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Structural Transition in Polyphenyls. II.* The Crystal Structure of the High-Temperature Phase of Quaterphenyl

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The crystal structure of quaterphenyl has been refined from new data collected at room temperature on a single-crystal diffractometer with a program taking account of curvilinear motions in the structure factor expression. 777 independent reflexions were used to yield a final R_w value of 0·045. A comparison is made between thermal-motion tensors of quaterphenyl and *p*-terphenyl. Translational terms are very similar for the two molecules. Librational terms about the directions perpendicular to the long molecular axis are approximately inversely proportional to the moments of inertia. Those of quaterphenyl are half those of *p*-terphenyl. For librations about the long molecular axis, the quaterphenyl central rings exhibit a large amplitude, $\langle\varphi^2\rangle = 178(°)^2$, which is however smaller than the exceptional value of $\langle\varphi^2\rangle = 260(°)^2$ for *p*-terphenyl. This is interpreted as resulting from a dynamic disorder, the rings oscillating in a double-well potential. The observation at 110 K of a superstructure confirms this interpretation.

Introduction

Refinement of the quaterphenyl [*p,p'*-bis(phenyl)-biphenyl] structure has been carried out to study the thermal vibrations of this compound and to compare them with those of isomorphous products: biphenyl (Messager, Sanquer, Baudour & Meinnel, 1973), *p*-terphenyl (Baudour, 1972; Baudour, Delugeard & Sanquer, 1974).

For these compounds, X-ray analysis at ordinary temperature assigns to the molecule a planar configuration associated with a high librational amplitude φ about the long axis: $\langle\varphi^2\rangle$ is 106 $(°)^2$ for biphenyl, 70 $(°)^2$ for the *p*-terphenyl outer ring. This amplitude becomes exceptionally high for the *p*-terphenyl central ring: $\langle\varphi^2\rangle = 260$ $(°)^2$. The unusual thermal motion found in this case reveals a dynamic disorder: the central ring moves in a double potential well and the planar configuration is only an average which does not correspond to a stable equilibrium in the crystal. At ordinary temperatures, both wells are randomly occupied. At low temperatures, the stabilization of the rings in one of these two wells results in the appearance of an ordered phase where the non-planarity of the molecules becomes obvious (Baudour, Delugeard & Cailleau, 1975). Therefore the thermal motion in quaterphenyl has been compared with that of other polyphenyls. For this, the crystal structure of quaterphenyl has been firstly refined from new experimental data.

Experimental

The quaterphenyl crystals were grown by sublimation. A crystal of approximate dimensions 0·6 × 0·3 × 0·1 mm was used both for lattice-constant determination and for intensity collection. The crystal system is

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* Part I: *Acta Cryst.* B**32**, 150–154.

monoclinic. Cell constants were obtained by a least-squares refinement from the positions of 39 reasonably intense reflexions.

Crystal data

$a=8\cdot110$ (6), $b=5\cdot610$ (4), $c=17\cdot910$ (10) Å, $\beta=95\cdot80$ (6)°. Space group $P2_1/a$, $Z=2$, $D_c=1\cdot25$ g cm^{-3}.

The intensities were collected on an Enraf–Nonius three-circle automatic diffractometer with Zr-filtered Mo $K\alpha$ radiation and the θ–2θ scan mode. In the range of measurements $2\cdot5° < \theta < 35°$, 777 reflexions were used in the crystal analysis, of which 660 had intensities above background. A control reflexion was measured every 50 reflexions and showed no significant change during data collection. Absorption effects were neglected ($\mu_r=0\cdot76$ cm^{-1} for Mo $K\alpha$ radiation).

Structure refinement

From the final coordinates of the 12 C atoms given by Pickett (1936) the structure was firstly refined by the least-squares program *ORFLS* (Busing, Martin & Levy, 1962). Some cycles of refinement with anisotropic temperature factors for C atoms reduced R from 0·26 to 0·17. At this stage the refinement was continued with the program *ANHAR* (Baudour, 1972) previously used for *p*-terphenyl. This program is based on Kay & Behrendt's formula and includes translational and librational tensors in the structure factor expression.

