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4-Bromobiphenyl; an Ordered Crystal with a Structure Similar to that of Biphenyl

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Abstract. $C_{12}H_9Br$, orthorhombic, $Pna2_1$, $a = 7{\cdot}531\,(2)$, $b = 11{\cdot}462\,(3)$, $c = 22{\cdot}219\,(6)$ Å at 152 (5) K, $Z = 8$, $M_r = 233{\cdot}11$, $D_c = 1{\cdot}615$ Mg m^{-3}. Molecules of 4-bromobiphenyl are packed in a layered structure very similar to that of biphenyl itself. The inter-ring dihedral angles of 20·4 and 17·8° for the two independent molecules are greatly compressed from the expected value of *ca* 40° and are among the smallest known for simple biphenyl derivatives.

Introduction. Biphenyl, $C_{12}H_{10}$ (Hargreaves & Rizvi, 1962), has long intrigued chemists because of the apparent decrease of 40° in the inter-ring dihedral angle upon crystallization. Recently this structure has been shown to be complicated by disorder and low-temperature phase changes (Charbonneau & Delugeard, 1976). Morphologically, the 4-bromo derivative of biphenyl appears to be very similar to the parent compound. We hoped that the presence of the Br atom would perturb the structure sufficiently to remove the crystallographic difficulties without leading to gross changes in the molecular packing. If so, the compression of the inter-ring angle upon crystallization could be studied in the absence of the problems associated with the $C_{12}H_{10}$ structure.

Small, colorless, plate-like crystals of $C_{12}H_9Br$ bounded by faces of the forms {120} and {001} were grown from ethanol. One of the more suitable of these poorly diffracting crystals (approximate dimensions 0·20 × 0·20 × 0·02 mm) was mounted on the Enraf–Nonius CAD-4 diffractometer and cooled to 152 (5) K with the LT-1 low-temperature attachment. This compound sublimes so rapidly, even inside capillaries, that room-temperature film work was impossible. The cell constants and crystal system were determined by indexing and refining the setting angles of 22 reflections centered with graphite-monochromatized Mo $K\alpha$ radiation and having $2\theta > 16°$. Intensities of the 1971 unique reflections contained in an octant of reciprocal space and having $\sin\theta/\lambda < 0{\cdot}595$ Å^{-1} (50° 2θ with Mo $K\alpha$) were measured; of these only 620 had $I \geq 3\sigma(I)$ where p was taken as 0·03 in the usual expression for the standard deviation (Brock & Webster, 1976). The data were corrected for absorption ($\mu = 49{\cdot}1$ mm^{-1}) and transmission factors ranged from 0·499 to 0·908.

Inspection of the intensities of various classes of reflections showed systematic absences for $0kl$, $k + l$ odd, and $h0l$, h odd, indicating the space group to be either $Pnam$ or $Pna2_1$. The Patterson function could not be solved in the former; however, when interpreted in the latter, noncentrosymmetric group, the map revealed the positions of two independent Br atoms. The phenyl rings were located in subsequent difference Fourier syntheses. All calculations were performed as described previously (Brock & Webster, 1976). The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o)^2$. Scattering factors were those of Cromer & Waber (1974) and anomalous terms for the Br atoms were included. Contributions were added for H atoms fixed at idealized positions (C–H = 1·00 Å; B's 0·5 Å^2 greater than the average temperature factor of the specific ring). Final agreement indices are $R_1 = \sum||F_o - F_c||/\sum |F_o| = 0{\cdot}052$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o^2|]^{1/2} = 0{\cdot}050$ for 620 data and 114 variables. The final value of R_2 based on F^2 is 0·132 for the 1729 data allowed by the space group; none of the reflections omitted from the refinement had $|F_o^2 - F_c^2| > 3{\cdot}7\sigma(F_o^2)$. The largest peaks in a final difference map have heights less than 0·5 e Å^{-3} and are associated with the Br atoms. No correction for extinction or decomposition appeared necessary. Atomic parameters and their standard deviations are given in Table 1.*

Discussion. The bond lengths and angles of the two independent 4-bromobiphenyl molecules are shown in Fig. 1. The precision of these values is low owing to the limited size of the data set and the severe absorption, but none differs significantly from expected values. The dihedral angles between the planes of the phenyl rings, however, are expected to be less sensitive to the uncertainties in the individual atom positions. The

