constituées par quatre atomes d'oxygène proches voisins. L'un des sommets est commun avec un octaèdre O(2) ou O(7). Par les trois autres sommets la pyramide est reliée à trois autres pyramides. L'ensemble des groupements TeO_4 constitue ainsi des couches bidimensionnelles parallèles au plan (a,b), observables en coupe sur les Figs. 1 et 2. Ces couches sont reliées entre elles par les groupements MoO_6, soit les atomes O(7) et O(2). Il se constitue ainsi une structure tridimensionnelle avec des liaisons relativement faibles Mo–O(2), Mo–O(7), Te(1)–O(2), Te(2)–O(7) (Tableau 4) mais qui confèrent une dureté plus grande à $MoTe_2O_7$ qu'à MoO_3 (fibreux) ou TeO_2.

Ainsi la structure de $MoTe_2O_7$ diffère notablement de celle des oxydes parents. Bien que la géométrie de l'environnement du molybdène varie peu, les liaisons dans la direction de l'axe **a** se relachent. Le Tableau 5 permet d'observer qu'une liaison Mo–O(6) passe de 2,33 dans MoO_3 à 2,589 Å dans $MoTe_2O_7$. Parallèlement le paramètre de maille **a** passe de 3,962 dans MoO_3 (molybdite) à 4,286 Å dans $MoTe_2O_7$.

Cette étude confirme un certain nombre de données et d'hypothèses émises par Bart *et al.* (1975); on observe bien que le tellure est tétravalent ce qui a été mis en évidence par analyse chimique par ces auteurs. Ainsi l'état du tellure varie peu de TeO_2 à $MoTe_2O_7$. Par contre celui du molybdène est plus notablement affecté.

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Structural Transition in Polyphenyls. III. Crystal Structure of Biphenyl at 110 K

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The crystal structure of biphenyl $C_{12}H_{10}$ has been determined at 110 K by X-ray diffraction. The data are: space group $P2_1/a$, $a = 7·82$ (2), $b = 5·58$ (1), $c = 9·44$ (2) Å, $\beta = 94·62$ (10)°, $Z = 2$. For the anisotropic refinement by block-diagonal least-squares technique, 684 independent reflexions were available. $R_w = 0·06$. A rigid-body model has been used for refinement. A comparison of translational and librational tensors, with those of biphenyl at 293 K and p-terphenyl at 113 K indicates that the structure, given by X-rays, might correspond to a non-equilibrium position.

Introduction

Biphenyl has been reported to be non-planar in the gas phase (Bastiansen & Trætteberg, 1962; Schmid & Brosa, 1972), in solution and in the melt (Barrett & Steele, 1972). A Raman temperature study from about 75 to 15 K reveals an unusual spectral change over this wide temperature region (Friedman, Kopelman & Prasad, 1974). Electron paramagnetic resonance and electron nuclear double resonance studies (Brenner, Hutchison & Kemple, 1974), at 1·9 K, show that the molecule does not have the idealized symmetry *mmm*. A two-dimensional structure analysis at room temperature (Trotter, 1961; Hargreaves & Rizvi, 1962) indicates that the molecules lie on symmetry centres and that the two phenyl rings in each molecule are coplanar.

A possibility is that the planar configuration given by X-rays is a statistically-centred arrangement: the two phenyl rings rotate independently around the single bond in a double minimum potential, so that at low temperature each ring occupies one of the two possible wells. In this case a structural change characterized by the molecule becoming non-centrosymmetric occurs in the crystal. Such a symmetry modification has been found with p-terphenyl (Baudour & Charbonneau, 1974; Baudour, Delugeard & Cailleau, 1976) and quaterphenyl (Delugeard, Desuché & Baudour, 1976). The present study of biphenyl has been undertaken at 110 K in order to obtain more accurate structural and thermal parameters and to examine the X-ray evidence for the planarity of the molecule in the solid phase.

Experimental

Crystals of biphenyl from a methanol solution are colourless large plates or thin needles elongated along the crystallographic b axis. Attempts to cut crystals to a size suitable for X-ray analysis were unsuccessful, because the crystals were easily damaged under very slight stress. For this reason, a needle of $10 \times 0.30 \times 0.20$ mm was used for the data collection. The specimen was sealed in a Lindemann glass capillary and mounted with $\mathbf{b}$ parallel to the φ axis of the goniostat.

The unit-cell dimensions were determined by a least-squares analysis of 23 reflexions measured on a three-circle diffractometer.

Crystal data at 110 K:
$a = 7.82$ (2), $b = 5.58$ (1), $c = 9.44$ (2) Å
$\beta = 94.62$ (10)°, space group $P2_1/a$, $Z = 2$
$M = 154.2$, $D_c = 1.25$ g cm^{-3}
$\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.76$ cm^{-1}.

