

A Refinement of the Structure of *meso*-3,3'-Di-(*p*-chlorophenyl)bi-3-phthalidyl

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The structure of *meso*-3,3'-di-(*p*-chlorophenyl)bi-3-phthalidyl has been refined from three-dimensional X-ray data by full-matrix least-squares methods to an *R* index of 0.099 for 912 observed reflexions. The compound crystallizes in the triclinic space group $P\bar{1}$, with a monomolecular cell of dimensions $a=7.89$, $b=8.06$, $c=9.65$ Å, $\alpha=86^\circ 18'$, $\beta=99^\circ 18'$ and $\gamma=105^\circ 44'$. The two halves of the molecule are related by a centre of symmetry and in each half the phenyl ring is tilted with respect to the phthalidyl ring system by $124^\circ 53'$. The lactone group is planar and exhibits the expected asymmetry of the C—O bonds. The thermal parameters of the atoms have been qualitatively explained in terms of the rigid-body oscillations about the single bond connecting the two halves of the molecule and that connecting the phenyl ring to the phthalidyl ring. The structure can be described as consisting of close-packed layers of molecules in the (100) plane repeated periodically along the crystallographic *X* direction. The molecular coordination number in this arrangement is 12 and the packing coefficient 0.68.

Introduction

It is well known that *o*-benzoylbenzoic acids and their acid chlorides are converted into 3,3'-diarylbiphtalidyls by the action of a variety of reducing agents like hydroiodic acid, hydrochloric acid, aluminum and sulphuric acid (Ullmann, 1896; Meyer, 1904; Bauer & Endres, 1913; Eckert & Pollak, 1917; Creighton & Jackman, 1960; Risinger & Thompson, 1963). These biphtalidyls can theoretically exist in two isomeric forms, *viz.* the racemic and the *meso* forms. A precise definition of their stereochemistry by X-ray diffraction methods would be of considerable value in understanding the steric factors involved in their formation, particularly because the two stereoisomers are formed in unequal proportions. The structure determination of the bromo derivative of *meso*-3,3'-di-(*p*-phenyl)bi-3-phthalidyl undertaken in this connexion has already been reported (Kalyani, Manohar & Mani, 1967). However, it was felt worth while to analyse the structure of the corresponding chloro derivative also in order to study the changes brought about in the geometry and packing of molecules as a result of the substitution of chlorine for bromine at the 3 and 3' positions. Another important consideration which prompted us to undertake this analysis is the following. One disconcerting feature of the refinement of the structure of the bromine compound which persisted till the end was the abnormal parametral shifts shown for some of the light atoms, particularly those of the phenyl ring. In retrospect, we feel that the reason for this anomaly lay, at least partly, in the fact that reflexions on both the halves of the upper level Weissenberg photographs were used in refinement procedures without allowing for the elongation or contraction of the spots. In the

present analysis, however, only the intensities of the elongated spots were measured and they were corrected for spot shape by the method due to Philips (1954) and hence, this study is expected to furnish a more accurate set of bond lengths and bond angles.

Experimental

Transparent and platy crystals of *meso*-3,3'-di-(*p*-chlorophenyl)bi-3-phthalidyl were kindly supplied to us by Prof. M. V. Bhatt and Mr K. M. Kamath of the Department of Organic Chemistry of this Institute. Examination of the oscillation and Weissenberg photographs taken about the *a* and *c* axes showed that the crystals are triclinic with a monomolecular unit cell of dimensions*

$$\begin{aligned} a &= 7.89 \pm 0.02 \text{ \AA} & \alpha &= 86^\circ 18' \pm 1^\circ \\ b &= 8.06 \pm 0.02 & \beta &= 99^\circ 18' \pm 1^\circ \\ c &= 9.65 \pm 0.02 & \gamma &= 105^\circ 44' \pm 1^\circ \end{aligned}$$

By analogy with the isomorphous bromo derivative the crystals were assigned to the centrosymmetric space group $P\bar{1}$.

Other crystal data:

$$\begin{aligned} M &= 487.32 & u &= 582.7 \text{ \AA}^3 \\ D_m &= 1.371 \text{ g.cm}^{-3} & D_x &= 1.381 \text{ g.cm}^{-3} \end{aligned}$$

Absorption coefficient for X-rays ($\lambda=1.5418$ Å):
 $\mu=26.96 \text{ cm}^{-1}$.