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* Lists of structure factors and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34914 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional and thermal parameters for the non-hydrogen atoms of* 4-*bromobiphenyl*

Estimated standard deviations in the least significant figure(s) are given in parentheses. The form of the anisotropic thermal ellipsoid is: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10^4.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	0·07155 (39)	−0·16658 (29)	$-\frac{1}{2}$	152 (8)	83 (3)	10·0 (6)	−3 (6)	−4 (2)	4 (2)
Br(2)	0·28268 (35)	0·14843 (27)	−0·12900 (16)	112 (6)	97 (3)	6·6 (5)	9 (5)	−6 (2)	−1 (2)

Table 1 (*cont.*)

	x	y	z	B (Å^2)
C(11)	−0·0416 (32)	−0·1248 (18)	−0·2925 (10)	1·0 (5)
C(12)	−0·0876 (38)	−0·0366 (21)	−0·3318 (11)	2·0 (6)
C(13)	−0·0489 (37)	−0·0499 (21)	−0·3957 (11)	1·8 (6)
C(14)	0·0264 (34)	−0·1486 (26)	−0·4137 (11)	2·1 (6)
C(15)	0·0720 (36)	−0·2373 (23)	−0·3753 (11)	2·0 (5)
C(16)	0·0299 (37)	−0·2291 (21)	−0·3152 (11)	2·0 (6)
C(21)	−0·0793 (37)	−0·1181 (20)	−0·2265 (11)	1·6 (5)
C(22)	−0·1995 (43)	−0·0361 (24)	−0·2044 (13)	3·5 (7)
C(23)	−0·2436 (34)	−0·0284 (22)	−0·1432 (10)	1·4 (6)
C(24)	−0·1505 (31)	−0·0957 (20)	−0·1020 (10)	0·8 (5)
C(25)	−0·0295 (37)	−0·1734 (23)	−0·1205 (13)	3·7 (7)
C(26)	0·0021 (32)	−0·1843 (21)	−0·1852 (11)	1·6 (5)
C(31)	0·4713 (32)	0·1254 (19)	−0·3289 (9)	0·9 (5)
C(32)	0·3852 (34)	0·0321 (21)	−0·3003 (11)	2·0 (6)
C(33)	0·3287 (31)	0·0389 (19)	−0·2411 (10)	0·5 (5)
C(34)	0·3585 (33)	0·1387 (21)	−0·2099 (11)	1·6 (6)
C(35)	0·4452 (34)	0·2355 (20)	−0·2338 (9)	1·2 (5)
C(36)	0·4976 (30)	0·2260 (19)	−0·2953 (9)	0·9 (5)
C(41)	0·5220 (35)	0·1190 (21)	−0·3951 (11)	1·7 (6)
C(42)	0·4579 (33)	0·0331 (20)	−0·4311 (10)	1·2 (5)
C(43)	0·5158 (34)	0·0237 (21)	−0·4907 (15)	2·0 (6)
C(44)	0·6417 (33)	0·1016 (20)	−0·5108 (12)	1·2 (5)
C(45)	0·7071 (37)	0·1857 (21)	−0·4756 (11)	2·5 (6)
C(46)	0·6560 (33)	0·1966 (20)	−0·4154 (10)	1·4 (6)

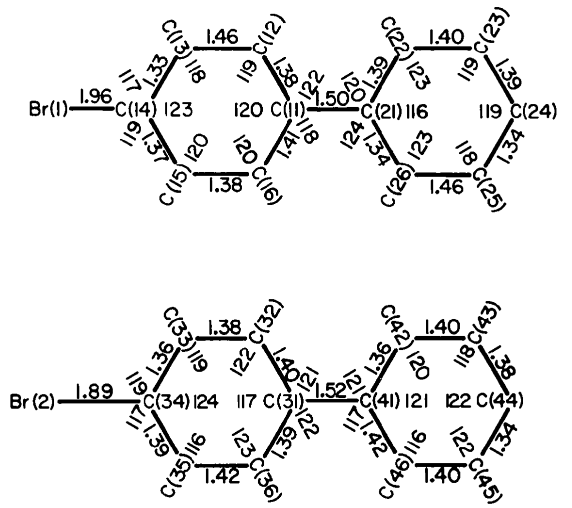

Fig. 1. Diagram showing the atom-numbering scheme, bond lengths (Å), and bond angles (°) in 4-bromobiphenyl. The average standard deviations of the bond lengths and angles are 0·03 Å and 2°.

average deviation of the C atoms from their six-atom least-squares planes is 0·013 Å; the largest such distance is 0·040 Å. The dihedral angles between the two rings of the two independent molecules have values of 20·4 and 17·8°.