The intensities were measured on an Enraf–Nonius three-circle automatic diffractometer with Zr-filtered Mo $K\alpha$ radiation, and θ–2θ scanning method (scan range $1.20°$). The crystal was cooled in a stream of cold nitrogen gas (van Bolhuis, 1971). The fluctuation in intensity of one standard reflexion measured after every 50 reflexions, over the period of data collection, was not larger than 8%. Of the 743 reflexions measured with $2\theta < 70°$, 684 were used for structure refinement. Corrections for the change in the volume of the crystal bathed by the X-ray beam were applied to the measured intensities; absorption effects were neglected.

Structure refinement

The refinement by the least-squares program *ORFLS* (Busing, Martin & Levy, 1962) started with the atomic coordinates given by Trotter (1961). With anisotropic temperature factors for the carbon atoms, and without a weighting scheme, some cycles stabilized the residual to the value $R = 0.15$. At this stage, the *ANHAR* program (Baudour, 1972) based on Kay & Behrendt's formula (Kay & Behrendt, 1963) was introduced in the refinement. This program used for p-terphenyl and quaterphenyl includes translational and librational

tensors of the assumed rigid-body molecule in the structure factor expression, and takes the internal degree of freedom due to the single bond into account. A weighting scheme was then employed in which $w = 1/\sigma^2(|F_o|)$ and $\sigma^2(|F_o|) = (1/N) (F_o^2/4I^2) (CN + B_1 + B_2 + I^2/400)$. CN is the total number of counts collected during the scan, B_1 and B_2 are the background counts, I is the net intensity and N is the number of cycles of measurements for the reflexion. The final values of agreement indices were: $R_1 = \sum w(|F_o| - |F_c|)/\sum w|F_o| = 0.066$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2} = 0.075$.* Final positional parameters appear in Table 1, with their estimated standard deviations. The interatomic distances and bond angles are given in Fig. 1.

Results and discussion

Bond lengths and angles

The shorter intermolecular distances are shown in Fig. 2. From this can be seen a remarkable similarity
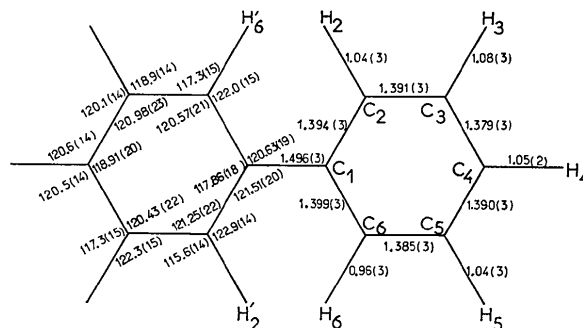
Fig. 1. Bond lengths (Å) and angles (°) of biphenyl. Estimated standard deviations are in parentheses.
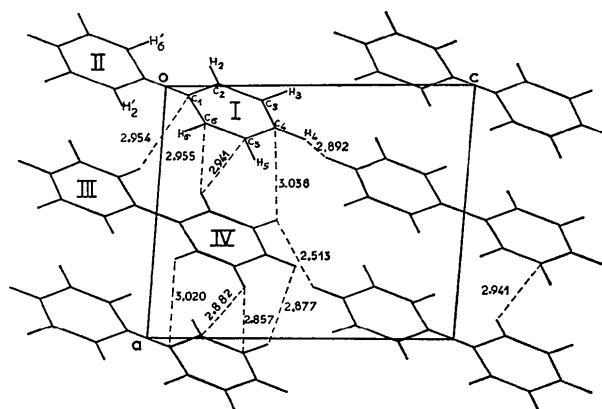
Fig. 2. A projection of the molecular arrangement along the b axis.

Table 1. *Final atomic parameters* ($\times 10^4$) *of biphenyl*

Estimated standard deviations are given in parentheses.

	x	y	z
C(1)	354.9 (27)	−9.8 (42)	759.6 (19)
C(2)	−50.3 (31)	1783.3 (47)	1704.8 (22)
C(3)	600.9 (32)	1743.3 (47)	3120.0 (23)
C(4)	1670.2 (30)	−85.5 (46)	3621.1 (22)
C(5)	2093.2 (32)	−1876.9 (47)	2687.4 (23)
C(6)	1438.8 (30)	−1859.2 (44)	1279.8 (22)
H(2)	−745 (38)	3316 (53)	1386 (27)
H(3)	305 (39)	3121 (54)	3868 (27)
H(4)	2149 (31)	−133 (45)	4697 (24)
H(5)	2916 (38)	−3261 (56)	3042 (25)
H(6)	1707 (36)	−3197 (50)	704 (25)

