In phenothiazine, the three bonds around the N atom are approximately planar in configuration. However, the piperidylmethyl group is in a 'boat-axial' conformation with respect to the thioxanthene ring. The torsion angles of the piperidyl ring and the methylene link between the two ring systems are given in Table 2.

The C–H bond lengths range from 0·84 to 1·14 Å with a mean value of 0·98 Å and a r.m.s. standard deviation of 0·03 Å. The C–C–H bond angles involving benzene rings range from 108 to 131° with a mean value of 120°, and the C–C–H and H–C–H bond angles involving tetrahedral C atoms range from 100 to 125° with a mean value of 109°. The r.m.s. standard deviation of these bond angles is 2°.

The packing of the molecules in the crystal is illustrated in Fig. 3. There are no intermolecular contacts less than van der Waals distances. The closest intermolecular distances are 3·56 and 3·47 Å between C(1) and C′(8) and between C(11) and C′(8) respectively. There is no close contact between the Cl^- and the rest of the molecule. The closest contacts are 3·62 and 3·74 Å between Cl^- and C′(2) and between Cl^- and C(15) respectively.

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References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Chu, S. S. C. (1972). *Acta Cryst.* **B28**, 3625–3632.

Chu, S. S. C. & van der Helm, D. (1975). *Acta Cryst.* **B31**, 1179–1183.

Chu, S. S. C. & van der Helm, D. (1976). *Acta Cryst.* **B32**, 1012–1016.

Chu, S. S. C. & van der Helm, D. (1977). *Acta Cryst.* **B33**, 873–876.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Shiono, R. (1971). Tech. Rep. 49, Crystallography Department, Univ. of Pittsburgh.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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4,4′-Dichlorobiphenyl: Crystal Packing in *para*-Substituted Biphenyls

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Abstract. $C_{12}H_8Cl_2$, monoclinic, $P2_1/n$, $a = 15{\cdot}780$ (4), $b = 13{\cdot}740$ (4), $c = 9{\cdot}682$ (3) Å, $\beta = 96{\cdot}23$ (3)°, $Z = 8$, $M_r = 233{\cdot}10$, $D_c = 1{\cdot}420$, $D_m = 1{\cdot}39$ (1) g cm^{-3}. The molecules are arranged in the unit cell with their long directions approximately parallel to **b**; in projection on the *ac* plane these axes form a pseudohexagonal array. This crystal is isostructural with several other biphenyl derivatives, and like them has a twist angle between the phenyl rings close to the expected mean gas-phase value of 42°.

Introduction. Biphenyl, $C_{12}H_{10}$, has long intrigued chemists since X-ray data suggest that an important conformational change, a decrease in the inter-ring twist angle from 42 to 0°, occurs upon crystallization (Hargreaves & Rizvi, 1962). More recently, a disordered model has been put forth to explain the apparent molecular planarity (Charbonneau & Delugeard, 1977). We decided to study the 4,4′-dihalobiphenyls with the aim of investigating the effect of the size of the *para* substituent on the crystal packing, and consequently on the molecular geometry. Being located on the periphery of the molecule, the halogen atoms should perturb only intermolecular contacts and should have little direct influence on the conformational preference of these biphenyl species.

Preliminary photographs of colorless $C_{12}H_8Cl_2$ crystals grown from benzene showed absences corre-

Table 1. *Cell constants of* 4,4'*-disubstituted biphenyls*

Substituents	Cl,Cl(a)	Br,Br(b)	Br,CN(c)	CH_3,CH_3(d)	F,F(e)	H,H(f)
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/a$	$P2_1/a$
a (Å)	15·780 (4)	15·79 (5)	15·556 (12)	16·11 (2)	7·76 (5)	8·12 (2)
b (Å)	13·740 (4)	14·11 (4)	14·635 (7)	13·67 (3)	5·81 (5)	5·63 (1)
c (Å)	9·682 (3)	9·76 (2)	9·597 (4)	9·77 (1)	9·96 (5)	9·51 (2)
β (°)	96·23 (3)	96·9 (4)	97·66 (9)	94·0 (1)	92·6 (5)	95·1 (3)
Z	8	8	8	8	2	2
V/Z (Å^3)	260·9	269·8	270·7	268·3	224·3	216·5
φ (°)	39,42	38,42	42,42	36,40	*	*