Intensity data were collected on multiple-film equi-inclination Weissenberg photographs using Cu $K\alpha$ radiation for reciprocal levels hkl , $h=0$ through -5 and hkl , $l=0$ through -7 , from specimens cut along the

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* The values of interaxial angles quoted in Kalyani, Manohar & Mani (1967) were found to be slightly inaccurate. The redetermined values are given here.

a and c axes and ground to cylinders of radii 0.014 and 0.015 cm respectively. The intensities were estimated visually using calibrated time-exposure strips prepared from the same specimens. As mentioned earlier, only the intensities of the elongated spots on one side of the upper level pictures were measured. However, this did not unduly restrict the volume of reciprocal space that could be explored as data were collected about two crystallographic axes. Out of the total number of 2664 non-equivalent reflexions in the Cu $K\alpha$ sphere, 2010 were accessible in this way, of which 912 were in the measurable range. The intensities were corrected for the Lorentz-polarization factor, spot shape in the upper level photographs and absorption (*International Tables for X-ray Crystallography*, 1959). Initially the data were put on the absolute scale by comparison with those of the bromine compound.

Refinement

The final positional parameters and the equivalent isotropic temperature factors of the isomorphous *meso*-3,3'-di-(*p*-bromophenyl)bi-3-phthalidyl were taken as the initial parameters in refinement procedures. Structure factor calculations with these parameters gave a residual index, defined as

$$\Sigma ||F_o| - |F_c|| / \Sigma |F_o|,$$

of 0.229 for $hk0$ and $0kl$ reflexions. The structure was refined from these zonal data to an R index of 0.160 by two cycles of isotropic structure-factor least-squares calculations done on the Elliott 803-B computer at Hindustan Aeronautics Ltd., Bangalore, using a general block-diagonal SFLS 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 installation at the Tata Institute of Fundamental Research, Bombay, using a full-matrix least-squares program, *ORFLS*, written by Busing, Martin & Levy (1962), modified by W. C. Hamilton, J. A. Ibers and C. K. Johnson and adapted for the CDC-3600 computer by S. Srikanta of the Nuclear Physics Division of the Bhabha Atomic Research Centre, Bombay. The first three-dimensional isotropic structure-factor calculations gave an R value of 0.170 for the 912 measured reflexions. This value was reduced to 0.147 in two isotropic least-squares cycles. At this stage individual anisotropic temperature factors of the form

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

were introduced and the structure was refined to an R index of 0.099 in four anisotropic cycles. In the final cycle the average and the maximum parametral shifts were 0.185σ and 0.692σ respectively. In these calculations, reflexions with F_o 's greater than 4 and less than 40 were given unit weights and those with F_o 's greater

than 40 and less than 4 were given half weights. The scattering factors used were those of Cromer & Waber (1965).

Results

The final positional and anisotropic thermal parameters of the atoms in the asymmetric part of the unit cell are listed in Tables 1 and 2 respectively. The amplitudes $(\overline{u_i^2})^{1/2}$ of thermal vibration along the principal axes of the B -ellipsoids, along with their orientations with respect to the direct cell edges, are given in Table 3. The last column of Table 3 gives the average B 's defined as $B = (B_1 + B_2 + B_3)/3$. A list of the final observed and calculated structure factors is presented in Table 4. The unobservable reflexions are not included in the Table.

Table 1. *Final fractional coordinates*
(e.s.d.'s $\times 10^5$ in parenthesis)

	x	y	z
Cl	0.52721 (51)	0.23577 (50)	0.56529 (37)
O(1)	-0.35607 (108)	0.26578 (108)	-0.02935 (87)
O(2)	-0.15868 (87)	0.10933 (84)	0.05134 (69)
C(1)	0.37639 (158)	0.18847 (141)	0.41289 (127)
C(2)	0.44441 (146)	0.19532 (143)	0.28498 (129)
C(3)	0.32453 (137)	0.16735 (142)	0.16256 (114)
C(4)	0.14369 (137)	0.12669 (119)	0.16198 (98)
C(5)	0.07603 (142)	0.11640 (134)	0.29292 (104)
C(6)	0.19475 (181)	0.15055 (144)	0.41485 (123)
C(7)	0.01531 (139)	0.09238 (124)	0.02607 (108)
C(8)	0.06162 (141)	0.22932 (131)	-0.09065 (103)
C(9)	0.20677 (152)	0.27449 (130)	-0.17034 (118)
C(10)	0.20239 (170)	0.40694 (147)	-0.27217 (114)
C(11)	0.06482 (184)	0.49083 (150)	-0.30283 (118)
C(12)	-0.08430 (167)	0.44501 (146)	-0.22664 (122)
C(13)	-0.07783 (135)	0.31184 (129)	-0.12463 (104)
C(14)	-0.21460 (155)	0.23367 (146)	-0.03303 (115)

