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Structural Phase Transition in Polyphenyls. X. Potential Barrier Heights in Crystalline Polyphenyls and in Gaseous Biphenyl Determined Uniquely from Diffraction Data

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Abstract

The analysis from X-ray or neutron diffraction data, of the librational motion around the long molecular axis of the *p*-terphenyl central ring permits resolution of its disorder: the phenyl rotation angle on either side of the average molecular plane is $\varphi = \pm 13{\cdot}3^\circ$. This disorder is associated with a double-well potential between two twisted conformations, and the overall libration on each site, at the bottoms of the double well, has the mean-square amplitude $\langle\theta^2\rangle = 52{\cdot}5\ \deg^2$ at room temperature. The analysis also permits separation in $\langle\theta^2\rangle$ of the mean-square amplitude of the torsional *g* mode $\langle\theta_i^2\rangle = 35\ \deg^2$ from that of the external mode $\langle\theta_e^2\rangle = 17{\cdot}5\ \deg^2$. Thus it becomes possible to scale the parameters of a simple model describing inter- and intramolecular interactions in the whole family of polyphenyls. It is shown that the intramolecular potential between two adjacent phenyl rings cannot be described by a simple sinusoidal function but exhibits a steeper gradient near the planar conformation. This double potential well model accounts for disorder and libration in crystalline *p*-terphenyl and *p*-quaterphenyl. It gives

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an estimation of potential barrier heights: $V = 4{\cdot}57$ kJ mol^{-1} in *p*-terphenyl and $7{\cdot}91$ kJ mol^{-1} in *p*-quaterphenyl in good agreement with NMR results. It agrees with the displacive nature of the biphenyl transition by giving in this case a barrier height, $V = 1{\cdot}25$ kJ mol^{-1}, significantly less than the thermal energy kT and a singly peaked probability density function associated with a large libration amplitude as observed experimentally. Combined with the estimation of librational amplitude from diffraction data it predicts a large increase of intermolecular interactions in biphenyl at low temperature and gives an estimation of the interactions involved in the low-temperature incommensurate phase of biphenyl. Indirectly it is one of the very few experimental determinations of the potential-energy curve for gaseous biphenyl, giving $V_0 = 10{\cdot}82$ kJ mol^{-1} for the planar conformation in agreement with the results of gas-phase electron diffraction for deuterated biphenyl.

Introduction

Since the pioneering work of Cruickshank (1956*a*) establishing with his *TL* model how anisotropic Gaussian vibration parameters could be used for estimating rigid-body librational and translational motion of molecules in crystals, followed by the more general *TLS* model of Schomaker & Trueblood (1968) when interactions between translations and rotations are allowed, X-ray and neutron diffraction data have been used extensively to analyze thermal vibrations of rigid molecules and the riding motion of rigid blocks such as methyl groups (Dunitz, 1979; Johnson, 1970; Willis & Pryor, 1975). The simplest interpretation of these thermal parameters can be made through the one-particle potential (OPP) approximation in which a rigid molecule (or a rigid block) vibrates with an averaged potential of which some characteristics can be estimated: quadratic force constants, torsional frequencies, potential barrier heights to internal molecular motions (see, for example, Trueblood & Dunitz, 1983). The OPP approximation which neglects dispersion can be tested by comparison with spectroscopic or thermodynamic results as shown for the first time on naphthalene (Cruickshank, 1956*b*,*c*). This method has the advantage of rapidly giving interesting parameters concerning thermal motion. It is much simpler to apply than complete lattice-dynamics calculations which are sometimes problematic in disordered systems.

In the case of a rigid or approximately rigid molecule such as naphthalene or anthracene or of a light rigid block (CH_3, NH_3, ...) riding on a much heavier molecule, libration around a particular axis can be reasonably described as a single mode governed by a single force constant in the OPP approximation. On the other hand, in the case of molecules such as polyphenyls (biphenyl, *p*-terphenyl, *p*-quaterphenyl) formed of rigid blocks (phenyl rings) having the same masses and linked by single bonds, a picture of the librations of a particular phenyl ring around the long molecular axis in terms of an OPP has no physical meaning. Indeed, because of the inter-ring coupling, the overall libration observed for a phenyl ring is a superposition of several molecular motions resulting from different modes generally mixing intermolecular and intramolecular forces which, as we shall see, are of the same order.

In this study, we shall use the very complete and accurate information obtained from diffraction data on the disordered high-temperature phase of *p*-terphenyl to estimate the parameters of a very simplified model which accounts for disorder and libration about the long molecular axis. It will be shown that the total librational motion of *p*-terphenyl rings can be resolved into contributions from individual modes and that the characteristics associated with each librational mode can be derived from diffraction data. As the model is also applicable to other polyphenyls, the molecular conformations of biphenyl and *p*-quaterphenyl in the crystal will be deduced, as well as the potential-energy function for internal rotation about the inter-ring C—C bond in gaseous biphenyl. Thus this study is an attempt to give a general and coherent view of the inter- and intramolecular interactions in crystalline polyphenyls, as regards rotations about the long molecular axes, only on the basis of diffraction data. Our results will be compared with those obtained by other authors from theoretical studies and from other experimental techniques.

Starting point: the characteristics of disorder in the high-temperature phase of p-terphenyl

For a long time, polyphenyl molecules have been considered, from diffraction results, as being planar in the crystal at room temperature, this planarity being associated with large librational amplitudes (Pickett, 1936; Trotter, 1961; Robertson, 1961; Hargreaves & Rizvi, 1962; Dejace, 1969; Rietveld, Maslen & Clews, 1970). The space group for the monoclinic room-temperature structures is $P2_1/a$, which is very common for planar organic molecules. Later it was established, in the case of *p*-terphenyl, that the room-temperature planar configuration is only an average resulting from disorder between twisted equilibrium conformations. Accurate analyses of libration around the long molecular axis for the *p*-terphenyl central phenyl ring have revealed a doubly peaked probability density function (shown in Fig. 1), allowing the resolution of two components in the overall libration: a process of jumps between two sites at $\varphi = \pm 13^\circ$ on either side of the average molecular plane and genuine libration on each site [$\langle\theta^2\rangle \simeq 52$ deg^2 at 300 K]. By considering a linear variation of $\langle\theta^2\rangle$ with temperature T, very good agreement is observed between X-ray diffraction results at room temperature: $\varphi = \pm 13{\cdot}3^\circ$, $\langle\theta^2\rangle = 52{\cdot}5$ deg^2 ($\sigma = 7{\cdot}8$ deg^2), neutron diffraction results at $T = 200$ K: $\varphi = \pm 13{\cdot}2^\circ$, $\langle\theta^2\rangle = 36{\cdot}2$ deg^2 ($\sigma = 4{\cdot}0$ deg^2) (Baudour, Cailleau & Yelon, 1977) and X-ray diffraction results at $T = 200$ K: $\varphi = \pm 13{\cdot}3^\circ$, $\langle\theta^2\rangle = 35{\cdot}1$ deg^2 ($\sigma = 6{\cdot}6$ deg^2) (Baudour, Toupet, Délugeard & Ghémid, 1986). Thus, these concordant estimates of φ and $\langle\theta^2\rangle$ can be considered to be very reliable.