References: (*a*) This work. (*b*) Kronebusch, Gleason & Britton (1976*b*). (*c*) Kronebusch, Gleason & Britton (1976*a*). (*d*) Casalone, Mariani, Mugnoli & Simonetta (1969). (*e*) Halstead, Spiess & Haeberlen (1976). (*f*) Hargreaves & Rizvi (1962).

* Molecules are located at a center of inversion and are probably non-planar and disordered; φ has not been accurately determined.

sponding to the presence of a glide plane and a screw axis. Axes corresponding to space group $P2_1/n$ were chosen since the more conventional $P2_1/c$ cell has a very large β angle.* Absences for the $P2_1/n$ cell are $h0l$, $h + l$ odd, and $0k0$, k odd. The data crystal was bounded by {110} faces and was broken off perpendicular to the elongated **c** direction; its dimensions were 0·26 × 0·26 × 0·41 mm. The cell constants (Table 1) and crystal-orientation matrix were determined by a least-squares fit of the setting angles of eight reflections having 2θ values in the range 21–38°, as measured with Mo $K\alpha$ (λ = 0·7107 Å) radiation on the Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). Intensities of 3696 reflections having $\sin\theta/\lambda \le 0·595$ Å^{-1} were measured in the θ–2θ mode with Nb-filtered Mo $K\alpha$ radiation. Of these, 1654 had $I \ge 3\sigma(I)$ where p was taken as 0·04 in the usual expression for the standard deviation (Brock & Webster, 1976). Data were corrected for decomposition (<10%) and absorption μ = 5·76 cm^{-1}) using the program *DATALIB* by H. A. Levy and R. D. Ellison.

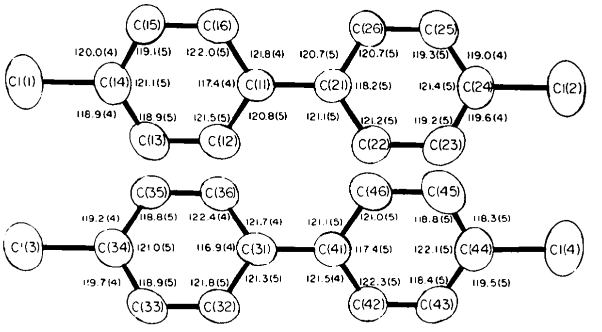

Fig. 1. A drawing of the two independent molecules of $C_{12}H_8Cl_2$ showing the atom-numbering scheme and bond angles (°). In this and the following figures the shapes of the atoms represent 50% probability contours of thermal motion and H atoms have been omitted for the sake of clarity.

The structure was solved by placing idealized C_6H_4 phenyl rings in the positions found for the isostructural 4,4'-dimethylbiphenyl crystal (Casalone, Mariani, Mugnoli & Simonetta, 1969) and Cl atoms at the positions of the *para* methyl groups. In the final cycles the Cl and C atoms were refined independently and anisotropically while the H atoms were fixed 1·04 Å from the C atoms and given isotropic temperature factors 1·0 Å^2 larger than those of the attached C atoms. All crystallographic calculations were performed with programs described previously (Brock & Webster, 1976). Scattering factors were taken from the usual compilation (Cromer & Waber, 1974), and anomalous contributions were included for the Cl atoms. The function minimized in the full-matrix least-squares procedure was $\Sigma\, w(|F_o| - k|F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and k is a variable scale factor; only reflections having $F_o^2 \ge 3\sigma(F_o^2)$ were included. Inspection of the data revealed that the backgrounds around the 101 and $\bar{2}02$ reflections were very unbalanced, and they were therefore omitted from the final cycles.