Table 2. *Anisotropic thermal parameters* ($\times 10^5$)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cl	3198	3581	1784	1384	-750	-770
O(1)	1444	3150	2370	1206	413	46
O(2)	1092	1645	1385	327	600	69
C(1)	1724	1758	1681	367	-340	-215
C(2)	1615	1964	1634	282	42	-123
C(3)	865	2201	1482	-261	164	-21
C(4)	1305	1278	989	189	90	-163
C(5)	1841	2004	903	766	267	95
C(6)	2657	1874	1529	665	10	-147
C(7)	1192	1616	1492	502	558	-42
C(8)	1533	1647	1075	340	317	-120
C(9)	1918	1260	1615	177	904	219
C(10)	2970	1601	1207	146	549	92
C(11)	2859	1919	1262	530	402	105
C(12)	2235	1834	1300	-23	-189	-208
C(13)	1223	1593	1196	216	506	13
C(14)	1271	2142	1551	759	174	-96

Fig. 1 gives the superimposed sections of the final three-dimensional electron density map. Atomic positions are also indicated. Fig. 2 is a composite diagram of the three-dimensional $(F_c - F_o)$ synthesis giving peaks corresponding to the hydrogen atoms. However, it

might be mentioned that two additional peaks of heights more than $0.3 \text{ e.}\text{\AA}^{-3}$ appeared in this diagram which could not be accounted for. The positions of

Table 3. The *r.m.s.* amplitudes of the principal vibration ellipsoids and their orientations relative to direct cell edges

	Axis <i>i</i>	$(\overline{u_i^2})^{1/2}$	θ_{ia}	θ_{ib}	θ_{ic}	<i>B</i>
Cl	1	0.2264	56.75	85.99	44.73	7.480
	2	0.2453	51.16	152.91	109.31	
	3	0.3825	123.59	116.75	51.59	
O(1)	1	0.1686	8.84	114.25	97.11	6.184
	2	0.3108	98.84	150.40	73.49	
	3	0.3317	89.73	74.08	18.06	
O(2)	1	0.1509	19.94	94.47	115.56	3.713
	2	0.2255	77.27	173.52	87.54	
	3	0.2597	74.91	85.32	25.70	
C(1)	1	0.1990	41.86	79.17	65.69	4.956
	2	0.2358	67.20	168.68	86.22	
	3	0.3051	122.91	86.73	24.64	
C(2)	1	0.2103	33.52	77.25	80.17	4.908
	2	0.2530	63.69	166.57	87.37	
	3	0.2799	109.24	85.84	10.19	
C(3)	1	0.1442	30.43	75.64	92.97	4.529
	2	0.2603	91.76	78.14	162.91	
	3	0.2889	120.37	18.79	73.19	
C(4)	1	0.1816	57.75	55.20	70.85	3.279
	2	0.2084	147.74	46.84	66.95	
	3	0.2195	90.37	117.02	30.72	
C(5)	1	0.2008	100.91	95.42	10.10	3.958
	2	0.2132	156.42	51.98	87.78	
	3	0.2542	69.36	38.55	80.16	
C(6)	1	0.2355	99.11	11.24	78.22	5.400
	2	0.2526	124.75	78.76	135.77	
	3	0.2931	143.73	89.67	48.16	
C(7)	1	0.1574	14.32	110.22	112.77	3.824
	2	0.2223	94.54	159.61	88.23	
	3	0.2666	76.45	92.51	22.85	
C(8)	1	0.2006	28.87	99.41	127.61	3.755
	2	0.2163	103.78	134.21	122.38	
	3	0.2361	114.84	45.65	125.72	
C(9)	1	0.1699	56.91	55.90	117.85	4.340
	2	0.2225	46.66	145.88	114.32	
	3	0.2941	61.28	91.06	38.51	
C(10)	1	0.2063	73.61	46.04	123.36	5.116
	2	0.2394	84.12	125.40	146.22	
	3	0.3074	17.47	115.29	85.26	
C(11)	1	0.2294	97.47	126.26	41.85	5.239
	2	0.2514	82.38	140.03	131.82	
	3	0.2886	10.70	104.52	88.62	
C(12)	1	0.1982	61.44	58.59	60.63	5.103
	2	0.2535	93.28	49.33	135.62	
	3	0.3005	28.78	123.44	119.90	
C(13)	1	0.1658	27.81	86.43	118.49	3.616
	2	0.2254	75.66	167.11	106.24	
	3	0.2431	66.70	102.36	33.57	
C(14)	1	0.1737	10.23	114.49	94.27	4.416
	2	0.2550	96.28	148.81	112.01	
	3	0.2695	98.04	108.09	22.46	