At low temperature, polyphenyls undergo phase transitions ($T_C \simeq 40$ K for biphenyl, $T_C \simeq 193$ K for hydrogenated *p*-terphenyl, $T_C \simeq 238$ K for hydrogenated *p*-quaterphenyl) where the molecules are stabilized in non-planar conformations. There had been indications of a low-temperature phase transition in biphenyl from EPR and ENDOR studies (Brenner, Hutchison & Kemple, 1974) and from Raman spectroscopy (Friedman, Kopelman & Prasad, 1974; Bree & Edelson, 1977). The low-temperature polyphenyl structures have been determined by X-ray or neutron diffraction (Baudour, Délugeard & Sanquer, 1974; Baudour, Délugeard & Cailleau, 1976; Baudour, Délugeard & Rivet, 1978; Cailleau, Baudour & Zeyen, 1979; Baudour & Sanquer, 1983).

The *p*-terphenyl transition is clearly of an order–disorder type since, as we have seen, diffraction studies reveal disorder in the high-temperature phase. With a view to understanding the transitional mechanism, it must be noted that the information on the structural and thermal characteristics of the disorder for the *p*-terphenyl central ring in the high-temperature phase is unique in the whole family of polyphenyls. Indeed the orientational disorder which very probably also affects the *p*-terphenyl end rings cannot be resolved from diffraction data. In the same way, such a disorder has never been revealed in the high-temperature phase of biphenyl, nor in *p*-quaterphenyl. In biphenyl it is commonly believed that the equilibrium conformation is planar, the transition being of a displacive type since there is evidence of soft-mode behaviour (Bree & Edelson, 1977; Cailleau, Girard, Moussa & Zeyen, 1979). In *p*-quaterphenyl, although the transition is of an order–disorder type (Toudic, Gallier, Rivet & Cailleau, 1983), the disorder cannot be resolved in the high-temperature phase, probably being masked by larger librations on either site. Thus, for our purpose, which is to estimate the potential barrier heights that polyphenyl molecules must overcome in the high-temperature phase in order to change their twisted conformation ($+\varphi$) into the opposite one ($-\varphi$) (this barrier possibly being equal to zero in the case of biphenyl if $\varphi = 0$), we only have the crystallographic results describing disorder in *p*-terphenyl.

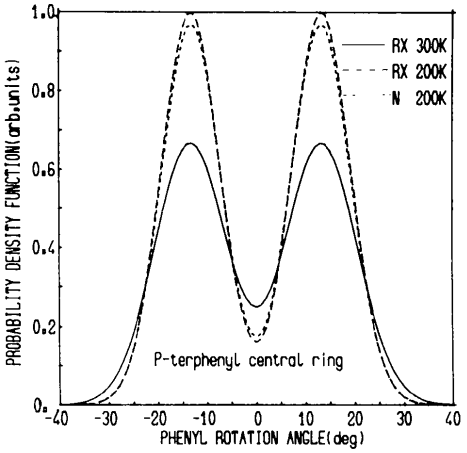

Fig. 1. Doubly peaked probability density function for the *p*-terphenyl central-ring librations around the long molecular axis, from X-ray data (300 and 200 K) and neutron diffraction data (200 K).

A simple model for p-terphenyl

As is now well established (Cailleau, Baudour, Meinnel, Dvorkin, Moussa & Zeyen, 1980; Raich & Bernstein, 1984), the equilibrium conformation of a polyphenyl molecule in the crystal results from a delicate balance between two competing interactions: the intramolecular forces which tend to twist the molecule [the phenyl–phenyl torsion angle is about 43° in the gaseous biphenyl (Bastiansen, 1949)] and intermolecular forces which tend to make it planar. We assume that for rotation φ about the long molecular axis (measured from the average molecular plane) each *p*-terphenyl phenyl ring is subject to harmonic intermolecular forces $C_e\varphi$ governed by a single force constant C_e. Besides this, we postulate that the intermolecular torsional potential between two adjacent phenyl rings has a simple sinusoidal shape and can be written as:

$$V_i = 0{\cdot}5B(1 - \cos\pi\theta_t/\theta_0), \qquad (1)$$

where θ_t is the torsion angle between two adjacent phenyl rings with $\theta_t = \theta_0$ at the minimum of V_i. As B is negative, B is the internal potential barrier height corresponding to a single phenyl–phenyl interaction.

From the symmetry of the molecular geometry two types of molecular equilibrium conformations can be anticipated, symbolized by the rotations of the three phenyl rings: (φ', 0, $-\varphi'$) and (φ'', $-2\varphi''$,

φ''). These conformations are represented schematically in Fig. 2; intermolecular forces are schematized by solid vectors always directed towards $\varphi = 0$, and intramolecular forces, always repulsive between two adjacent phenyl rings, are schematized by dashed or dotted pairs of opposite vectors. Each conformation has associated with it an equally probable conformation in which all the signs of rotations are changed, resulting in orientational disorder.

Diffraction results obtained in the high- and low-temperature phases indicated that only the (φ, -2φ, φ) type of conformation must be retained. Indeed, above the transition temperature T_C, the doubly peaked probability density function observed for the central ring indicates that the latter is localized far from $\varphi = 0$; in addition, below T_C, the *p*-terphenyl molecules are stabilized in twisted centrosymmetric configurations, the average of which is approximately of the (φ, -2φ, φ) form (Baudour *et al.*, 1976).

Librational contributions from individual modes

Now we write the two *p*-terphenyl equilibrium conformations associated with disorder as ($\varphi/2$, $-\varphi$, $\varphi/2$) and ($-\varphi/2$, φ, $-\varphi/2$). For librations around the long molecular axis each *p*-terphenyl molecule has three degrees of freedom and thus in the simple model considered, can vibrate according to three modes, around one of its two possible conformations. Using θ_1 and θ_3 to designate the rotations of the end rings and θ_2 the rotation of the central ring, these three modes are: a librational external mode $\theta_1 = \theta_2 = \theta_3$; a *g*-torsional mode $\theta_1 = -\theta_2/2 = \theta_3$; and a *u*-torsional mode $\theta_1 = -\theta_3$, $\theta_2 = 0$.

