Structural Phase Transition in Polyphenyls.
VI. Crystal Structure of the Low-Temperature Ordered Phase of *p*-Quaterphenyl at 110 K

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The crystal structure of the ordered phase of *p*-quaterphenyl has been determined from X-ray diffraction data collected at 110 K on a single-crystal diffractometer. This superstructure is very similar to that of *p*-terphenyl: the space group is also $P\bar{1}$ ($Z = 4$) with $a = 9.74$ (2), $b = 9.74$ (2), $c = 17.70$ (3) Å, $\alpha = 85.40$ (10), $\beta = 94.60$ (10), $\gamma = 110.11$ (10)°. However, for comparison with the high-temperature monoclinic cell a', b', c', β' ($P2_1/a$, $Z = 2$) it is more convenient to choose a pseudomonoclinic cell a, b, c, β centred on the face (001) with $Z = 8$ and $a = 15.97$ (3) ($\simeq 2a'$), $b = 11.16$ (2) ($\simeq 2b'$), $c = 17.70$ (3) Å ($\simeq c'$), $\beta = 95.61$ (8)° ($\simeq \beta'$). However, unlike *p*-terphenyl molecules, the *p*-quaterphenyl molecules do not conserve their centre of symmetry at low temperature. The average torsion angles are 17.1° between an external and an internal ring and 22.7° between two internal rings. All the long molecular axes remain parallel. As for *p*-terphenyl, the interpretation of the experimental result $I_{hkl} = I_{h\bar{k}l}$ requires the existence of two sorts of domains in the crystal, related by a mirror or glide plane perpendicular to **b** and equally probable.

Introduction

Polyphenyls are characterized at room temperature by a mean planar conformation associated with unusually high librational amplitudes about their long molecular axes (Dejace, 1969; Rietveld, Maslen & Clews, 1970; Delugeard, Desuche & Baudour, 1976; Charbonneau & Delugeard, 1977).

In the case of *p*-terphenyl, it has been established that this characteristic results from rotational disorder, each molecule librating in a double-well potential (Baudour, Cailleau & Yelon, 1977), the barrier height being about 0.6 kcal mol⁻¹. At low temperature, *p*-terphenyl undergoes a transition, molecules being stabilized in one of the two minima of the double well (Baudour, Delugeard & Cailleau, 1976).

p-Quaterphenyl [*p,p'*-bis(phenyl)biphenyl] also undergoes a transition in which, as for *p*-terphenyl, the
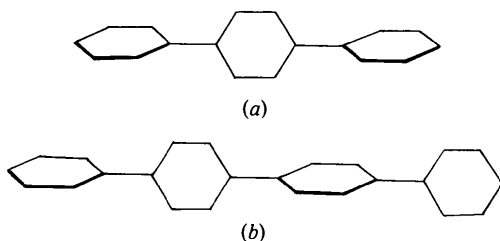

(a)

(b)

Fig. 1. (a) Low-temperature configuration of the *p*-terphenyl molecule (conservation of the centre of symmetry). (b) Supposed low-temperature configuration of the *p*-quaterphenyl molecule (loss of the centre of symmetry).

unit-cell parameters *a* and *b* each double at low temperature (Delugeard *et al.*, 1976; Parkinson & Rees, 1977). For these two systems the molecular configuration results essentially from the competition between two antagonistic effects: the repulsion between the *ortho* H atoms on two adjacent rings and the intermolecular forces which tend to restore planarity. For *p*-terphenyl, two adjacent rings in a molecule rotate in opposite senses and the molecule conserves its centre of symmetry (Fig. 1). But if this alternation in rotations subsists for *p*-quaterphenyl, the molecule cannot conserve its centre of symmetry (Fig. 1). This is a general result when the number of rings is even (quaterphenyl, biphenyl). However, it is possible that the centre of symmetry subsists outside the molecule and thus the structure can remain centrosymmetric. It seemed interesting to determine the crystal structure of the low-temperature phase of *p*-quaterphenyl and to compare the extent of the non-planarity with that of *p*-terphenyl.

Experimental

The quaterphenyl crystals were grown by slow evaporation from *p*-xylene. The crystal used for data collection was sealed in a Lindemann-glass capillary and mounted with **b** parallel to the φ axis of the goniostat. The unit-cell dimensions were determined by a least-squares refinement from the positions of 45 reflexions. At 110 K, the supercell is pseudomonoclinic with: $a = 15.97$ (3), $b = 11.16$ (2), $c = 17.70$ (3) Å, $\beta = 95.61$ (8)°.