the hydrogen atoms were not refined and their coordinates given in Table 5 and used in the subsequent discussion are those fixed from geometrical considerations assuming a C-H distance of 1.08 \AA .

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.

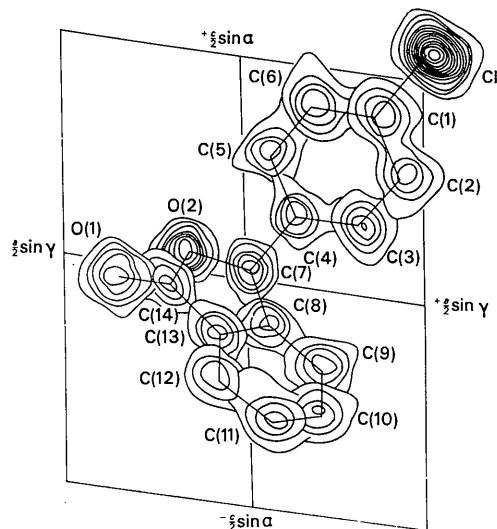


Fig. 1. Superimposed sections of the final three-dimensional electron-density distribution projected on to the (010) plane. Contours start at $1.0 \text{ e.}\text{\AA}^{-3}$ and are at intervals of $1.0 \text{ e.}\text{\AA}^{-3}$. The asymmetric half of the molecules is also represented.

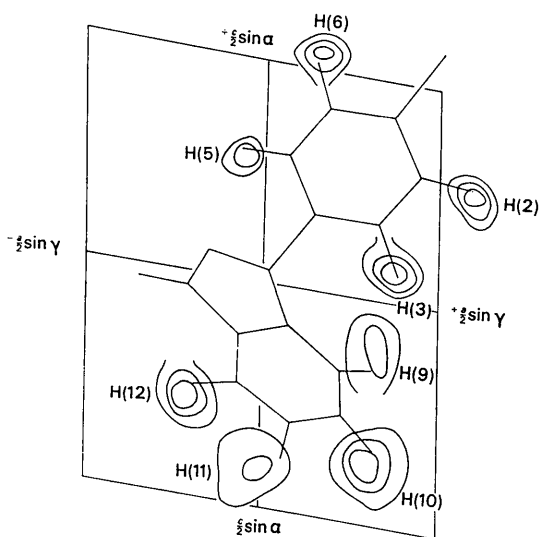


Fig. 2. Composite diagram of the final $(F_0 - F_c)$ synthesis. Contours start at $0.1 \text{ e.}\text{\AA}^{-3}$ and are at intervals of $0.1 \text{ e.}\text{\AA}^{-3}$. Atomic positions are indicated.

Table 5. *Calculated positions of hydrogen atoms in fractional coordinates*

	<i>x</i>	<i>y</i>	<i>z</i>
H(2)	0.5859	0.2256	0.2818
H(3)	0.3753	0.1740	0.0643
H(5)	-0.0653	0.0861	0.2960
H(6)	0.1443	0.1440	0.5129
H(9)	0.3136	0.2120	-0.1497
H(10)	0.3133	0.4447	-0.3303
H(11)	0.0661	0.5905	-0.3774
H(12)	-0.1911	0.5077	-0.2472

the six-membered and the five-membered parts of the fused ring system are planar within experimental error. The average C-C distance of 1.421 Å in the six-membered ring is slightly greater than the aromatic C-C distance. However, this discrepancy is not statistically significant.