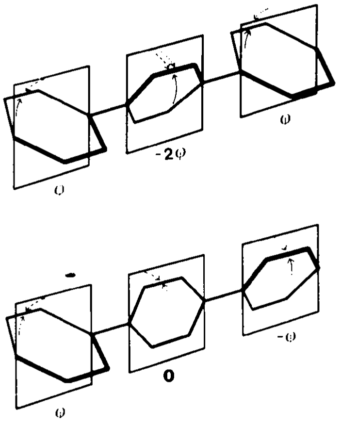

Fig. 2. Two possible molecular equilibrium conformations in the *p*-terphenyl crystal: (φ, -2φ, φ) and (φ, 0, $-\varphi$). Rectangles represent the plane $\varphi = 0$. Intermolecular forces (solid vectors) are always directed towards the plane $\varphi = 0$. In the range of torsion angles observed in the crystal, intramolecular forces (pairs of dashed or dotted opposite vectors) are repulsive between two adjacent phenyl rings.

It is clear that the only mode which permits the molecule to jump from the ($\varphi/2$, $-\varphi$, $\varphi/2$) conformation to the opposite one ($-\varphi/2$, φ, $-\varphi/2$) is the *g*-torsional mode. From the doubly peaked probability density function resolved from diffraction data, we know the amplitude of the jumps for the *p*-terphenyl central ring: $2\varphi = 26{\cdot}6°$ (Baudour *et al.*, 1977). Now, to determine completely the characteristics of the double potential well associated with this reorientational process, it is necessary to separate in the overall mean-square amplitude of libration $\langle\theta^2\rangle \simeq 52{\cdot}5\ \mathrm{deg}^2$, the contribution due to the external librational mode (which has no relation with the reorientational jumps) from that due to the torsional *g* mode. The contribution due to the torsional *u* mode does not need to be considered since it is equal to zero for the central ring.

Although there is generally no single way of resolving the total vibrational motion into contributions from individual modes, this can be done with reasonable accuracy for the *p*-terphenyl central ring. From the potential given in equation (1), the internal torque acting on each external phenyl ring is given by:

$$\Gamma_i = \mathrm{d}V_i/\mathrm{d}\theta_t = 0{\cdot}5B(\pi/\theta_0)\sin(\pi\theta_t/\theta_0), \qquad (2)$$

where θ_t is the torsion angle between two adjacent phenyl rings.

The distorting intramolecular forces acting on the central phenyl ring are double the magnitude of those for the outer rings, and go in the opposite direction. This is expected since the effects of π-electron delocalization and the repulsive terms between *ortho*-H atoms on two adjacent rings are effectively double ended for the central ring. θ_0, which is the dihedral angle in gaseous biphenyl, is about 43° (Bastiansen, 1949); arguments based on a comparison of previous crystallographic results in *p*-terphenyl and *p*-quaterphenyl, indicating that θ_0 is about 45° are also given in the *Appendix*. θ_t, the dihedral angle between two adjacent phenyl rings in *p*-terphenyl, is obtained by adding the rotation of the central ring at the equilibrium (13·3° from diffraction data in the high-temperature phase) and the rotation of the end rings in the opposite direction [$13{\cdot}3/2 = 6{\cdot}65°$ from the model which imposes a conformation ($-\varphi/2$, φ, $-\varphi/2$)]. Thus $\theta_t = 19{\cdot}95°$.

It is to be noted that this θ_t value is very near $\theta_0/2 \simeq 21{\cdot}5°$ which corresponds to the maximum value of the internal torque Γ_i. Thus at equilibrium in the crystal the intermolecular repulsion between two adjacent phenyl rings is practically at its maximum value and hence exhibits very little variation around this position. As a consequence, as a first approximation, the only active restoring forces when a molecule librates around its long axis are the intermolecular forces. This is true not only for the external mode as usual, but also for the torsional modes.

With C_e designating the external force constant acting on a phenyl ring, the variation of the potential energy for a set of small rotations (θ_1, θ_2, θ_3) measured from either possible equilibrium conformation, is:

$$V = (1/2)C_e(\theta_1^2 + \theta_2^2 + \theta_3^2), \tag{3}$$

the intramolecular contributions being neglected as indicated above. Thus the potential energy of the whole molecule vibrating in the external mode (θ_e, θ_e, θ_e) is:

$$V_e = (3/2)C_e\theta_e^2, \tag{4}$$

and the potential energy of the whole molecule vibrating in the torsional g mode ($-\theta_i/2$, θ_i, $-\theta_i/2$) is

$$V_i = (3/4)C_e\theta_i^2. \tag{5}$$

As the average potential energy of a mode is $(1/2)kT$ in the high-temperature limit, where k is the Boltzmann constant, we obtain:

$$\langle\theta_e^2\rangle = kT/3C_e, \tag{6}$$

$$\langle\theta_i^2\rangle = 2kT/3C_e. \tag{7}$$

Thus, two thirds of the crude librational term $\langle\theta^2\rangle$ must be attributed to the torsional g mode and one third to the external mode, which gives: $\langle\theta_e^2\rangle \simeq 52{\cdot}5/3 = 17{\cdot}5$ deg^2; $\langle\theta_i^2\rangle \simeq (2/3)52{\cdot}5 = 35$ deg^2, at room temperature.

Potential barrier height in crystalline p-terphenyl

The probability density function describing the reorientational jumps of the central *p*-terphenyl ring in the model used for interpreting diffraction data (Baudour *et al.*, 1977) is the sum of two Gaussian functions written as:

$$P(\theta) = k_1\left\{\exp\left[\frac{-(\theta+\varphi)^2}{2\langle\theta^2\rangle}\right] + \exp\left[\frac{-(\theta-\varphi)^2}{2\langle\theta^2\rangle}\right]\right\}, \tag{8}$$

each Gaussian function being associated with the harmonic librations θ around a particular equilibrium site: φ or $-\varphi$; $\langle\theta^2\rangle$ being the mean-square amplitude of libration on either site and k_1 a normalization constant. The crude probability density function directly extracted from X-ray or neutron diffraction data corresponds to $\langle\theta^2\rangle = 52{\cdot}5$ deg^2 and includes all contributions from external and torsional modes. However the probability density function associated with reorientational jumps is obtained by taking $\langle\theta^2\rangle = 35$ deg^2, the value calculated for the torsional g mode in the previous section. These two functions are represented in Fig. 3. The g-mode probability density function can be related to a potential $V(\theta)$ by the classical Boltzmann formula:

$$P(\theta) = k_2\exp[-V(\theta)/kT], \tag{9}$$

where k is the Boltzmann constant and k_2 is a normalization factor.