In comparison with the high-temperature cell (Delugeard *et al.*, 1976) and neglecting the thermal contraction, the *a* and *b* parameters are doubled while the *c* parameter is unaltered. This result is similar to that for *p*-terphenyl (Baudour *et al.*, 1976). The condition limiting possible reflexions is also $h + k = 2n$.

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 (scan range 1·50°). The crystal was cooled in a stream of cold nitrogen gas (van Bolhuis, 1971). Two control reflexions were measured after every 50 reflexions and their intensities showed no unusual fluctuations or decay with time. (The maximum deviation of any standard from its mean intensity was about 4%.) Of the 4528 reflexions collected with $\theta < 30°$, 1018 have net intensities significantly non null, of which 336 (*h* and *k* odd) were superstructure reflexions. These 1018 reflexions were used in the structure analysis. It will be noted that, in comparison with the total number of data measured, only a small number of reflexions were used for the refinement. This can be explained by the weak intensities of superstructure reflexions. For example, the intensity ratio between the strongest structure and superstructure reflexions is 63. The data were corrected for Lorentz and polarization effects but not for absorption ($\mu = 0·37$ cm^{-1} for Mo $K\alpha$ radiation).

Structure determination and refinement

The steps in the structure determination are the same as those previously described for *p*-terphenyl (Baudour *et al.*, 1976). At first each molecule must be distorted from its mean planar high-temperature configuration. It is clear that the larger the libration amplitude at room temperature, the larger is the rotation of the ring at low temperature. Consequently, the rotation angles imposed at the beginning were 5° for the two end rings [$\langle \theta^2 \rangle = 71·5$ (°)^2 at room temperature] and 10° for the two inner rings [$\langle \theta^2 \rangle = 178·3$ (°)^2 at room temperature]. Two adjacent rings were rotated in opposite senses. We have seen that under these conditions the molecular centre of symmetry disappears. Secondly, the simplest hypothesis is to conserve the centres of symmetry between two molecules (Fig. 2). These centres of symmetry transform a molecule of configuration +, −, +, − (signs of the four rotations from the mean planar high-temperature configuration) into a molecule of the opposite configuration −, +, −, +, the molecular centres being translated by a/2 or b/2. In terms of double-well potential the molecules are alternately stabilized in a right well and in a left well. This agrees with the doubling of parameters *a* and *b* at low temperature. In fact, with this hypothesis, the true space group is $P\bar{1}$, but for comparison with the high-temperature cell a', b', c' it is more convenient to use a pseudomonoclinic mesh $a \simeq 2a'$, $b \simeq 2b'$, $c \simeq c'$ (Fig. 2). Thus there are two independent complete molecules in the unit cell. (In *p*-terphenyl there are four independent half molecules, each molecule being situated on a centre of symmetry.)

By this procedure, two sublattices are obtained (Fig. 2): one from the molecule at ($\frac{1}{4}$,0,0) and the other from the molecule at ($\frac{1}{2}$,$\frac{1}{4}$,0). The relative positions of these two sublattices give two possible structures, α and β, which are related by a mirror plane. However,
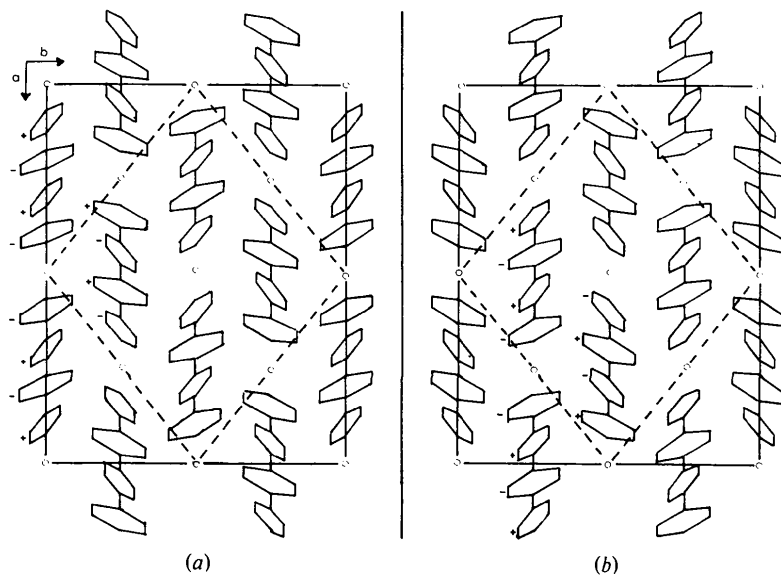