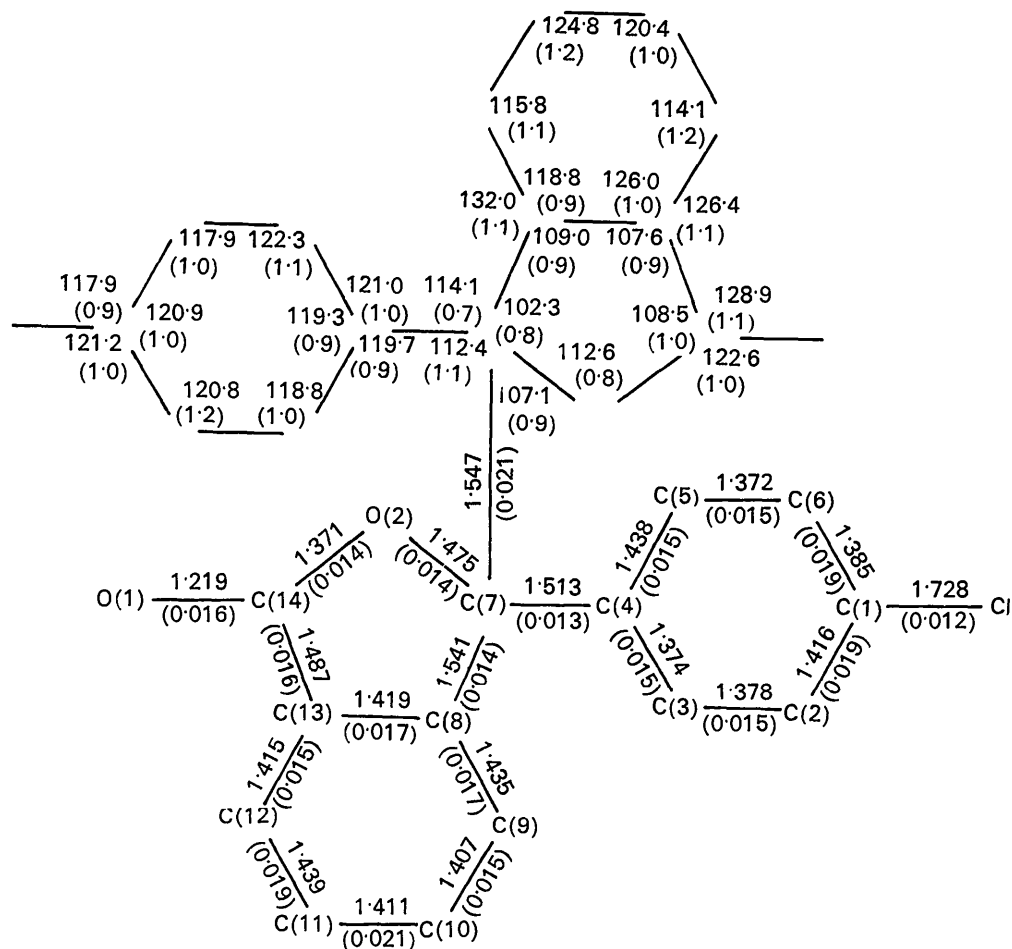
As in the case of the bromine compound, the lactone group in the molecule, constituting the atoms C(7),

O(2), C(14), O(1) and C(13), exhibits perfect planarity, the root mean square and the maximum displacements of the atoms being 0.004 and 0.007 Å respectively. Also, the two C-O bonds about O(2) show the expected asymmetry, the one adjacent to the C=O bond being 0.104 Å less than the other. The length of the C(14)-

Table 6. *Short intramolecular contact distances*

The centrosymmetric equivalent ones are not given. Primes refer to atoms related by centre of symmetry.

C(3)-C(14')	3.377 Å
C(5)-C(9')	3.482
C(5)-C(8')	3.360
C(8)-O(2')	3.015
O(2)-C(9')	3.174
O(2)-C(4')	2.929
H(3)-O(2')	2.641
H(5)-C(8')	3.332
H(5)-C(9')	3.070
H(9)-O(2')	2.728



$$\text{C}(8)-\text{C}(7)-\text{C}(7') = 111.9(1.1)$$

$$\text{C}(4)-\text{C}(7)-\text{O}(2) = 108.3(0.9)$$

Fig. 3. Bond lengths (Å) and bond angles (°); values in parenthesis denote the standard deviations.