For $\theta = \varphi = 13{\cdot}3°$ (or $\theta = -\varphi$), taking $\langle\theta^2\rangle = 35$ deg^2, one Gaussian function of equation (8) is completely negligible ($\simeq 4 \times 10^{-5}$) compared to the other which is equal to 1. Thus from (8)

$$P(\theta = \pm\varphi) = k_1. \tag{10}$$

Fixing the origin of the potential energy at the equilibrium conformations by imposing $V(\theta = \pm\varphi) = 0$ in (9), gives:

$$P(\theta = \pm\varphi) = k_2. \tag{11}$$

Thus the normalization factors k_1 and k_2 are equal. (This would not be true in the case of a non-negligible overlap of Gaussian functions at $\theta = \pm\varphi$.) The potential barrier height given by the value of $V(\theta)$ at $\theta = 0$ is estimated by identifying the two expressions of $P(\theta)$ [equations (8) and (9)].

$$2\exp(-\varphi^2/2\langle\theta^2\rangle) = \exp[-V(0)/kT] \tag{12}$$

or

$$V(0) = kT[(\varphi^2/2\langle\theta^2\rangle) - \log 2]. \tag{13}$$

Taking $kT = 2{\cdot}494$ kJ mol^{-1} at room temperature, $\varphi = 13{\cdot}3\,(0{\cdot}2)°$, $\langle\theta^2\rangle = 35\,(1{\cdot}5)$ deg^2, we obtain for the barrier height $V(0) = 4{\cdot}57 \pm 0{\cdot}5$ kJ mol^{-1}. This value is in good agreement with NMR results (Toudic *et al.*, 1983) which indicate that far above the transition

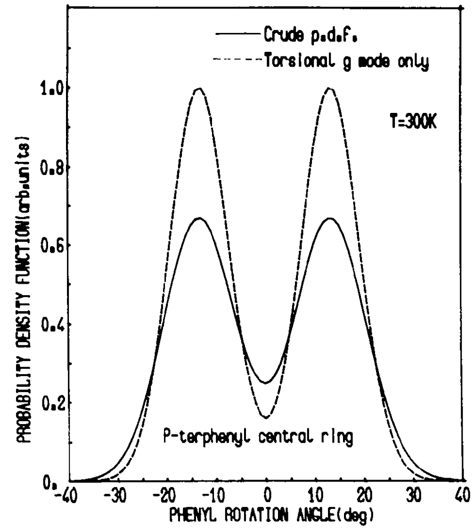

Fig. 3. Crude probability density function (solid line) for the *p*-terphenyl central-ring librations at room temperature. Probability density function (dashed line) associated with reorientational jumps in the *g*-torsional mode.

temperature ($T_C \simeq 193$ K) the mean residence time τ_R in a potential well follows an Arrhénius law with an activation energy $E_{\mathrm{act}} = 4{\cdot}39 \pm 0{\cdot}42$ kJ mol^{-1}. It must be noted that if, as in a previous study (Baudour *et al.*, 1977), we take the crude value $\langle\theta^2\rangle = 52{\cdot}5$ deg^2 given by diffraction data instead of $(2/3)\langle\theta^2\rangle$ which corresponds to the torsional *g* mode, we obtain a significantly inferior barrier height $V(0) = 2{\cdot}47$ kJ mol^{-1}, which does not agree with the NMR results.

Shape of the torsional potential

In the previous sections, by assuming a sinusoidal shape [equation (1)] for the intramolecular torsional potential between two adjacent phenyl rings, we have resolved the contribution due to the external mode from that due to the torsional *g* mode in the crude librational term $\langle\theta^2\rangle$ of the *p*-terphenyl central ring. This has allowed the estimation of the potential barrier height in crystalline *p*-terphenyl. However, a quantitative estimate of inter- and intramolecular interactions has not been given. In addition, in our reasoning the sinusoidal shape of the internal torsional potential is not necessary. The reasoning is still valid provided that the internal couple derived from the potential exhibits no or little variation near the equilibrium conformation θ_t in the crystal. For example, a square-function torque also satisfies the above condition. In this section, we will discuss the shape and the parameters associated with this intramolecular potential, from experimental arguments based on diffraction data. This problem which concerns polyphenyls in general, has been extensively studied in the case of gaseous biphenyl during the last decades, particularly by theoretical chemists. The results of theoretical calculations of different degrees of sophistication, show some scatter in the torsion angles and considerable differences in the two barrier heights; the torsional potential function exhibits maxima at both $\theta_t = 0°$ (planar) and $\theta_t = 90°$ (perpendicular configuration) [see, for example, Häfelinger & Regelmann (1985) for a review of these numerous studies]. On the other hand, to our knowledge, there have been very few experimental determinations of the potential energy for biphenyl. Katon & Lippincott (1959) reporting the Raman spectra of the pure liquid and the infrared spectra of biphenyl in solution, have estimated the barrier heights about planar and perpendicular forms to be 4–8 kJ mol^{-1} by comparing observed and calculated thermodynamic functions. Carreira & Towns (1977) examining the gas-phase vibrational spectra of biphenyl by Raman spectroscopy and assuming a torsion angle of 45°, have calculated two equal barrier heights of 6 kJ mol^{-1}. More recently Almenningen, Bastiansen, Fernholt, Cyvin, Cyvin & Samdal (1985) and Bastiansen & Samdal (1985) using electron diffraction data in the vapour phase found a twist angle of 44·4 (1·2)° for $C_{12}H_{10}$, 45·5 (1·6)° for $C_{12}D_{10}$ and two barrier heights of 6·0 (2·1) kJ mol^{-1} ($\theta_t = 0°$) and 6·5 (2·0) kJ mol^{-1} ($\theta_t = 90°$) for $C_{12}H_{10}$, the corresponding values being 9·9 (3·0) and 9·2 (2·6) kJ mol^{-1} for $C_{12}D_{10}$. Like Carreira & Towns (1977), they used a simple potential function to analyze the torsional data. The function is written as:

$$V(\theta_t) = (V_2/2)(1 - \cos 2\theta_t) + (V_4/4)(1 - \cos 4\theta_t), \qquad (14)$$

where θ_t is the torsional angle. As V_2 was found to be less than its standard deviation and hence practically equal to zero, $V(\theta_t)$ could be considered as having a simple sinusoidal shape, V_4 being negative.

