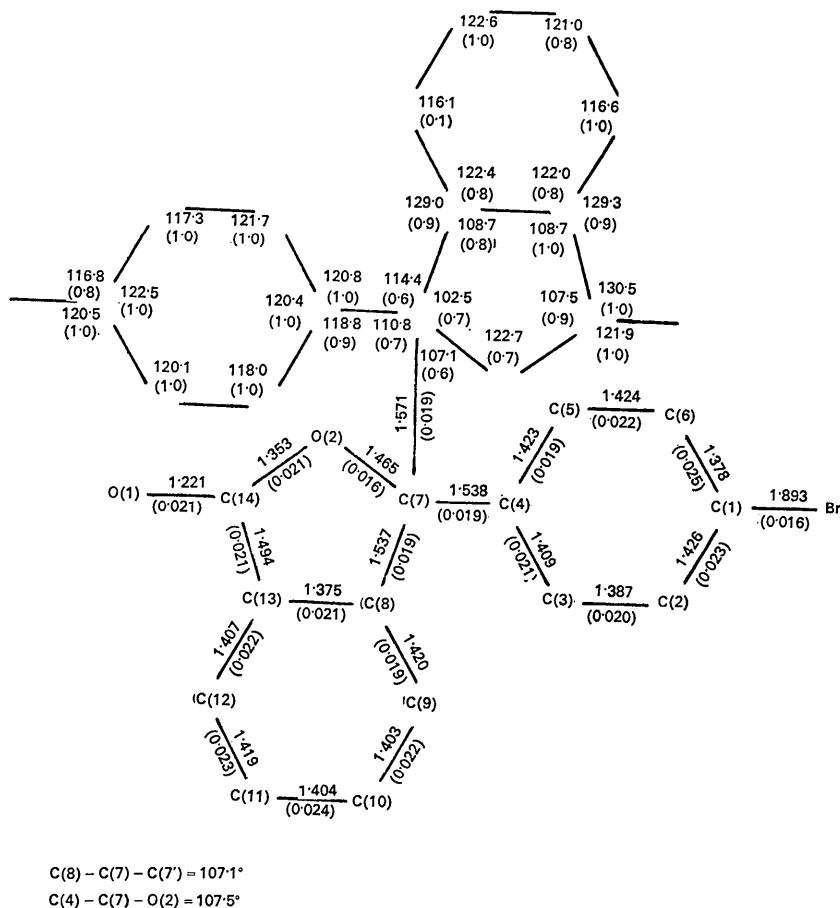
Fig. 2. Bond lengths (Å) and bond angles (°); values in parenthesis denote the estimated standard deviations.

axes X', Y', Z' where X' coincides with the crystallographic X direction, Y' lies in the XY plane and Z' is perpendicular to the XY plane. The equations are as follows:

Phenyl ring:
$$0.2303X' - 0.9678Y' + 0.1017Z' + 0.7201 = 0$$

Fused ring system:
$$0.2180X' + 0.7041Y' + 0.6758Z' - 0.6376 = 0$$

Lactone group:
$$0.1937X' + 0.7097Y' + 0.6773Z' - 0.6673 = 0$$

A projection of the molecule (excluding hydrogen atoms) in the plane of the fused ring system and the out-of-plane distances of the atoms are given in Fig. 3. The phenyl ring, the fused ring system and the lactone group are essentially planar, the displacement of the atoms from the respective mean planes being, in general, less than their standard deviations normal to the planes. However, the bromine and the oxygen atom O(1) are off the mean plane of the phenyl ring and the fused ring system by 0.116 and 0.080 Å respectively.

The phenyl ring is inclined at an angle of 124.2° to the plane of the fused ring system belonging to the same half of the molecule. This orientation of the benzene plane and the centrosymmetrical conformation of the molecule correspond to a position of least steric hindrance. Any deviation from this configuration would only shorten some of the intramolecular contacts while increasing the others. The short intramolecular non-bonded distances are given in Table 6.