Table 7. The displacements (Å) of atoms from different mean planes

	Displacement from mean planes				
	I	II	III	IV	V
Cl	0.069				
O(1)		0.058		0.015	0.005
O(2)		0.016		0.000	-0.002
C(1)	0.002				
C(2)	-0.014				
C(3)	0.013				
C(4)	0.000				
C(5)	-0.013				
C(6)	0.011				
C(7)		-0.014		0.001	0.004
C(8)		-0.031	-0.019	-0.001	
C(9)		0.020	0.014		
C(10)		0.011	-0.004		
C(11)		0.003	-0.002		
C(12)		-0.016	-0.003		
C(13)		-0.007	0.014	0.002	0.000
C(14)		0.018		-0.001	-0.007

O(2) bond (1.371 ± 0.014 Å) corresponds to a double bond character of 10% (Curl, 1959) which means a 10% contribution from the valence-bond resonance form $C-C=O^+-C$. However, the C(14)-O(1) length of



1.219 ± 0.016 Å agrees well with the C=O bond length of 1.23 Å within experimental error. This suggests that the lactone group can be entirely represented by the formula $C-C-O-C$. The precision with which the



atomic positions have been determined is not high enough to permit any rigorous estimate to be made regarding the contribution from the two canonical forms. However, it is felt that the asymmetry of the C-O bond distances about O(2) is partly due to a small contribution from the form $C-C=O^+-C$ and partly due



to the smaller covalent radius of the sp^2 hybridized C(14) compared with that of the sp^3 hybridized C(7). The C(7)-O(2) length (1.475 ± 0.014 Å) is considerably greater than the C-O single bond distance of 1.43 Å (*International Tables for X-ray Crystallography*, 1962). This is a common feature found in many lactone compounds (Fridrichsons, Mathieson & Sutor, 1963; Kartha & Haas, 1964; Jeffrey, Rosenstein & Vlasse, 1967; Kim, Jeffrey, Rosenstein & Corfield, 1967) and is probably due to the strain introduced as a result of the group being part of a ring system. Further, the exocyclic angles around C(14) are considerably greater than the internal angle O(2)-C(14)-C(13) ($108.5 \pm 1.0^\circ$) and of the two exocyclic angles, the one nearer to O(2) is 6.3° less than the other. This is also a feature encountered in many compounds containing γ -lactone (Przybylska & Ahmed, 1958; Gabe, 1962; Fridrichsons

& Mathieson, 1962; Karle & Karle, 1966; Asher & Sim, 1965).

The phenyl ring is oriented with respect to the fused ring system at an angle of 124.9° . The two rings are connected by a pure single C-C bond and hence this orientation should completely be determined by steric effects. The group is in steric contact with various atoms of the fused ring system in the same half of the molecule and in the centrosymmetrically related half of the molecule, with the oxygen atom O(1) in the molecule related by a translation along the *a* axis and with the atoms in the six-membered part of the fused ring system related by the *b* translation. A careful examination showed that any rotation of the phenyl group about C(4)-C(7) bond will give rise to greater steric interactions.

The two centrosymmetric halves of the molecule are related by a C-C single bond of length 1.547 ± 0.02 Å. In this conformation, the oxygen atom O(2) in one of the halves is in close contact with the carbon atoms C(8) and C(9) of the other half of the molecule (Table 6).

It can be clearly seen from Fig. 4 that any departure from centrosymmetry caused by the rotation of one half relative to the other about the C(7)-C(7') bond would prohibitively shorten these contacts and hence

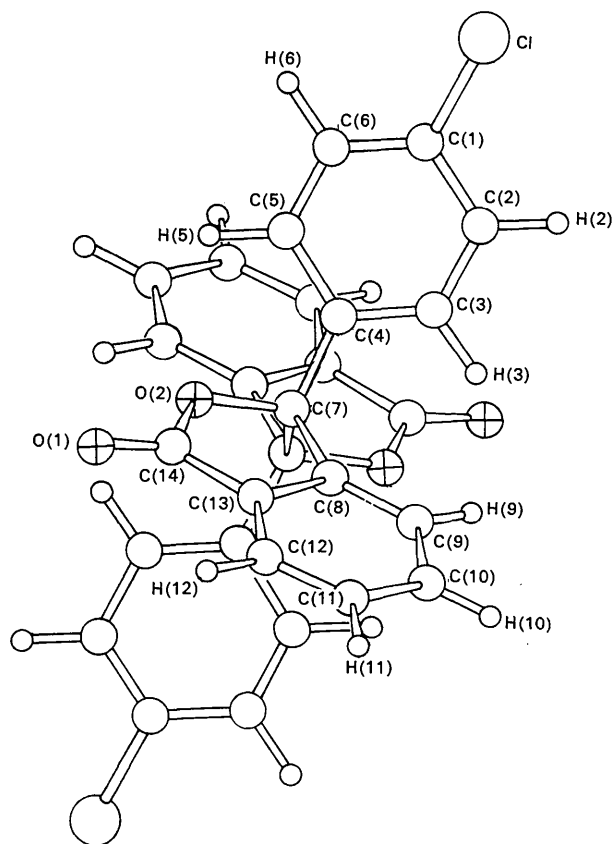


Fig. 4. A perspective view of the molecule as seen normal to the plane of the phenyl rings.

a centrosymmetrical arrangement is sterically favoured. An examination of a wire model confirmed this conclusion.