The nine H atoms of the half-molecule have been introduced at their theoretical positions and alternately refined with the C atoms. Under these conditions, the refinement was complete after a few cycles. The final

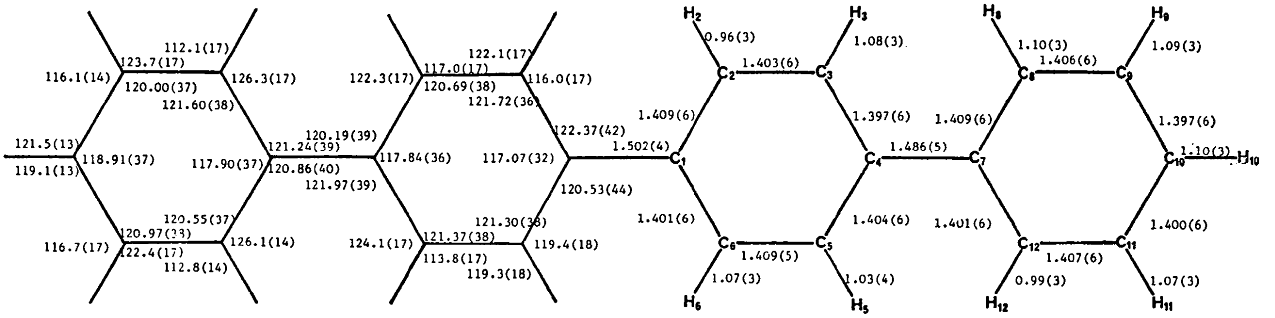

Fig. 1. Bond lengths (Å) and angles(°) in quaterphenyl. The corresponding e.s.d.'s are given in parentheses and refer to the last decimal positions.

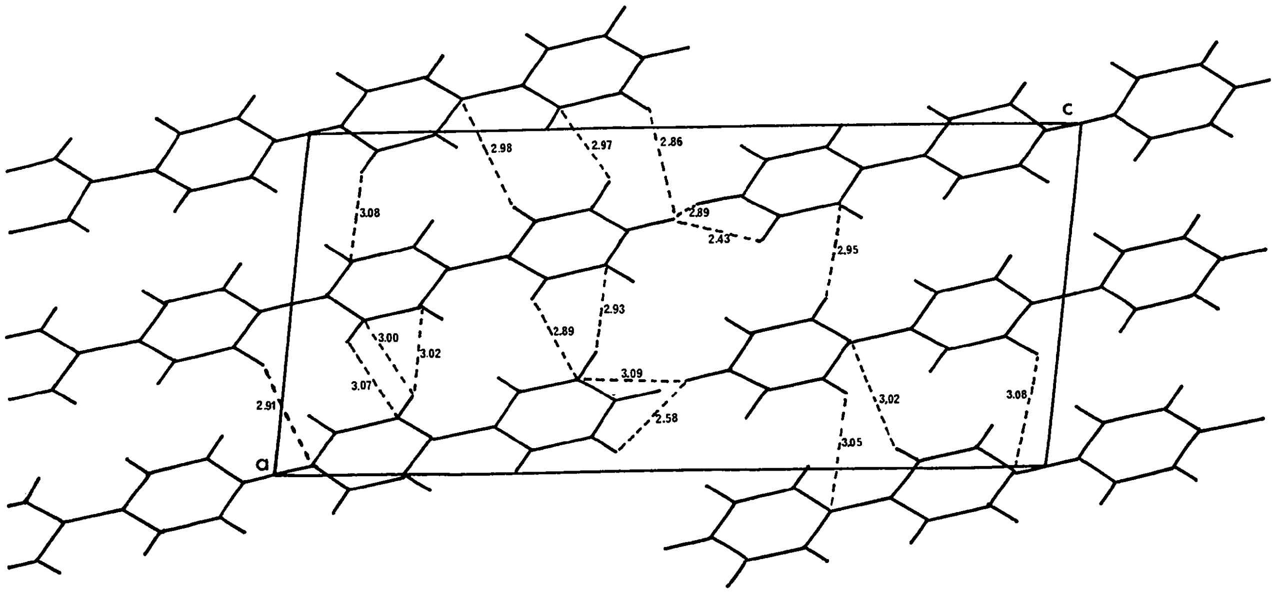

Fig. 2. Projection of the crystal structure on the (010) plane, showing some of the intermolecular contacts.

agreement indices are $R_1=\sum w||F_o|-|F_c||/\sum w|F_o|=0{\cdot}032$, $R_2=|\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2|^{1/2}=0{\cdot}045$.