However, as outlined by Bastiansen & Samdal (1985) the potential-energy function from the electron data is essentially obtained from θ_t value areas where the population is high, *i.e.* around the minimum ($\theta_t \simeq 45°$). They note that if the curvature at the minimumn is determined with some degree of accuracy, the barrier heights are to a great extent dependent on the mathematical expression selected to describe the potential-energy function. In the *p*-terphenyl crystal the torsional potential between two adjacent phenyl rings is very probably similar to that of biphenyl. However, as the torsion angle between the *p*-terphenyl rings is $\theta_t = 19{\cdot}95°$ at equilbrium instead of $\theta_t \simeq 45°$ in gaseous biphenyl, crystal diffraction probes a different zone of the potential function and can give complementary information to that given by electron diffraction.

The problem of interactions is more easily comprehended by representing, on the same figure, the inter- and intramolecular forces acting on the *p*-terphenyl phenyl rings when the molecule librates to jump the potential barrier in the crystal. The two possible equilibrium conformations being represented by $(-\varphi_e/2, \varphi_e, -\varphi_e/2)$ and $(\varphi_e/2, -\varphi_e, \varphi_e/2)$, the *g*-torsional mode, which is the mode of interest in overcoming the potential barrier, has the same form ($\theta_1 = \theta_3 = -\theta_2/2$) as the equilibrium conformation. Thus a molecule librating in this particular *g* mode has an instantaneous conformation $(-\varphi/2, \varphi, -\varphi/2)$ (φ now designating any rotation from the average planar configuration and not only the rotation at equilibrium). The intermolecular couple acting on any phenyl ring (outer or central) in position φ is $\Gamma_e = C_e\varphi$ in the harmonic approximation. For an outer ring in position φ, the torsion angle is $\theta_t = 3\varphi$ (φ for the outer ring plus 2φ for the central one) and the intramolecular couple Γ_i is given by (2). For the central ring in position φ, the torsion angle is $\theta_t = (3/2)\varphi$ (φ for the central ring plus $\varphi/2$

Table 1. *Parameters obtained from diffraction data*

Intermolecular force constant: $C_e = kT/3\langle\theta_e^2\rangle = 0{\cdot}259$ mdyn Å rad^{-2}; crystalline *p*-terphenyl central-ring position $\varphi_e = 13{\cdot}3°$; gaseous biphenyl torsion angle $\theta_0 = 45°$ (*p*-terphenyl, $T = 297$ K).

Shape of the intra-molecular potential	Parameters of the intramolecular potential	Molecular conformations and potential barrier heights obtained from the model: Crystalline *p*-terphenyl	Crystalline biphenyl	Crystalline *p*-quaterphenyl	Gaseous biphenyl
Sinusoidal shape: $V_t = 0{\cdot}5B \times (1 - \cos\pi\theta_t/\theta_0)$ where θ_t is the torsion angle	$B = -9{\cdot}20$ kJ mol^{-1}	Conformation: ($-6{\cdot}65$, $13{\cdot}3$, $-6{\cdot}65°$) Potential barrier height: $V = 1{\cdot}26$ kJ mol^{-1}	Twist angle: $\theta_t = 0$ Potential barrier height: $V = 0$ kJ mol^{-1}	Conformation: ($-6{\cdot}64$, $13{\cdot}16$, $-13{\cdot}16$, $6{\cdot}64°$) Potential barrier height: $V = 2{\cdot}96$ kJ mol^{-1}	Twist angle: $\theta_t = 45$ Potential barrier height: $V(0°) = 9{\cdot}20$ kJ mol^{-1}, $V(90°) = 9{\cdot}20$ kJ mol^{-1}, $k = (\partial^2V/\partial\theta_t^2)V = V_{\min} = 0{\cdot}122$ mdyn Å rad^{-2}
Steeper gradient near the planar conformation: $V_t = 0{\cdot}5B(1 - \cos\pi\theta_t/\theta_0) + A\theta_t'^2(\theta_0^3/16 - \theta_0^2\theta_t'/4 + 3/8\theta_0\theta_t'^2 - \theta_t'^3/5)$ with $\theta_t' = \theta_t$ for $\theta_t < \theta_0/2$, $\theta_t' = \theta_0/2$ for $\theta_t \geq \theta_0/2$	$B = -9{\cdot}14$ kJ mol^{-1} $A = -3595$ kJ mol^{-1} rad^{-5}	Conformation: ($-6{\cdot}65$, $13{\cdot}3$, $-6{\cdot}65°$) Potential barrier height: $V = 4{\cdot}57 \pm 0{\cdot}5$ kJ mol^{-1}; from NMR (1) $V = 4{\cdot}39 \pm 0{\cdot}42$ kJ mol^{-1}	Twist angle: $\theta_t = 13{\cdot}3$ Maximum of the p.d.f.: ($T = 297$ K) at $\theta_t = 0$ Potential barrier height: $V = 1{\cdot}25 \pm 0{\cdot}2$ kJ mol^{-1}	Conformation: ($-6{\cdot}64$, $13{\cdot}13$, $-13{\cdot}13$, $6{\cdot}64°$) Potential barrier height: $V = 7{\cdot}91 \pm 0{\cdot}6$ kJ mol^{-1}; from NMR (1) $V = 7{\cdot}75 \pm 0{\cdot}42$ kJ mol^{-1}	Twist angle: $\theta_t = 45°$ Potential barrier heights: $V(0°) = 10{\cdot}82 \pm 1{\cdot}1$ kJ mol^{-1}, $V(90°) = 9{\cdot}14 \pm 0{\cdot}9$ kJ mol^{-1}, $k = 0{\cdot}121$ mdyn Å rad^{-2}; from electron diffraction (2): $V(0°) = 6{\cdot}2 \pm 2{\cdot}1$ kJ mol^{-1}, $V(90°) = 6{\cdot}5 \pm 2{\cdot}0$ kJ mol^{-1} for $C_{12}H_{10}$, $k = 0{\cdot}083$ (31) mdyn Å rad^{-2} for $C_{12}H_{10}$, $V(0°) = 9{\cdot}9 \pm 3{\cdot}0$ kJ mol^{-1} for $C_{12}D_{10}$, $V(90°) = 9{\cdot}2 \pm 2{\cdot}6$ kJ mol^{-1} for $C_{12}D_{10}$, $k = 0{\cdot}127$ (48) mdyn Å rad^{-2} for $C_{12}D_{10}$; from STO-3G *ab initio* calculations (3) $V(0°) = 11{\cdot}01$ kJ mol^{-1}, $V(90°) = 10{\cdot}32$ kJ mol^{-1}

References: (1) Toudic, Gallier, Rivet & Cailleau (1983). (2) Almenningen, Bastiansen, Fernholt, Cyvin, Cyvin & Samdal (1985); Bastiansen & Samdal (1985). (3) Häfelinger & Regelmann (1985).

for the outer one) and the intramolecular couple Γ_i is given by (2), this expression being multiplied by a factor of two since the central ring is adjacent to two phenyl rings. Hence the intermolecular as well as the intramolecular couples acting on any phenyl ring can be represented on the same figure as a function of the position φ of this ring. For the central ring, $|\Gamma_e|$ and $|\Gamma_i|$ intersect at $\varphi = 13{\cdot}3°$, the equilibrium position. For an outer ring, $|\Gamma_e|$ and $|\Gamma_i|$ intersect at $\varphi = 13{\cdot}3/2 = 6{\cdot}65°$. Taking $C_e = 0{\cdot}259$ mdyn Å rad^{-2} from equation (6) in which $\langle\theta_e^2\rangle = 17{\cdot}5$ deg^2, $\theta_0 = 45°$ (torsion angle in gaseous biphenyl), the parameter B can easily be calculated from (2) by using $|\Gamma_e| = |\Gamma_i|$ at equilibrium, which determines the intramolecular potential completely [equation (1)].