At convergence $R = \Sigma||F_o| - |F_c||/\Sigma\,|F_o| = 0·042$ and $R_w = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, wF_o^2]^{1/2} = 0·049$ for 1652 reflections and 253 variables; the error in an observation of unit weight was calculated to be 1·46. The peaks and troughs in a final difference electron density map were less than 0·20 e Å^{-3} in size. Of the reflections omitted from the refinement, eight were obviously measured incorrectly [*i.e.* intensity negative by an amount greatly exceeding $3\sigma(F_o^2)$]. Of the others,

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* Cell constants for the corresponding $P2_1/c$ unit cell are a = 9·682, b = 13·740, c = 17·595 Å, β = 116·93°. The two cells are related by the transformation

$$\mathbf{a}_{P2_1/c} = \mathbf{M}\mathbf{a}_{P2_1/n},\ \text{where}\ \mathbf{M} = \begin{vmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & -1 \end{vmatrix}.$$

The general positions in $P2_1/n$ are x,y,z; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\bar{x},\bar{y},\bar{z}$; and $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

Table 2. *Atomic positions* ($\times 10^4$) *for non-hydrogen atoms* (*estimated standard deviations are given in parentheses*)

	x	y	z
Cl(1)	1066 (1)	−1711 (1)	930 (2)
Cl(2)	1527 (1)	5916 (1)	1462 (1)
Cl(3)	1072 (1)	793 (1)	−4149 (2)
Cl(4)	1397 (1)	8417 (1)	−3377 (2)
C(11)	1220 (3)	1568 (3)	1034 (5)
C(12)	681 (3)	1064 (4)	1829 (5)
C(13)	630 (3)	57 (4)	1799 (5)
C(14)	1110 (3)	−450 (4)	936 (6)
C(15)	1636 (3)	23 (4)	123 (5)
C(16)	1691 (3)	1025 (4)	187 (5)
C(21)	1292 (3)	2646 (3)	1118 (4)
C(22)	583 (3)	3223 (4)	1247 (5)
C(23)	651 (3)	4226 (4)	1341 (5)
C(24)	1433 (4)	4652 (4)	1319 (5)
C(25)	2146 (3)	4110 (4)	1194 (5)
C(26)	2075 (3)	3101 (3)	1083 (5)
C(31)	1242 (3)	4068 (3)	−3778 (5)
C(32)	1003 (3)	3498 (4)	−2695 (5)
C(33)	939 (3)	2500 (4)	−2800 (5)
C(34)	1146 (3)	2051 (4)	−3995 (5)
C(35)	1393 (3)	2586 (4)	−5082 (5)
C(36)	1438 (3)	3583 (4)	−4958 (5)
C(41)	1273 (3)	5141 (3)	−3676 (5)
C(42)	1612 (3)	5607 (4)	−2462 (5)
C(43)	1656 (3)	6597 (4)	−2354 (5)
C(44)	1345 (3)	7143 (4)	−3478 (6)
C(45)	1003 (3)	6729 (4)	−4698 (6)
C(46)	977 (3)	5724 (4)	−4798 (5)

Table 3. *Bond lengths* (Å) *in* $C_{12}H_8Cl_2$

Distances enclosed in brackets have been corrected for thermal motion.