During refinement the weighting scheme was

$$w^{-1}=\sigma^2(|F_o|)=\frac{1}{N}\frac{F_o^2}{4I^2}\left(\mathrm{CN}+B_1+B_2+\frac{I^2}{400}\right)$$

where 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 measurement for the reflexion. The final coordinates are shown in Table 1, the bond distances and angles in Fig. 1. Fig. 2 shows the structure projected on (010) with some intermolecular contacts.*

Table 1. *Final fractional atomic coordinates with e.s.d.'s in parentheses*

	x	y	z
C(1)	−0·02032 (59)	−0·00025 (103)	0·04000 (16)
C(2)	0·04117 (49)	0·17999 (80)	0·09007 (24)
C(3)	0·00559 (46)	0·18121 (70)	0·16513 (25)
C(4)	−0·09063 (50)	0·00252 (85)	0·19342 (21)
C(5)	−0·15008 (49)	−0·18048 (79)	0·14438 (22)
C(6)	−0·11511 (46)	−0·18049 (72)	0·06891 (21)
C(7)	−0·12802 (52)	0·00027 (85)	0·27295 (21)
C(8)	−0·06523 (48)	−0·17870 (72)	0·32338 (26)
C(9)	−0·10040 (48)	0·17473 (74)	0·39867 (24)
C(10)	−0·19623 (50)	−0·00718 (84)	0·42545 (22)
C(11)	−0·26237 (47)	−0·18228 (72)	0·37541 (25)
C(12)	−0·22547 (47)	−0·17969 (72)	0·30033 (25)
H(2)	0·1088 (43)	0·3042 (58)	0·0725 (16)
H(3)	0·0424 (46)	0·3429 (63)	0·1949 (16)
H(5)	−0·2174 (48)	−0·3216 (64)	0·1617 (16)
H(6)	−0·1668 (43)	−0·3100 (57)	0·0293 (16)
H(8)	−0·0021 (40)	0·3433 (58)	0·3086 (14)
H(9)	−0·0542 (43)	0·3102 (64)	0·4390 (15)
H(10)	−0·2303 (30)	0·0030 (43)	0·4832 (15)
H(11)	−0·3469 (41)	−0·3047 (58)	0·3967 (13)
H(12)	−0·2743 (40)	−0·3180 (58)	0·2716 (14)

Description of the structure

The C–C bond lengths in the two benzene rings are in the range 1·397–1·409 Å and agree well with the 1·398 Å expected value. The endocyclic bond angles on the long molecular axis are less than the normal 120° value (they vary from 117·07 to 118·91°) while those situated out of this long molecular axis are equal to or greater than 120° (in the range 120·00–121·72°). This result agrees with those obtained for biphenyl (Robertson, 1961; Trotter, 1961), *p*-terphenyl (Baudour, 1972) and for some other polyphenyls (Domenicano, Vaciago & Coulson, 1975).

The C–H bond lengths vary from 0·96 to 1·10 Å and their mean is 1·05 Å. Here the agreement is satisfactory, the H atoms being difficult to locate by X-ray diffraction.

The equation of the least-squares plane through the two aromatic rings and the distances of atoms from this plane are listed in Table 2. The molecule is approximately planar, the largest deviation being 0·02 Å. The angle between the two benzene ring planes is 1·37°. Allowing for the standard deviations on atomic coordinates, this value agrees with a planar configuration of the molecule. A comparable result has been obtained for *p*-terphenyl where the angle between the outer and central rings is also about 1°.

Table 2. *Least-squares plane of the molecule and deviations of atoms from this plane*

X,Y,Z are expressed in Å relative to orthogonal axes parallel to **a**, **b** and **c***.

Plane through atoms C(1)–C(12)

$$-0{\cdot}80163X+0{\cdot}54375Y-0{\cdot}24844Z=0{\cdot}01095$$

C(1)	0·0014 Å	C(7)	0·0099 Å
C(2)	0·0024	C(8)	−0·0041
C(3)	0·0141	C(9)	−0·0116
C(4)	0·0103	C(10)	−0·0232
C(5)	−0·0154	C(11)	0·0216
C(6)	−0·0182	C(12)	0·0130
H(2)	−0·0061	H(8)	0·1319
H(3)	0·1796	H(9)	−0·0187
H(5)	−0·0595	H(10)	0·0576
H(6)	0·0409	H(11)	0·1343
		H(12)	−0·0061

Translational and librational tensors

Table 3 compares translational and librational tensors for quaterphenyl and *p*-terphenyl. The analogy between the translational amplitudes is explained by the similarity of the molecular arrangements in the two systems. Concerning librations, the Ω_{11} et Ω_{33} terms define motions about axes perpendicular to the long molecular axis and do not interfere with the internal dynamics of the benzene rings. Square amplitudes for quaterphenyl are about half those of *p*-terphenyl. They are approximately inversely proportional to the moments of inertia, as expected. In these two isostructural systems, the force constants involved are approximately equal. The Ω_{22} term corresponds to librations about the long molecular axis. For these motions the quaterphenyl and *p*-terphenyl molecules

Table 3. *Molecular thermal motion tensors*

The axes are OX perpendicular to molecular plane, OY in the direction of the long molecular axis, $OZ=OX\wedge OY$. The direction cosines of OX,OY,OZ in a,b,c^* are respectively −0·800, +0·545, −0·251, −0·296, +0·005, +0·955, +0·521, +0·839, +0·157. The standard deviations are given in parentheses.