The potential barrier heights are immediately calculable for the *p*-terphenyl molecule in the crystal and for the biphenyl molecule in the gaseous state. Results are given in Table 1, which shows that the so-calculated values ($V_0 = V_{90} = 9{\cdot}2$ kJ mol^{-1}) of the potential barrier heights in gaseous biphenyl are in reasonable agreement with recent theoretical calculations ($V_0 = 11{\cdot}01$, $V_{90} = 10{\cdot}32$ kJ mol^{-1}) (Häfelinger & Regelmann, 1985). On the other hand the calculated value ($1{\cdot}265$ kJ mol^{-1}) of the potential barrier height in crystalline *p*-terphenyl is much less than the values obtained from our estimation of $\langle\theta_g^2\rangle$ in the *g*-torsional mode: $4{\cdot}57\,(0{\cdot}5)$ kJ mol^{-1} and from NMR measurements: $4{\cdot}39\,(0{\cdot}42)$ kJ mol^{-1}. The latter values being considered to be reasonably accurate, the origin of the discrepancy can be examined by noting that the work done by resultant forces in the crystal is given by $\int||\Gamma_e| - |\Gamma_i||\mathrm{d}\varphi$ and the work done by intramolecular forces by $\int|\Gamma_i|\mathrm{d}\varphi$. Thus the potential barrier height in crystalline *p*-terphenyl is represented in Fig. 4 by the sum of surfaces $S_A + 2S_B$, corresponding respectively to the central and to the two external phenyl rings. In the same way, the intramolecular couple in crystalline or gaseous biphenyl in the torsional mode (displacements from the equilibrium $\theta_1 = -\theta_2$) is given by (2) in which $\theta_t = 2\varphi$ (φ giving the position of a phenyl ring). Thus, the potential barrier height in gaseous biphenyl is represented in Fig. 4 by the surface $2S_C$, the factor two corresponding to the two rings of biphenyl. For the parameters of the model in biphenyl, $|\Gamma_e|$ is always greater than $|\Gamma_i|$ as shown in Fig. 4, which implies a planar conformation for biphenyl in the crystal. The integration of the couples represented in Fig. 4 gives the potential curves represented in Fig. 5.

There are two ways of resolving the discrepancy concerning the crystalline *p*-terphenyl potential barrier heights. The first consists of multiplying the inter- and intramolecular interactions by the same factor of about 3·5, which does not change the equilibrium conformation. This corresponds to a simple change of scale on the Γ axis of Fig. 4, with the consequence that all surfaces and thus all potential barrier heights are also multiplied by the same factor of 3·5. Under these conditions the gaseous biphenyl barrier height takes on an unreasonably high value of about 32 kJ mol^{-1}. Besides, the frequency ω_e associated with the external mode and calculated from $\omega_e^2 = C_e/I$ increases from $\omega_e = 70$ to $\sim 130\ \text{cm}^{-1}$ and disagrees with inelastic neutron scattering measurements in *p*-terphenyl which give ω_e in the 70–89 cm^{-1} range (Reynolds & White, 1972). The second possibility involves modifying the shape of the intramolecular couple between adjacent rings by giving it a steeper gradient towards the planar conformation and a larger level near $\theta_t = \theta_0/2$. The latter solution is the only one to be considered as it greatly increases the value of the crystalline *p*-terphenyl barrier height without considerably changing the gaseous biphenyl barrier height. In addition, a high value of the repulsive intramolecular couple near the planar conformation is easily accounted for by the steric hindrance between H atoms in *ortho* positions on adjacent rings. Modification of the internal couple near $\theta_t = 0°$ only slightly affects the results of gaseous biphenyl electron diffraction, which probes the potential near a twist angle θ_t of 45°.

Thus the shape of the intramolecular couple has been modified by adding, after some adjustments, an empirical function in the expression (2), for a torsion angle θ_t less than $\theta_0/2$.

$$\Gamma_i = 0{\cdot}5B(\pi/\theta_0)\sin(\pi\theta_t/\theta_0) + A\theta_t[(\theta_0/2) - \theta_t]^3, \tag{15}$$

for $\theta_t \le \theta_0/2$. For $\theta_t > \theta_0/2$ equation (2) is not modified.

At equilibrium in the *p*-terphenyl crystal, the value of Γ_i is fixed, since $|\Gamma_i| = \Gamma_e$. Thus A and B are not independent parameters: A being given, B is calculable. The value of A has been adjusted to obtain a potential barrier height of 4·57 kJ mol^{-1} in crystalline *p*-terphenyl, in agreement with our estimate based on the probability density function for the torsional *g* mode. Resulting couples and potentials appear in Figs. 6 and 7, respectively. Results are discussed in the next section.

Results and discussion

We will discuss successively the results obtained in the case of crystalline *p*-terphenyl, crystalline *p*-quaterphenyl, gaseous biphenyl and crystalline biphenyl. These results are summarized in Table 1.