C(11)–C(21)	1·487 (6) [1·489]	C(31)–C(41)	1·478 (6) [1·480]
C(11)–C(12)	1·391 (6) [1·399]	C(31)–C(32)	1·394 (6) [1·400]
C(12)–C(13)	1·387 (7) [1·388]	C(32)–C(33)	1·379 (6) [1·380]
C(13)–C(14)	1·376 (7) [1·383]	C(33)–C(34)	1·381 (6) [1·389]
C(14)–C(15)	1·369 (7) [1·375]	C(34)–C(35)	1·374 (6) [1·381]
C(15)–C(16)	1·381 (7) [1·382]	C(35)–C(36)	1·376 (6) [1·378]
C(16)–C(11)	1·383 (6) [1·390]	C(36)–C(31)	1·386 (6) [1·394]
C(21)–C(22)	1·388 (6) [1·395]	C(41)–C(42)	1·394 (6) [1·401]
C(22)–C(23)	1·385 (7) [1·386]	C(42)–C(43)	1·365 (7) [1·368]
C(23)–C(24)	1·369 (7) [1·375]	C(43)–C(44)	1·368 (7) [1·376]
C(24)–C(25)	1·365 (6) [1·373]	C(44)–C(45)	1·368 (7) [1·376]
C(25)–C(26)	1·394 (7) [1·396]	C(45)–C(46)	1·385 (7) [1·387]
C(26)–C(21)	1·389 (6) [1·395]	C(46)–C(41)	1·389 (6) [1·397]
C(14)–Cl(1)	1·733 (5) [1·750]	C(34)–Cl(3)	1·737 (5) [1·753]
C(24)–Cl(2)	1·746 (5) [1·764]	C(44)–Cl(4)	1·754 (5) [1·772]

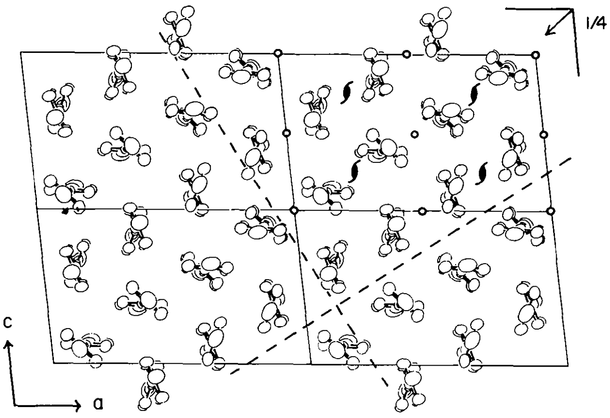

Fig. 2. A projection of the structure perpendicular to **b**. Typical positions of approximate local glide planes relating two independent molecules are indicated by dashed lines.

none had $|F_o^2 - F_c^2| > 4{\cdot}3\sigma(F_o^2)$.* No evidence of extinction was observed and no correction was applied. Atomic coordinates for the non-hydrogen atoms varied in the refinement are given in Table 2. The numbering scheme for the atoms is shown in Fig. 1.

A rigid-body thermal-motion analysis was performed using C. K. Johnson's (1970) program *ORSBA*. A moderate fit (r.m.s. deviations between observed and calculated U_{ij}'s of 0·0028 and 0·0029 Å^2 for the two molecules) was obtained when the twelve C atoms of the two phenyl rings were treated as a single rigid body. The resulting translation tensors are nearly isotropic, having r.m.s. amplitudes of 0·24, 0·23, 0·20 and 0·25, 0·20, 0·20 Å for the two molecules. The libration tensors are more anisotropic, the r.m.s. amplitudes being 6·1, 2·8, 1·1 and 6·3, 2·8, 1·4° respectively. The principal axis for the largest of these is the long molecular axis, which is the direction with the smallest moment of inertia. This model was not significantly improved when the molecule was treated as a segmented body. Distances were corrected for thermal motion and are given in Table 3. The bond angles were not significantly affected; the uncorrected values are shown in Fig. 1. The thermal motions of the Cl atoms, which were not considered in the analysis, are much larger than those of the C atoms. The lengths of the C–Cl bonds were corrected assuming a riding model. A similar analysis was carried out for 4,4′-dimethylbiphenyl using the published thermal parameters (Casalone, Mariani, Mugnoli & Simonetta, 1969). The agreement between observed and calculated values was not as good as in the dichloro case, but the results (*i.e.* magnitudes and anisotropy of translation and libration tensors, and the absence of important differences between the two rings within a single molecule) are the same. None of the other compounds given in Table 1 was refined anisotropically.