of the arrangement of molecules for biphenyl, p-terphenyl and quaterphenyl. The aromatic ring carbon–carbon bond distances are normal. They vary from 1·379 Å to 1·399 Å. In particular the C(2)–C(3) and C(5)–C(6) distances are significantly different from those obtained at room temperature by Trotter (1961) and Hargreaves & Rizvi (1962) (1·406, 1·425 Å and 1·418, 1·423 Å respectively). The mean estimated standard deviation is 0·0031 Å in bond lengths and 0·21° in bond angles involving only carbon atoms. It is interesting to note the endocyclic bond angles: the angles situated on the long molecular axis are smaller than 120° (118·9° and 117·9°), while the other angles at C(2), C(3), C(6), C(5) are slightly greater (121·5°, 120·4°, 121·0°, 120·6°); this feature has been observed in p-terphenyl, quaterphenyl, and in some other substitued polyphenyls (Casalone, Mariani, Mugnoli & Simonetta, 1969; Domenicano, Vaciago & Coulson, 1975).

The least-squares mean planes relative to the biphenyl molecule and deviations of atoms from these planes are given in Table 2. The maximum deviation is 0·0049 Å for the carbon atoms. However the hydrogen atoms H(2) and H(6) deviate significantly from this plane (0·102 Å and 0·063 Å respectively). This feature can be explained by a steric repulsion between the hydrogen atoms H(2)–H'(6) and H'(2)–H(6). The H(2)–H'(6) distance in a regular model is 1·80 Å, while the distance calculated from the coordinates of Table 1 is 2·056 Å. This increase is in agreement with the opening of angles C(1)–C(2)–H(2) = 122·9° and C(1)–C(6)–H(6) = 122·0°. It must be noted that the average value of the other hydrogen–hydrogen distances is 2·40 Å.

Table 2. *Least-squares planes of the molecule with atomic deviations* (Å)

The plane constants $(Ax + By + Cz = D)$ are referred to crystal axes a,b,c* and coordinates in Å.

(I) Carbon atoms C(1) to C(6):
$0·8144X + 0·5291Y - 0·2383Z = 0·0052.$
(II) 12 carbon atoms of the molecule:
$0·8138X + 0·5291Y - 0·2402Z = 0·0000.$

	(I)	(II)		(I)	(II)
C(1)	0·0064	0·0043	H(2)	0·1023	0·1055
C(2)	0·0015	0·0038	H(3)	0·0036	0·0020
C(3)	-0·0005	-0·0009	H(4)	-0·0198	-0·0237
C(4)	-0·0027	-0·0046	H(5)	0·0190	0·0175
C(5)	0·0049	0·0045	H(6)	-0·0634	-0·0603
C(6)	-0·0039	-0·0016			

All the intermolecular distances correspond to normal van der Waals interactions.

Thermal motions

A comparison of the translational and librational tensors of biphenyl at 110 K with those of biphenyl at 293 K and p-terphenyl at 113 K shows some interesting features (Table 3).

Table 3. *Molecular thermal motion tensors*

The axes are OX perpendicular to molecular plane
OY in the direction of the long molecular axis
$OZ = OX \wedge OY.$

Standard deviations are given in parentheses.

Translation ($\times 10^4$ Å²)			
	Biphenyl 110 K (a)	Biphenyl 290 K (b)	p-Terphenyl 113 K (c)
T_{11}	133 (10)	470 (60)	70 (30)
T_{22}	281 (4)	560 (20)	230 (10)
T_{33}	216 (8)	320 (50)	250 (20)
T_{12}	7 (3)	50 (20)	-40 (40)
T_{13}	20 (4)	-30 (20)	-40 (40)
T_{23}	15 (4)	-50 (20)	20 (10)

Librations (°)²			
L_{11}	3·45 (0·40)	8·0 (1·8)	1·04 (0·4)
L_{22}	45·70 (2·06)	105·9 (10·7)	19·3 (8·0) central ring 12·1 (5·9) outer ring
L_{33}	2·46 (0·43)	11·1 (2·2)	0·99 (0·5)

(a) Present work; (b) Messager, Sanquer, Baudour & Meinnel (1973) from Hargreaves & Rizvi's (1962 data). (c) Baudour *et al.* (1975).

The results concerning translational tensors at low temperature are very similar for both biphenyl and p-terphenyl studies. The term L_{22} which corresponds to a libration around the long axis of the molecule appears with an unusually large value 45·70(°)² in biphenyl, when compared with the corresponding libration motion in p-terphenyl, 19·3(°)² and 12·1(°)², calculated with a non-planar molecule in the ordered phase.