It might be mentioned that the bond lengths and bond angles obtained from the present analysis are similar to those found in the bromine compound. Considerable deviations are observed in individual values, but their significance cannot be ascertained in view of the high standard deviations of lengths and angles in the analysis of the bromine compound. The standard deviations obtained from the present analysis are much smaller on account of the higher precision attained in the location of atomic positions, presumably as a result of the more accurate treatment of the reflexion data from the upper level Weissenberg pictures and also owing to the lower scattering power of chlorine compared with that of bromine.

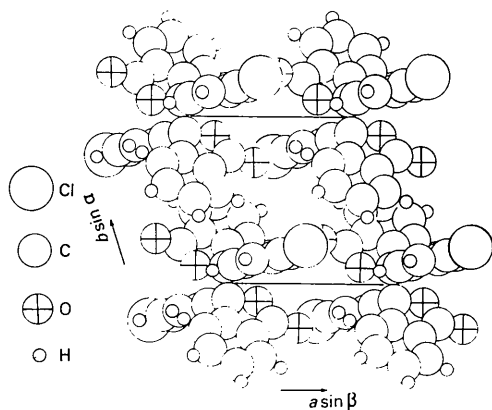


Fig. 5. Arrangement of the molecules in the unit cell as seen normal to the (001) plane.

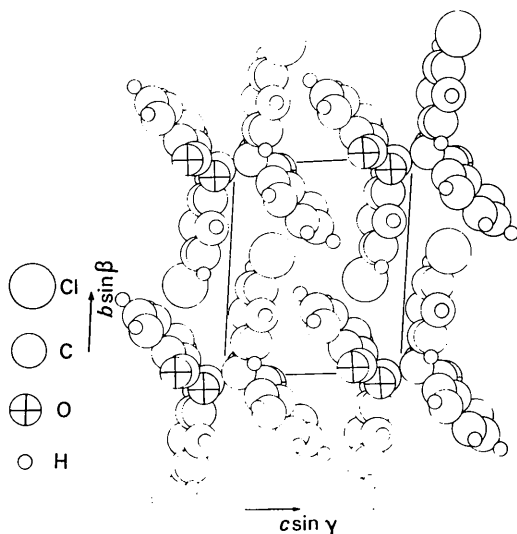


Fig. 6. Arrangement of the molecules in the unit cell as seen normal to the (100) plane.

Thermal vibrations

The single-bond character of the C–C link that connects the centrosymmetrically related halves permits a twisting motion of the two halves about it. Further, the phenyl ring is connected to the fused ring system through a C–C single bond which facilitates rigid body oscillations of the ring. The temperature factors of most of the atoms in the structure can be satisfactorily explained on the assumption that the main contribution to the thermal vibration amplitudes is from these two types of rigid body oscillations.

An examination of Table 3 shows that the chlorine atom attached to the phenyl ring has the largest thermal vibration amplitude in the structure. This is only to be expected when it is remembered that the twisting motion of the two halves of the molecule gives rise to the maximum amplitude of motion to the chlorine atom as it is situated farther away from the centre of the molecule. Further, this atom is endowed with more freedom of motion as it is located at a free end of the molecule. The only other atom which does not form part of any ring system is the lactonic oxygen O(1) and consequently, it has the second largest average B value in the structure.

Among the phenyl carbon atoms, the end atoms C(1), C(2) and C(6) exhibit large vibration amplitudes. C(3) and C(5) are nearer to the centre of the molecule and have lesser temperature factors. C(4) is the phenyl carbon atom nearest to the centre and has the smallest B value. Even a cursory examination clearly shows that the earlier assumption regarding the rigid body oscillations is quite compatible with the observed thermal parameters of these atoms.

In the fused ring system C(10), C(11) and C(12) are farther away from the centre of the molecule and consequently, have the largest thermal vibration amplitudes. It is noticed that this amplitude decreases as one approaches the C(7)–C(7') bond. The carbon atoms C(8) and C(13) have smaller temperature factors than would be expected from the above picture, probably because they are covalently linked to three neighbouring atoms. The slightly higher B value of C(14) compared with those of the neighbouring ring atoms may be explained as due to the fact that the free oxygen atom O(1) is attached to it.