Translation

	Quaterphenyl		*p*-Terphenyl
T_{11}	320 (15) 10^{-4} Å^2	T_{11}	335 (13) 10^{-4} Å^2
T_{22}	442 (6)	T_{22}	416 (6)
T_{33}	378 (11)	T_{33}	356 (10)
T_{12}	21 (6)	T_{12}	20 (5)
T_{13}	10 (5)	T_{13}	8 (6)
T_{23}	−3 (5)	T_{23}	−12 (5)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31257 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3 (*cont.*)

Libration

	Quaterphenyl		*p*-Terphenyl
Ω_{11}	1·43 (0·16) $(°)^2$ ($I_X=12{\cdot}8\ 10^{-44}$ kg m^2)	Ω_{11}	3,58 (0·20) $(°)^2$ ($I_X=5{\cdot}5\ 10^{-44}$ kg m^2)
Ω_{22}	178·3 (4·7) (central ring)	Ω_{22}	260·3 (7·5) (central ring)
Ω_{22}	71·5 (4·6) (outer ring)	Ω_{22}	68·9 (3·8) (outer ring)
Ω_{33}	1·59 (0·16) ($I_Z=12{\cdot}0\ 10^{-44}$ kg m^2)	Ω_{33}	2·74 (0·27) ($I_Z=5{\cdot}0\ 10^{-44}$ kg m^2)

are not rigid because of the important part of torsional movements of rings. In *p*-terphenyl the very large value of Ω_{22} for the central ring cannot be interpreted as resulting from usual harmonic motion even when taking into account low-frequency internal modes (Baudour *et al.*, 1974). Only a dynamic disorder can explain this result. The central ring moves in a double potential well whose minima are located at about 15° on either side of the mean position determined by X-ray diffraction. In quaterphenyl the value of Ω_{22} for the inner ring, 178 $(°)^2$, although smaller than that in *p*-terphenyl is, however, large and shows unusual librational behaviour. Because of the similarity between the two molecular configurations we can interpret this as resulting from a dynamic disorder similar to that of *p*-terphenyl. Consequently for the two quaterphenyl central rings it can be shown that the minima of the double potential well are at about 11° on either side of the mean position determined by X-ray diffraction.

Structural transition in quaterphenyl

Oscillation and Weissenberg photographs obtained at low temperature (110 K) with the Renaud–Fourme apparatus (Renaud & Fourme, 1967) revealed a pseudomonoclinic superstructure. Neglecting the thermal contraction, this supercell corresponds to a doubling of the *a* and *b* high-temperature cell parameters. This structural transition is comparable to that existing in *p*-terphenyl (Baudour *et al.*, 1975). Three-dimensional measurements are now in progress.

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Sodium Silicate Hydrates. V. The Crystal Structure of $Na_2O.SiO_2.8H_2O$

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The title compound is monoclinic, $P2_1/c$, $a=8{\cdot}96$, $b=13{\cdot}54$, $c=9{\cdot}99$ Å, $\beta=119{\cdot}6°$, $Z=4$. X-ray analysis shows that its constitutional formula is $Na_2(H_2SiO_4).7H_2O$; it thus resembles other members of the series $Na_2O.SiO_2.nH_2O$ in containing isolated $H_2SiO_4^{2-}$ groups. Each Na is surrounded, roughly octahedrally, by six O atoms, mostly of water molecules. The geometries of the $H_2SiO_4^{2-}$ groups and of the Na–O frameworks of all the known members of the series are compared.

Introduction

The structures of all except one of the series of sodium silicate hydrates $Na_2O.SiO_2.nH_2O$ have been determined and the constitutional formulae shown to be $Na_2(H_2SiO_4).xH_2O$, where $x=n-1$ (for $x=4$ see Jost & Hilmer, 1966; $x=5$, Jamieson & Dent Glasser, 1967, and Williams & Dent Glasser, 1971; $x=8$, Jamieson & Dent Glasser, 1966*a*). The present work completes our knowledge of the structures of this series, and enables them to be compared.

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