Crystalline p-terphenyl

In crystalline *p*-terphenyl the potential barrier height is extremely sensitive to the shape of the potential near the planar conformation, as clearly illustrated in Figs. 4–7. One parameter A in (15) must be adjusted to obtain a single value (4·57 kJ mol^{-1}) for the barrier heights determined from the model and from the p.d.f. given by X-ray or neutron diffraction. This barrier height agrees with that obtained from NMR results: 4·39 (0·42) kJ mol^{-1} (Toudic *et al.*, 1983). It is also interesting to note (as shown in Fig. 8) that the

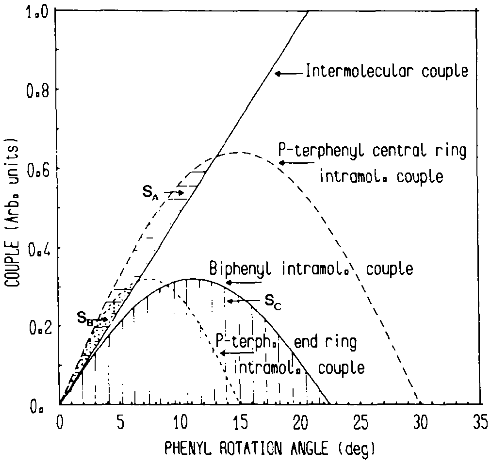

Fig. 4. Intermolecular couple (straight solid line) acting on a phenyl ring in the crystal as a function of the phenyl rotation angle φ, and intramolecular couples acting on the *p*-terphenyl central ring and outer rings, in the *g*-torsional mode, and intramolecular couple acting on a phenyl ring in biphenyl in the torsional mode (assuming a simple sinusoidal intramolecular potential). The surface S_A is hatched horizontally, S_B is dotted and S_C is hatched vertically. The potential barrier height in crystalline *p*-terphenyl is given by $S_A + 2S_B$. There is no potential barrier in crystalline biphenyl, its equilibrium conformation being planar. The potential barrier height in gaseous biphenyl is given by $2S_C$.

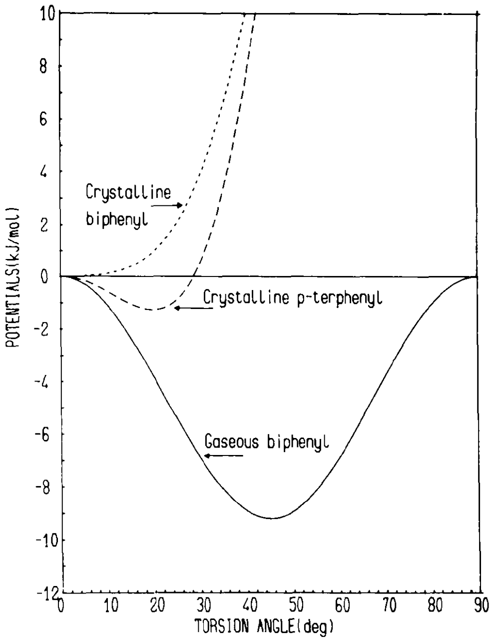

Fig. 5. Potential curves deduced from the couples represented in Fig. 4, assuming a simple sinusoidal intramolecular potential between two adjacent phenyl rings.

shapes of the potential curves deduced from the model, by integration of (15), and from the p.d.f. associated with diffraction data [equations (8) and (9)], agree very well in the range of torsional angles θ_t probed by X-ray or neutron diffraction: about $0 < \theta_t < 30°$. The barrier height in crystalline *p*-terphenyl is significantly higher than the thermal energy ($kT = 2{\cdot}49$ kJ mol^{-1} at room temperature). Hence, in the high-temperature phase of *p*-terphenyl, each molecule is rather well localized in either bottom of the double well, thermal activation inducing a dynamical disorder between the two minima. An order–disorder transition results when one of the potential minima is preferred to the other at $T_C \simeq 193$ K. Thus, the parameters of the simple model described in the previous sections can, precisely because of its simplicity, only be evaluated from diffraction results on *p*-terphenyl. Now we can apply the model to obtain a general and coherent picture of the inter- and intramolecular interactions in the whole family of polyphenyls.

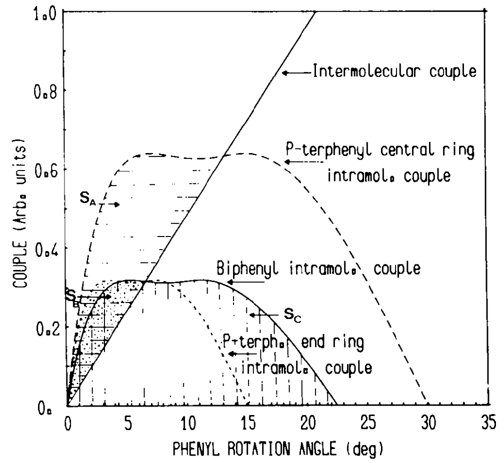

Fig. 6. Intermolecular couple (straight solid line) acting on a phenyl ring in the crystal, and modified intramolecular couples exhibiting a steeper gradient than the sinusoidal couples of Fig. 4, towards the planar conformation. Surfaces S_A and S_B, and hence the potential barrier height in crystalline *p*-terphenyl, are greatly enhanced. S_C, and hence the potential barrier height in gaseous biphenyl, is slightly enhanced. The biphenyl equilibrium conformation is not planar, the intermolecular couple and the biphenyl intramolecular couple intersecting at $\varphi = 6{\cdot}65°$.

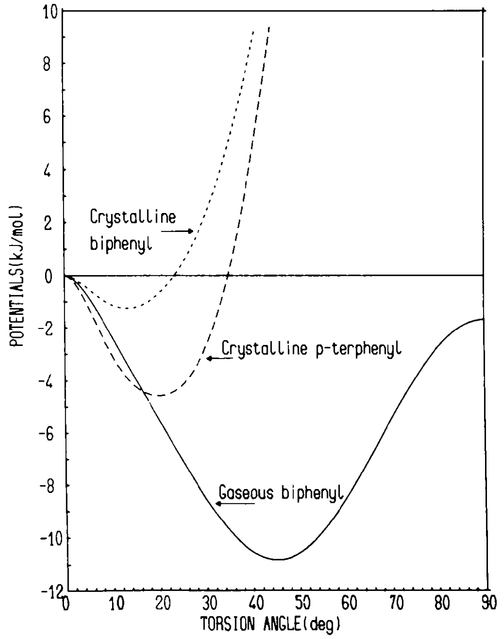

Fig. 7. Potential curves deduced from the couples represented in Fig. 6, with a non-sinusoidal intramolecular potential.