No attempt has, however, been made to explain the thermal oscillations in terms of T and ω tensors (Cruickshank, 1956) as the assumptions involved in the calculation of these tensors are not strictly applicable to the present case.

Molecular packing

The arrangement of molecules in the structure as seen normal to the (001) and (100) planes are shown in Figs. 5 and 6 respectively. The arrangement is similar to that found in the bromine compound. The intermolecular contact distances with a maximum limit specified as 0.2 Å greater than the sum of the van der Waals radii of the relevant atoms are listed in Table 8.

The only distances which are significantly shorter than the sum of the van der Waals radii of the atoms involved are H(3)A—O(1)B and ClA—C(12)F.

Table 8. *Intermolecular contact distances*

Primes refer to atoms related by inversion.

$A = x, y, z$	
$B = 1+x, y, z$	
$C = x, 1+y, z$	
$D = x, y, 1+z$	
$E = 1+x, 1+y, z$	
$F = 1+x, y, 1+z$	
$G = x, 1+y, 1-z$	
C(3)A—O(1)B	3.262 Å
H(3)A—O(1)B	2.355
H(9)A—O(1)B	2.610
C(4)A—C(12')C	3.712
C(4)A—H(12')C	3.020
C(5)A—C(11')C	3.640
C(5)A—H(11')C	3.081
C(5)A—C(12)C	3.537
C(5)A—H(12)C	2.945
C(11)A—C(5')C	3.640
C(12)A—C(14')C	3.763
ClA—H(10)D	2.999
ClA—C(10)D	3.798
C(6)A—C(10)D	3.751
H(5)A—H(6')D	2.553
H(6)A—C(5')D	3.082
H(6)A—C(10)D	2.955
C(2)A—C(10')E	3.643
H(2)A—C(11')E	3.054
H(2)A—C(10')E	2.983
ClA—C(12)F	3.453
ClA—C(1')F	3.691
ClA—C(2')F	3.732
H(11)A—C(11')G	3.143
C(11)A—C(11')G	3.782

The structure can most adequately be described as consisting of close-packed layers of the molecules in the (100) plane repeated periodically along the crystallographic *X* direction. In each layer, each molecule is in contact with six other molecules surrounding it, as required by the theory of close packing of molecules (Kitaigorodskii, 1955). The molecules in this layer, as can be seen from Fig. 6, are very closely packed and obey the principle of 'bumps' in 'hollows'. In three dimensions each molecule is in contact with 12 neighbours at distances $\pm(a, b, c, a+b, a+c$ and $b-c)$, thus giving a molecular coordination number of 12. According to Kitaigorodskii, a coordination number of 12 is assumed to provide adequately close packing. The packing coefficient *k* of the structure defined as

$$k = ZV_0/V,$$

where *Z* is the number of molecules in the cell, *V*₀ the molecular volume and *V* the cell volume (Kitaigorod-

skii, 1955) is 0.68. The corresponding value for the bromine compound is 0.69.

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References

- ASHER, J. D. M. & SIM, G. A. (1965). *J. Chem. Soc.* p. 1584.
 BAUER, H. & ENDRES, G. (1913). *J. prakt. Chem.* **87**, 545.
 BLOW, D. M. (1960). *Acta Cryst.* **13**, 168.
 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.
 CREIGHTON, A. M. & JACKMAN, L. M. (1960). *J. Chem. Soc.* p. 3138.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747.
 CURL, R. F. (1959). *J. Chem. Phys.* **30**, 1529.
 ECKERT, A. & POLLAK, R. (1917). *Mh. Chem.* **38**, 11.
 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.
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.
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.
 KARLE, I. & KARLE, J. (1966). *Acta Cryst.* **20**, 555.
 KARTHA, G. & HAAS, D. J. (1964). *J. Amer. Chem. Soc.* **86**, 3630.
 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.
 MEYER, H. (1904). *Mh. Chem.* **25**, 1177.
 PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746.
 PRZYBYLSKA, M. & AHMED, F. R. (1958). *Acta Cryst.* **11**, 718.
 RISINGER, G. E. & THOMPSON, J. A. (1963). *Rec. Trav. chim. Pays-Bas*, **82**, 801.
 ULLMANN, F. (1896). *Liebig's Ann.* **291**, 17.