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* Lists of structure factors, anisotropic thermal parameters for C and Cl atoms, and calculated parameters for the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33132 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. The crystal structure of 4,4′-dichlorobiphenyl shows significant pseudosymmetry. The long molecular axes of the two independent molecules are nearly parallel to **b**, the deviations being 5 and 4° respectively. Their centers are separated by a translation of approximately $0, \frac{1}{4}, \frac{1}{2}$, and the $0k0$, $k \neq 4n$ reflections are absent. As can be seen in Fig. 2, neighboring molecules of different types are approximately related by local pseudo glide reflections through planes parallel to (101) and ($\bar{1}03$) and by pseudo twofold screw rotations about axes parallel to [101] and [$\bar{1}03$]. The angle between these directions is 90·09°. The result is an approach to orthorhombic symmetry similar to that observed previously in glycolic acid (Ellison, Johnson & Levy, 1971). Fig. 2 also shows the approximate hexagonal close packing of the molecular long axes. Parallel to the *b* axis the molecules are ordered in columns, the molecules within each stack being related by translation only. Each Cl atom lies approximately over the center of an adjacent phenyl ring as can be seen in Fig. 3.

This crystal is isostructural with those of the 4,4′-dibromo-, 4-bromo-4′-cyano-, and 4,4′-dimethylbiphenyl derivatives. The cell constants for these compounds are given in Table 1; it can be seen that changes in bond lengths and van der Waals radii of the substituents are reflected in the unit-cell dimensions. However, when the Cl atoms are replaced by Br atoms the *b* axis does not expand as much as anticipated. Rather the intermolecular halogen contacts in this direction shorten from *ca* 94% of the van der Waals distance (Pauling, 1960) in the dichloro compound to less than 90% of the van der Waals distance in the dibromo crystal, the greater compressibility of the Br atoms allowing the increase in packing efficiency. There is no significant difference in molecular orientation relative to the crystal axes in the series, and in all cases the molecules are linear along their long axes to within a few degrees. The dihedral angles φ between the phenyl rings in these four compounds are all very close to the average gas-phase value of 42° (Almenningen & Bastiansen, 1958).

When F atoms are substituted at the *para* positions the molecules adopt a different packing arrangement which is also found for biphenyl itself (see Table 1). The long molecular axes remain parallel, in this case by symmetry, and the space group is the same, but Z changes from 8 to 2, the molecules line up approximately perpendicular, rather than parallel, to the unique axis, and the twist angle φ between the two rings is almost certainly decreased substantially from its gas-phase value.

A comparison of the two groups of compounds in Table 1 suggests that the $Z = 8$ structure is stabilized by substituents of moderate size at the *para* positions of the phenyl rings; compounds in the $Z = 2$ structure have smaller groups in this location. Since derivatives with electron-withdrawing and electron-releasing groups are found in each structure type, the electronic nature of the *para* substituent seems to be of secondary importance in determining the crystal packing. The $Z = 8$ arrangement is also found for 4,4′-dimethoxybenzophenone (Karle, Hauptman, Karle & Wing, 1958). In spite of the central carbonyl group, this molecule is similar in size and shape to the 4,4′-biphenyl derivatives, and its packing arrangement is apparently also determined by the bulky *para*-substituted phenyl rings.

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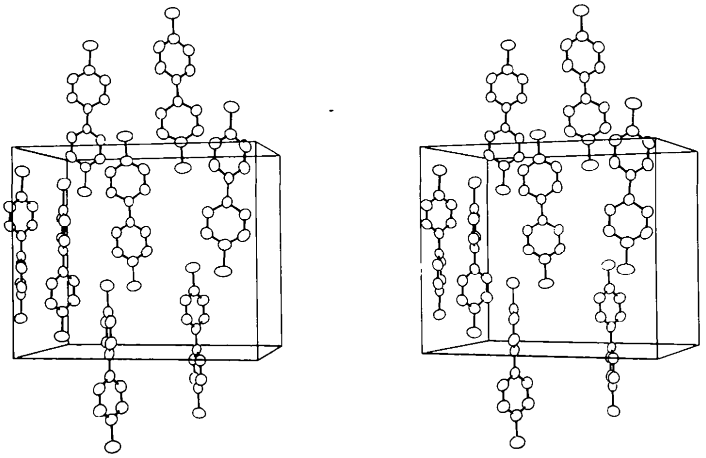

Fig. 3. A stereoscopic view of the unit cell of $C_{12}H_8Cl_2$. The *a* axis is horizontal, the *b* axis is vertical, and the *c* axis points out of the paper.