Table 6. *Short intermolecular contacts*

BrA ——C(1′)D	3.681 Å
BrA ——C(10)C	3.838
C(2)A—C(10′)B	3.709
C(2)A—O(1)B	3.409
C(3)A—O(1)B	3.151
C(1′)A–C(9′)B	3.500
C(12)A–C(4′)E	3.729
C(12)A–C(5′)E	3.661
C(11)A–C(5′)E	3.638

The coordinates of the atoms of molecule A are related to those of molecules B to E by the following symmetry relations:

Molecule	Coordinates		
A	x	y	z
B	$1+x$	y	z
C	x	y	$1+z$
D	$1+x$	y	$1+z$
E	x	$1+y$	z

The arrangement of molecules in the unit cell as seen in the $h0l$ and $hk0$ projections is shown in Figs. 4 and 5. It can be seen that the structure is based purely on packing considerations which are decided by the shape of the molecule, fragments of one filling the concavity of its neighbours. The close intermolecular contacts less than 4 Å are marked in the two figures and also listed in Table 7. None of them is abnormal.
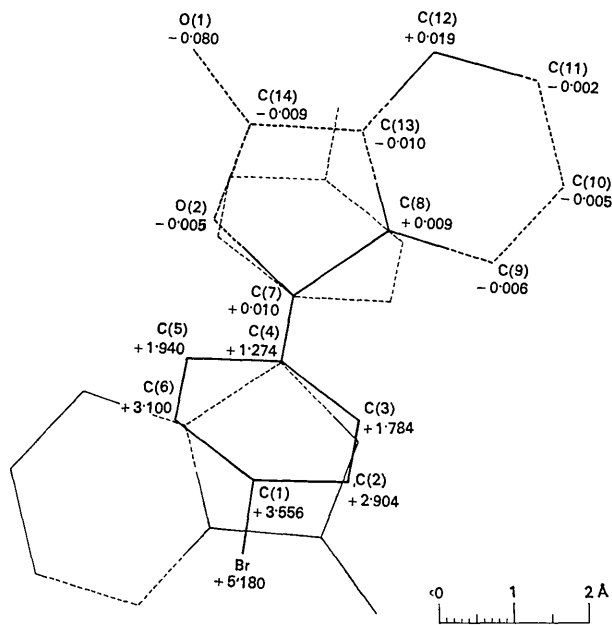
Fig. 3. Mean plane of the 'phthalidyl' ring system showing the perpendicular distances (Å) of the atoms of one half molecule from the plane.
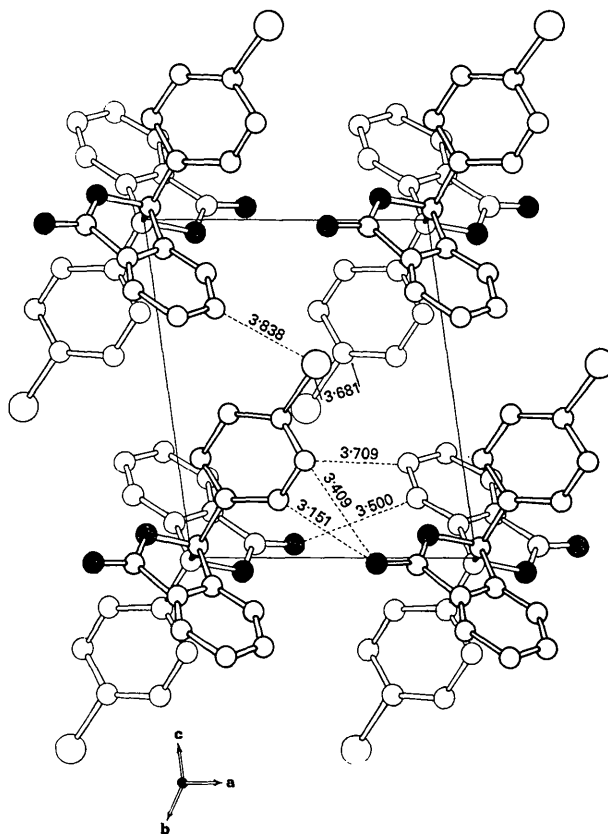
Fig. 4. View of the structure along [010] showing the packing arrangement and short intermolecular contacts. The hydrogen atoms are not shown. The large open circles denote the bromine atoms and the smaller open and black circles represent the carbon and oxygen atoms respectively.
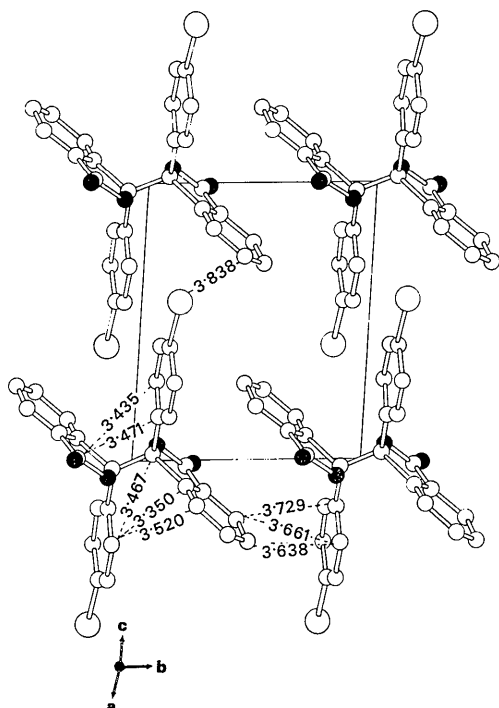
Fig. 5. View of the structure along [100] to illustrate the packing arrangement. Short intermolecular and intramolecular contacts are also indicated.