(a)   (b)

Fig. 2. Construction of two possible structures (*a*) α and (*b*) β, each without a mirror or glide plane but related to each other by a mirror plane perpendicular to **b**. A pseudomonoclinic mesh a,b,c is used for comparison with the high-temperature cell a',b',c': $a = 2a'$, $b = 2b'$, $c = c'$. The true unit cell corresponding to the space group $P\bar{1}$ is represented by broken lines.

neither of these structures α and β satisfies the experimental result: $I_{hkl} = I_{h\bar{k}l}$, since the glide planes of the high-temperature space group $P2_1/a$ have disappeared. It is necessary to consider two sorts of domains equally probable in the crystal, with the structures α and β respectively. The intensities of the domains must be added and not the amplitudes, for a phase relation between domains would cancel the superstructure reflexions. The calculated structure factor expression is given by: $\mathscr{F}_c(hkl) = |F_{c,\alpha}^2(hkl) + F_{c,\beta}^2(hkl)|^{1/2} = |F_c^2(hkl) + F_c^2(h\bar{k}l)|^{1/2}$, where $F_c(hkl)$ is the structure factor of domain α or β.

In the low-temperature ordered phase, the number of independent atoms is four times that of the high-temperature disordered phase, but the number of measured reflexions having a significant intensity is approximately the same. It is therefore necessary to carry out a constrained refinement. Bond lengths and angles are imposed: C—C 1·50 Å between the phenyl rings, 1·40 Å in the rings, C—H 1·05 Å; angles 120°.

For each molecule the variable geometrical parameters are the three angles between two adjacent rings and the three Eulerian angles to allow the molecule to take up any arbitrary orientation in the crystal. Then the total number of geometrical parameters is 12 for the two independent molecules. In addition the same isotropic temperature factor is attributed to each pair of C atoms which were related by the glide plane in the high-temperature disordered phase. H atoms are given a common unrefined isotropic temperature factor $B_H = 2·50$ Å^2. The total number of variable thermal parameters is arbitrarily limited to 24.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

The function used for minimization was $\Sigma w(|F_o| - |F_c|)^2$. Several cycles of refinement were calculated. The latter calculations yielded R values of 0·104 for the 1018 observed reflexions and 0·138 for the 336 superstructure reflexions, with corresponding weighted R_w values of 0·113 and 0·144.*

At this stage, attempts were made to refine the structure in the noncentrosymmetric space group $P1$, with four independent molecules in the asymmetric unit. The application of Hamilton's (1965) statistical test did not result in a significant improvement of the R and R_w factors. We conclude that the structure is centrosymmetric. However, this conclusion based on statistical arguments has to be confirmed by other methods such as Raman and IR spectroscopy.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33060 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Description of the structure

The atoms are numbered in accordance with Fig. 3. The atomic coordinates and isotropic temperature factors are given in Table 1. A projection of the molecular arrangement along the c axis and the extent of the nonplanarity of the p-quaterphenyl molecules are given in Fig. 4. The average rotation angle from the mean planar high-temperature configuration is 5·8° for the end rings and 11·3° for the internal rings. The mean torsion angle between an external and an internal ring is 17·1°. The mean torsion angle between two internal rings is 22·7°.

In the low-temperature phase, all the long molecular axes remain almost parallel: the difference in orientations of the two independent molecules is 0·7°, of the same order as two e.s.d.'s ($\sigma = 0·3°$).

Thus, when p-quaterphenyl undergoes its phase transition, the structural modification results essentially from rotations of the rings about the long molecular axes, as for p-terphenyl. Isotropic thermal parameters
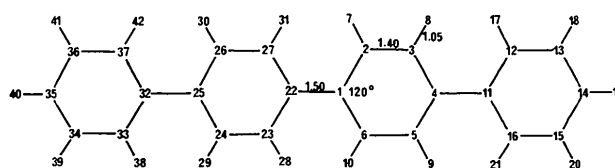