Thus the planar configuration given by X-rays at 110 K would still correspond to a non-equilibrium position. At about 75 K a structural change would then occur so that the molecule would become non-centrosymmetric in the crystal. This hypothesis would be in agreement with Raman infrared, EPR and ENDOR studies.

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1,7-Dibromo-4-dibromomethyl-3,3-dimethylnorbornan-2-one

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$C_{10}H_{12}Br_4O$, orthorhombic, $P2_12_12_1$, $a=10\cdot270$ (2), $b=26\cdot614$ (7), $c=9\cdot881$ (3), Å, $d_x=2\cdot30$ g cm^{-3}, $Z=8$, μ(Cu $K\alpha$) = 153·6 cm^{-1}. The norbornane skeleton is slightly twisted in both independent molecules with normal bond lengths and angles. The C–C–C bridge angles are 97 and 95° respectively.

Introduction

Small, colourless, well formed crystals were obtained by slow crystallization from a solution in diethyl ether. The density was measured as approximately 2 g cm^{-3} by flotation in aqueous thallous formate. Unit-cell and intensity data were measured on a Datex-automated G.E. XRD 6 diffractometer using Cu $K\alpha$ radiation and the θ–2θ scan technique. Unit-cell parameters were refined by least squares from the observed 2θ values of 17 reflexions. A standard reflexion monitored periodically throughout the data collection decreased in intensity by 21% and the data were accordingly scaled. Of the 2297 independent reflexions with $2\theta < 120°$, 1529 had intensities greater than $3\sigma(I)$ above background $[\sigma^2(I) = S + B + (0\cdot04S)^2$, where S=scan and B=background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. Owing to the high value of the absorption coefficient and the crystal dimensions $(0\cdot016 \times 0\cdot019 \times 0\cdot022$ cm) an absorption correction was applied by a computer program using a Gaussian integration method (Coppens, Leiserowitz & Rabinovich, 1965; Busing & Levy, 1957).

The structure was solved by direct methods using symbolic addition and tangent refinement techniques. Origin-defining reflexions and starting symbols for this procedure were chosen manually. The eight Br atoms were located on the best E map and the solution proceeded by conventional Fourier methods. The non-hydrogen atoms were refined by the full-matrix least-squares procedure where the function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F)$, where $\sigma(F)$ values were derived from the previously calculated

$\sigma(I)$ values. All non-hydrogen atoms were included with anisotropic temperature factors and the scattering factors for Br were corrected for anomalous dispersion. H atoms were included in the structure-factor calculations with calculated geometry and fixed posi-

Table 1. *Final positional parameters (fractional* $\times 10^4$) *with estimated standard deviations in parentheses*

	x	y	z
Br(1)	8807 (2)	7009 (1)	8365 (3)
Br(2)	6418 (3)	6855 (1)	10931 (3)
Br(3)	6059 (4)	7727 (1)	4291 (3)
Br(4)	7172 (3)	6661 (1)	4945 (3)
Br'(1)	9133 (3)	5500 (1)	5525 (3)
Br'(2)	6612 (3)	5559 (1)	8024 (3)
Br'(3)	13293 (3)	5050 (1)	8318 (4)
Br'(4)	12259 (3)	6087 (1)	7211 (4)
C(1)	6135 (25)	7168 (9)	9242 (23)
C(2)	6394 (27)	7723 (10)	9205 (31)
C(3)	6467 (24)	7889 (7)	7698 (30)
C(4)	6404 (23)	7357 (7)	6989 (23)
C(5)	4950 (24)	7161 (9)	7132 (31)
C(6)	4738 (24)	7093 (10)	8630 (27)
C(7)	6927 (22)	6984 (9)	8008 (23)
C(8)	5328 (25)	8248 (9)	7539 (33)
C(9)	7695 (27)	8188 (9)	7416 (27)
C(10)	6974 (24)	7317 (10)	5563 (26)
O	6550 (17)	7984 (7)	10153 (21)
C'(1)	8358 (22)	5367 (8)	8317 (25)
C'(2)	8573 (19)	4811 (10)	8124 (23)
C'(3)	10095 (21)	4724 (9)	8074 (28)
C'(4)	10570 (20)	5300 (7)	8094 (24)
C'(5)	10420 (25)	5522 (10)	9526 (23)
C'(6)	8887 (22)	5519 (10)	9758 (28)
C'(7)	9427 (25)	5590 (8)	7409 (28)
C'(8)	10456 (25)	4413 (10)	9287 (31)
C'(9)	10510 (23)	4421 (8)	6811 (26)
C'(10)	11928 (18)	5380 (10)	7421 (25)
O'	7807 (15)	4475 (6)	7988 (19)