Table 7. *Short non-bonded intramolecular distances*

C(3)–C(14′)	3·435 Å
C(4)–C(14′)	3·471
C(5)–C(7′)	3·467
C(5)–C(9′)	3·520
C(5)–C(8′)	3·350

References

ASHER, J. D. M. & SIM, G. A. (1965). *J. Chem. Soc.* p. 1584.
BLOW, D. M. (1960). *Acta Cryst.* **13**, 168.
BOND, W. L. (1959). *Acta Cryst.* **12**, 375.
BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
CURL, R. F. (1959). *J. Chem. Phys.* **30**, 1529.
DEWAR, M. J. S. & SCHMEISING, H. N. (1959). *Tetrahedron*, **5**, 166.
FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412.
FRIDRICHSONS, J. & MATHIESON, A. McL. (1962). *Acta Cryst.* **15**, 119.
FRIDRICHSONS, J., MATHIESON, A. McL. & SUTOR, D. J. (1963) *Acta Cryst.* **16**, 1075.
GABE, E. J. (1962). *Acta Cryst.* **15**, 759.
HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
KANNAN, K. K., VIJAYAN, M. & NAMBUDIRI, M. M. G. (1966). *A Unified Set of Crystallographic Programmes.* Bangalore: Indian Institute of Science. To be published.
KARLE, I. & KARLE, J. (1966). *Acta Cryst.* **20**, 555.
KARTHA, G. & HAAS, D. J. (1964). *J. Amer. Chem. Soc.* **86**, 3630.
LIPSON, H. & COCHRAN, W. (1957). *The Determination of Crystal Structures.* London: Bell.
MATHIESON, A. McL. & TAYLOR, J. C. (1963). *Acta Cryst.* **16**, 524.
McCONNELL, J. F., MATHIESON, A. McL. & SCHOENBORN, B. P. (1964). *Acta Cryst.* **17**, 472.
MILLS, O. S. & ROLLETT, J. S. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 117. Oxford: Pergamon Press.
PRZYBYLSKA, M. & AHMED, F. R. (1958). *Acta Cryst.* **11**, 718.
SCHOENBORN, B. P. & McCONNELL, J. F. (1962). *Acta Cryst.* **15**, 779.
SUTTON, L. E. (1958). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* London: The Chemical Society.
WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.