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References

Almenningen, A. & Bastiansen, O. (1958). *K. Nor. Vidensk. Selsk. Skr.* **4**, 1–16.
Brock, C. P. & Webster, D. F. (1976). *Acta Cryst.* B**32**, 2089–2094.
Busing, W. R., Ellison, R. D., Levy, H. A., King, S. P. & Roseberry, R. T. (1968). *The Oak Ridge Computer-Controlled Diffractometer.* Report ORNL-4143. Oak Ridge National Laboratory, Tennessee.
Casalone, G., Mariani, C., Mugnoli, A. & Simonetta, M. (1969). *Acta Cryst.* B**25**, 1741–1750.
Charbonneau, G.-P. & Delugeard, Y. (1977). *Acta Cryst.* B**33**, 1586–1588.
Cromer, D. T. & Waber, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.
Ellison, R. D., Johnson, C. K. & Levy, H. A. (1971). *Acta Cryst.* B**27**, 333–344.
Halstead, T. K., Spiess, H. W. & Haeberlen, U. (1976). *Mol. Phys.* **31**, 1569–1583.
Hargreaves, A. & Rizvi, S. H. (1962). *Acta Cryst.* **15**, 365–373.
Johnson, C. K. (1970). *Thermal Neutron Diffraction*, edited by B. T. M. Willis, pp. 132–160. Oxford Univ. Press.
Karle, I. L., Hauptman, H., Karle, J. & Wing, A. B. (1958). *Acta Cryst.* **11**, 257–263.
Kronebusch, P., Gleason, W. B. & Britton, D. (1976*a*). *Cryst. Struct. Commun.* **5**, 17–20.
Kronebusch, P., Gleason, W. B. & Britton, D. (1976*b*). *Cryst. Struct. Commun.* **5**, 839–842.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

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1-(α,α-Diphenylmethylene)-1,2-naphthoquinone*

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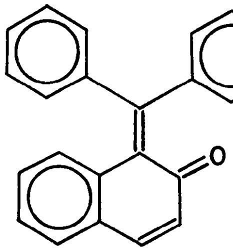
Abstract. $C_{23}H_{16}O$, M_r = 308·4, monoclinic, $P2_1/c$ (C^5_{2h}, No. 14), a = 9·360 (2), b = 10·183 (2), c = 17·823 (3) Å, β = 109·32 (1)°, Z = 4, D_c = 1·28 g cm^{-3}, μ(Mo $K\alpha$) = 0·8 cm^{-1}. The structure of the molecule shows considerable evidence of steric overcrowding at the exocyclic C=C double bond. In addition to a twist around this bond, there is a significant pyramidal distortion at the two sp^2 carbon atoms.

Introduction. The red-orange crystals (m.p. 199–200°C) of 1-(α,α-diphenylmethylene)-1,2-naphthoquinone (I) grow as long rods with well defined faces. The cell constants and intensity data out to $2\theta = 50°$ were obtained on a Picker FACS-1 diffractometer (Mo $K\alpha$, λ = 0·71069 Å) using a crystal of dimensions 0·5 × 0·3 × 0·3 mm. 2435 out of the possible 3703 reflections were above the $2\sigma(I)$ significance level. The structure was determined by direct methods (Germain, Main & Woolfson, 1971), the H atoms were located from a difference map, and the refinement by full-matrix least-squares methods gave final agreement factors of R = 0·060 and R_w = 0·064. The final value of $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m is the number of observations and n is the number of variables, was 1·79. The atomic scattering factors were from the compilation in *International Tables for X-ray Crystallography* (1974). The atomic coordinates are listed in Table 1.†



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* *Chemical Abstracts* name: 1-Diphenylmethylene-2(1*H*)-naphthalenone.

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33143 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.