Fig. 3. The molecule of p-quaterphenyl showing the numbering of the atoms. Bond lengths and angles were imposed in the constrained refinement.
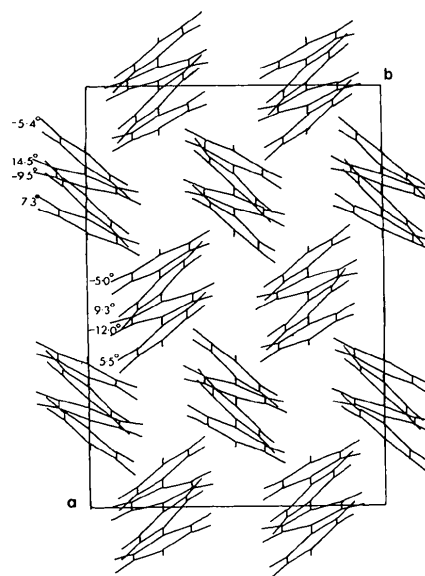

Fig. 4. A projection of the molecular arrangement along the c axis. The angles indicate the ring rotations measured from the high-temperature planar configuration.

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters*

Standard deviations of temperature factors are in parentheses.

	Molecule 1			Molecule 2			
	x	y	z	x	y	z	$B(\text{Å}^2)$
C(1)	2408	−5	407	4903	2497	406	0·8 (2)
C(2)	2087	−1041	720	4310	3298	648	1·2 (3)
C(3)	1915	−1051	1480	4128	3292	1406	1·0 (2)
C(4)	2064	−26	1929	4540	2485	1922	1·8 (2)
C(5)	2385	1010	1616	5133	1684	1680	1·7 (3)
C(6)	2557	1020	856	5314	1690	922	2·3 (3)
H(7)	1975	−1811	383	4001	3904	261	2·50
H(8)	1675	−1828	1714	3684	3893	1588	2·50
H(9)	2496	1780	1952	5442	1078	2067	2·50
H(10)	2797	1797	622	5759	1089	740	2·50
C(11)	1880	−37	2743	4346	2479	2734	0·8 (2)
C(12)	1330	−893	2996	3905	3436	3019	1·2 (2)
C(13)	1159	−903	3756	3724	3430	3777	1·5 (2)
C(14)	1536	−57	4265	3983	2467	4250	1·4 (2)
C(15)	2085	800	4012	4424	1510	3965	1·8 (2)
C(16)	2257	810	3252	4605	1516	3207	1·3 (2)
H(17)	1047	−1528	2614	3710	4158	2664	2·50
H(18)	747	−1546	3945	3393	4148	3991	2·50
H(19)	1407	−64	4835	3847	2463	4819	2·50
H(20)	2369	1435	4394	4619	788	4320	2·50
H(21)	2669	1453	3063	4936	798	2994	2·50
C(22)	2592	5	−407	5097	2503	−406	2·1 (2)
C(23)	3182	812	−649	5455	1491	−714	1·8 (3)
C(24)	3354	822	−1410	5637	1497	−1472	2·1 (3)
C(25)	2936	26	−1928	5460	2515	−1922	1·0 (2)
C(26)	2346	−781	−1687	5102	3527	−1614	1·3 (2)
C(27)	2174	−791	−926	4921	3521	−856	0·9 (3)
H(28)	3495	1410	−260	5588	728	−376	2·50
H(29)	3796	1428	−1591	5905	738	−1703	2·50
H(30)	2033	−1379	−2076	4969	4290	−1952	2·50
H(31)	1732	−1397	−745	4652	4280	−625	2·50
C(32)	3120	37	−2743	5654	2521	−2734	1·8 (2)
C(33)	3529	1021	−3033	6209	1673	−2987	2·1 (3)
C(34)	3701	1031	−3793	6391	1679	−3745	2·1 (2)
C(35)	3464	57	−4265	6017	2533	−4250	1·7 (2)
C(36)	3055	−928	−3975	5462	3381	−3997	1·9 (2)
C(37)	2883	−938	−3215	5280	3375	−3239	2·2 (2)
H(38)	3707	1752	−2679	6490	1032	−2608	2·50
H(39)	4008	1769	−4010	6807	1043	−3935	2·50
H(40)	3593	64	−4835	6153	2537	−4819	2·50
H(41)	2877	−1658	−4329	5181	4022	−4376	2·50
H(42)	2576	−1676	−2998	4864	4011	−3050	2·50

are generally slightly higher at the periphery than on the molecular axis, in agreement with a low librational amplitude about this axis. However, because of some anomalies involving thermal parameters, perhaps owing to the constraints imposed on molecular geometry, we have considered as useless an attempt to determine thermal tensors.

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