The inter-ring angles in 4-bromobiphenyl are among the smallest known for simple *meta* and *para* biphenyl derivatives (perhaps excepting those molecules required to be planar by symmetry; see below). Most such derivatives have considerably larger inter-ring angles which approach the expected gas-phase value of about 40° (Bastiansen, Seip & Boggs, 1971). The isostructural series of derivatives, 4,4′-dichloro-, 4,4′-dibromo-, 4,4′-dimethyl-, and 4-bromo-4′-cyanobiphenyl have angles between 36 and 42° (Brock, Kuo & Levy, 1978, and references therein). The three angles in 1,3,5-triphenylbenzene are also in this range (Lin & Williams, 1975), as is the angle in 4,4′-diamino-3,3′-dimethylbiphenyl (Chawdhury, Hargreaves & Sullivan, 1968). The 4-nitro- (Casalone, Gavezzotti & Simonetta, 1973) and 4,4′-dinitrobiphenyl (Boonstra, 1963) derivatives have somewhat smaller angles of 33°, and in 4,4′-diamino-3,3′-dichlorobiphenyl (Chawdhury, Hargreaves & Rizvi, 1968) the value is 21°. At the other end of the scale are a number of biphenyl derivatives which, like unsubstituted $C_{12}H_{10}$ (Hargreaves & Rizvi, 1962), crystallize with the molecules located at centers of symmetry. Members of this group include 4,4′-difluoro- (Halstead, Spiess & Haeberlen, 1976) and 4,4′-dihydroxybiphenyl (Farag & Kader, 1960) and the linear polyphenyls *p*-terphenyl (Baudour, Delugeard & Cailleau, 1976) and *p*-quaterphenyl (Baudour, Delugeard & Rivet, 1978). Although the center of symmetry implies molecular planarity, the molecules in these crystals are almost certainly disordered and the inter-ring angles are not well determined. In the low-temperature ordered phases of *p*-terphenyl and *p*-quaterphenyl, however, the ten independent angles range from 14 to 27° with an average of 19·7°. These latter values are very similar to those observed for $C_{12}H_9Br$. A recent study of biphenyl at 22 K (Cailleau, Baudour & Zeyen, 1979) gives interplanar angles of 10° for the two independent molecules in the low-temperature cell. At 22 K, however, the phase transformation is not complete and the average torsion angle may continue to increase as the temperature is lowered further.

As the inter-ring angles in $C_{12}H_9Br$ are similar in size to those known for the linear polyphenyls, so are the crystal structures of these compounds related. The packing arrangements in both *p*-terphenyl and *p*-quaterphenyl are the same as in biphenyl itself; their common $P2_1/a$ cell is elongated through the series in the direction of the long molecular axis. The $C_{12}H_9Br$ structure will be compared below with the biphenyl structure measured at 110 K (Charbonneau & Delugeard, 1976).

The overall packing in 4-bromobiphenyl is illustrated in Fig. 2. The molecules form layers perpendicular to *c*. The long molecular axes are perpendicular to *b* to within 5°, but are tipped *ca* 11 and 16° with respect to *c*. Alternate layers are tilted in opposite senses. The two independent molecules are related by approximate 2_1 axes. One such axis passes through $\frac{1}{4}$,0,0·30 and lies in the *ac* plane about 10–15° from *a*. The projection of the structure on the *ab* plane is shown in Fig. 3. The molecules within each layer are seen to form a herringbone arrangement. The layers are then stacked so that each molecule, which has four near neighbors within the layers, also has four near neighbors in each of the adjacent layers.

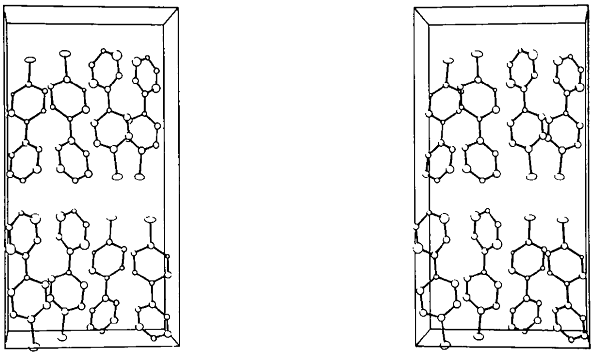
Fig. 2. A stereoscopic view of the unit cell of 4-bromobiphenyl. The *b* axis is horizontal, the *c* axis is vertical, and the *a* axis points out of the plane of the paper. In this and the following drawings the ellipsoids correspond to 50% probability contours of thermal motion and H atoms have been omitted for clarity.

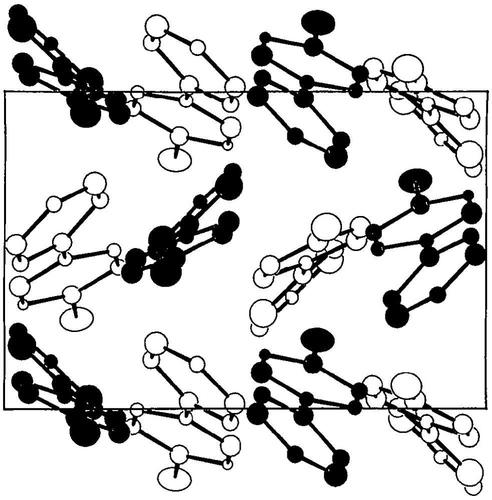
Fig. 3. A projection of the structure of 4-bromobiphenyl. The *a* axis is vertical and the *b* axis is horizontal. The dark and light molecules form layers which are separated by *c*/2.

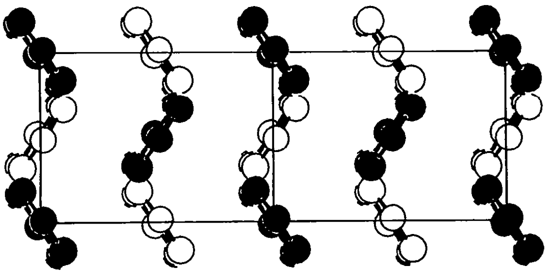
Fig. 4. A projection of the structure of biphenyl (Hargreaves & Rizvi, 1962) viewed parallel to [102]. The *b* axis points vertically upward and the projection of *a* runs from right to left; *a* itself makes an angle of 18·7° with its projection and points into the paper. The dark and light molecules form layers which are related by the lattice translation *c*. Molecules related by *a* are separated by 2·60 Å in the direction normal to the plane of the paper, [102].

The similarity of the $C_{12}H_9Br$ structure to the biphenyl structure, which is illustrated in Fig. 4, is striking. Neither the disposition of the molecules within the layers nor the stacking sequence varies much between the two packing arrangements. Minor differences include the tip of the $C_{12}H_9Br$ molecules mentioned above and the slip of the $C_{12}H_{10}$ molecules within each layer parallel to the long molecular axes. The comparable dimensions of the two structures are given below:

	$C_{12}H_9Br$		$C_{12}H_{10}$
a	7·53 Å	*b*	5·58 Å
b	11·46	$2\lvert b \times [102]\rvert$	14·83
c	22·22	[102]	19·84.

Strong evidence for the close relationship between the two structures is also given by the crystal morphology. Crystals of both compounds grow as thin plates, and in each case the large {001} faces are parallel to the molecular layers. The faces forming the edges of the plates, the {120} faces in $C_{12}H_9Br$ and the {110} in $C_{12}H_{10}$, cut through the layers in the same way, as can be seen from Figs. 3 and 4.

As hoped, the addition of the Br substituent to biphenyl perturbed the structure sufficiently to remove the crystallographic disorder without changing the overall packing. There is no evidence of strong interactions between the Br atoms; the shortest Br···Br contact is 3·73 Å which is only 0·17 Å shorter than twice the van der Waals radius. The stability of the crystals (as judged by ease of sublimation) is decreased by the substitution. Substitution of a Br atom at the *para* position of the second ring results in a gross change in crystal structure in which the layered structure is lost and the inter-ring angles revert to more normal values.

The comparison of the 4-bromo and linear polyphenyl structures suggests that the type of layered packing arrangement found in these compounds is associated with relatively small inter-ring dihedral angles. Apparently, sufficient energy is gained in this type of structure relative to some hypothetical arrangement having less planar molecules to offset the increase in intramolecular energy. The studies of $C_{12}H_9Br$ and of the low-temperature forms of *p*-terphenyl and *p*-quaterphenyl indicate that the average value for the inter-ring angle of molecules crystallizing in this type of structure is 20° and consequently suggest that the angle in biphenyl itself may be of this magnitude.

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References

BASTIANSEN, O., SEIP, H. M. & BOGGS, J. E. (1971). *Perspect. Struct. Chem.* **4**, 60–165.

BAUDOUR, J. L., DELUGEARD, Y. & CAILLEAU, H. (1976). *Acta Cryst.* B**32**, 150–154.

BAUDOUR, J. L., DELUGEARD, Y. & RIVET, P. (1978). *Acta Cryst.* B**34**, 625–628.

BOONSTRA, E. G. (1963). *Acta Cryst.* **16**, 816–823.

BROCK, C. P., KUO, M.-S. & LEVY, H. A. (1978). *Acta Cryst.* B**34**, 981–985.

BROCK, C. P. & WEBSTER, D. F. (1976). *Acta Cryst.* B**32**, 2089–2094.

CAILLEAU, H., BAUDOUR, J. L. & ZEYEN, C. M. E. (1979). *Acta Cryst.* B**35**, 426–432.

CASALONE, G., GAVEZZOTTI, A. & SIMONETTA, M. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 342–345.

CHARBONNEAU, G.-P. & DELUGEARD, Y. (1976). *Acta Cryst.* B**32**, 1420–1423.

CHAWDHURY, S. A., HARGREAVES, A. & RIZVI, S. H. (1968). *Acta Cryst.* B**24**, 1633–1638.

CHAWDHURY, S. A., HARGREAVES, A. & SULLIVAN, R. A. L. (1968). *Acta Cryst.* B**24**, 1222–1228.

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.

FARAG, M. S. & KADER, N. A. (1960). *J. Chem. UAR*, **3**, 1–9.

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.

LIN, Y. C. & WILLIAMS, D. E. (1975). *Acta Cryst.* B**31**, 318–320.

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2,3-Dihydro-3-hydroxy-5*H*-thiazolo[3,2-*a*]pyrimidin-5-one. A 3,S^2-‘Hydroxyethano’ Derivative of 2-Thiouracil

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Abstract. $C_6H_6N_2O_2S$, monoclinic, $P2_1/n$, a = 6·4676 (7), b = 8·268 (1), c = 13·617 (1) Å, β = 100·53 (1)°, V = 716·0 (1) Å^3, Z = 4, D_c = 1·59, D_m = 1·58 Mg m^{-3}. The final R was 0·034 for 846 reflexions. The cyclization through the hydroxyethano bridge changes the geometry of the thiouracil moiety. The pyrimidine ring is nearly planar while the thiazolidine ring adopts a half-chair conformation.

Introduction. Systematic studies on the mechanism of chloroacetaldehyde reactions with nucleic-acid components carried out by Wiewiórowski, Krzyżosiak and their co-workers (Biernat, Ciesiołka, Górnicki, Adamiak, Krzyżosiak & Wiewiórowski, 1978; Biernat, Ciesiołka, Górnicki, Krzyżosiak & Wiewiórowski, 1978; Krzyżosiak, Biernat, Ciesiołka, Górnicki & Wiewiórowski, 1979*a*) have recently led to the conclusion that the thio analogues of pyrimidines and pyrimidine nucleosides also react with chloroacetaldehyde (Krzyżosiak, Biernat, Ciesiołka, Górnicki & Wiewiórowski, 1979*b*) under conditions in which adenosine or cytidine is converted into the so-called ‘etheno’ derivative (Barrio, Secrist & Leonard, 1972). Following a suggestion made by Wiewiórowski and

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