Crystalline p-quaterphenyl

The previously determined parameters governing inter- (C_e) and intramolecular (A, B, θ_0) interactions in *p*-terphenyl have been used without making any modifications to model the high-temperature phase of *p*-quaterphenyl. This is justified by the identical molecular packing of the two crystals which exhibit the same a (8·11 Å) and b (5·61 Å) cell parameters in the $P2_1/a$ space group, the long molecular axes all being approximately parallel to the c axis which

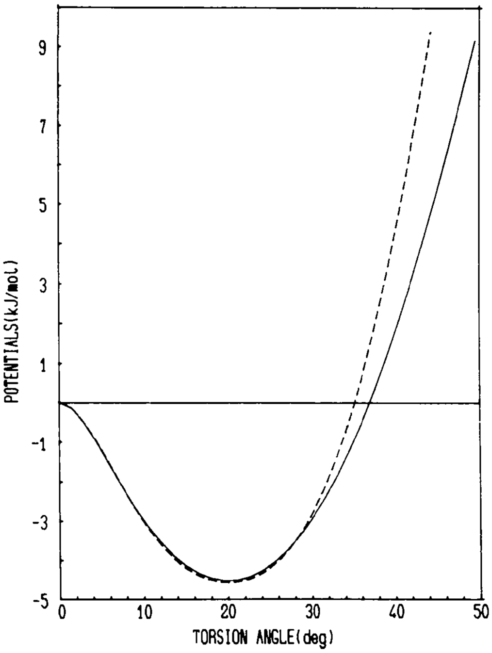

Fig. 8. A comparison of the shapes of the crystalline *p*-terphenyl potential curves deduced from the model (dashed line) assuming a non-sinusoidal intramolecular potential and from the probability density function derived from diffraction data. The agreement is good in the range of torsional angles probed by X-ray or neutron diffraction.

increases from 13·61 Å in *p*-terphenyl to 17·91 Å in *p*-quaterphenyl. The *p*-quaterphenyl conformation (φ_1, $-\varphi_2$, $+\varphi_2$, $-\varphi_1$), minimizing the potential energy, is obtained for $\varphi_1 = 6{\cdot}64$ and $\varphi_2 = 13{\cdot}13^\circ$. As already mentioned, X-ray diffraction data do not allow us, in the *p*-quaterphenyl high-temperature phase, to reveal and analyze disorder, which is probably masked by libration on each site of the double-well potential. However, this conformation is quite compatible with the average one obtained in the ordered low-temperature phase of *p*-quaterphenyl: $\varphi_1 = 5{\cdot}8$, $\varphi_2 = 11{\cdot}32^\circ$ (Baudour *et al.*, 1978), particularly if we consider that the thermal contraction, by increasing intermolecular interactions, must reduce torsional angles. The potential barrier height corresponds to a jump from the conformation (φ_1, $-\varphi_2$, φ_2, $-\varphi_1$) to the opposite one ($-\varphi_1$, φ_2, $-\varphi_2$, φ_1). Calculated from the model, it is found to be equal to 7·91 kJ mol^{-1}, in fair agreement with NMR results: 7·74 ± 0·42 kJ mol^{-1} (Toudic *et al.*, 1983). It is worthwhile noting that the undistorted sinusoidal shape ($A = 0$) of the intramolecular potential gives a barrier height of 2·96 kJ mol^{-1} which does not agree with NMR results. Hence, *p*-quaterphenyl as well as *p*-terphenyl analyses imply a modification of the intramolecular potential sinusoidal shape near the planar conformation. The *p*-quaterphenyl potential height being much greater than the thermal energy, the transition which takes place at low temperature ($T_c = 238$ K) is of the order–disorder type, like that of *p*-terphenyl.

Gaseous biphenyl

A picture of the biphenyl molecule in the gaseous state is obtained by considering only the intramolecular interactions between two adjacent phenyl rings in the previous model. The parameters governing these intramolecular interactions are the same as in the above analyses of crystalline *p*-terphenyl and *p*-quaterphenyl. In particular, the twist angle at equilibrium has been fixed at $\theta_0 = 45^\circ$ from considerations developed in the *Appendix*, in agreement with gaseous electron diffraction (GED) results (Almenningen *et al.*, 1985). Contrary to what is observed in the crystals of *p*-terphenyl and *p*-quaterphenyl the potential barrier height in gaseous biphenyl is only slightly sensitive to modification of the intramolecular potential shape near $\theta_t = 0^\circ$. The potential barrier heights for the planar and perpendicular conformations are found to be $V_0 = V_{90} = 9{\cdot}20$ kJ mol^{-1} for the sinusoidal torsion potential and $V_0 = 10{\cdot}82$, $V_{90} = 9{\cdot}14$ kJ mol^{-1} for the modified potential described in the previous sections. These energy barriers are significantly greater than those given for hydrogenated biphenyl $C_{12}H_{10}$ from GED [$V_0 = 6{\cdot}0\,(2{\cdot}1)$, $V_{90} = 6{\cdot}5\,(2{\cdot}0)$ kJ mol^{-1}, Almmenningen *et al.*, 1985], but compare well with those obtained for deuterated biphenyl $C_{12}D_{10}$ from GED [$V_0 = 9{\cdot}9\,(3{\cdot}0)$, $V_{90} = 9{\cdot}2\,(2{\cdot}6)$ kJ mol^{-1}]. They also agree reasonably well with values obtained from recent STO-3G *ab initio* calculations, for the minimum-energy parameters (Häfelinger & Regelmann, 1985): $V_0 = 11{\cdot}01$, $V_{90} = 10{\cdot}32$ kJ mol^{-1}. In addition, our model gives a value $k = 0{\cdot}121$ mdyn Å rad^{-2} for the torsional force constant $k = [\partial^2 V/\partial\theta_t^2]_{\theta_t = \theta_0}$, *i.e.* the curvature at the minimum of the potential-energy function. This value is intermediate between those given by GED for $C_{12}H_{10}$ [$k = 0{\cdot}083\,(31)$ mdyn Å rad^{-2}] and for $C_{12}D_{10}$ [$k = 0{\cdot}127\,(48)$ mdyn Å rad^{-2}].

Crystalline biphenyl

Crystalline biphenyl is a particularly interesting system which has been extensively studied by experiment and calculation in recent years. As the temperature is lowered the twist mode goes soft at wavevector $\pm q_b\mathbf{b}^* \pm (q_a\mathbf{a}^* - q_c\mathbf{c}^*)$ with a transition at 38 K to the incommensurate phase II where $q_b = 0{\cdot}46$ and q_a and q_c are small (Cailleau, Messager, Moussa, Bugaut, Zeyen & Vettier, 1986). At 21 K only the $q_b\mathbf{b}^*$ wavevector component subsists giving an incommensurate phase III. The form of the phase III modulation has been detemined in detail by Baudour & Sanquer (1983) from neutron diffraction experiments. Obviously the detailed mechanism of these transitions can be understood by only two methods. One consists of complete lattice-dynamical calculations in the high-temperature phase, using an intermolecular potential of the atom–atom type (Takeuchi, Suzuki, Dianoux & Allen, 1981; Natkaniec, Bielushkin & Wasiutynski, 1981; Bonadeo & Burgos, 1982; Plakida, Bielushkin, Natkaniec & Wasiutynski, 1983). The other consists of minimizing the energy of models explicity taking into account the orientation of phenyl rings of two neighbouring molecules in the low-temperature phase (Busing, 1983; Raich & Bernstein, 1984; Heine & Price, 1985; Benkert, Heine & Simmons, 1987). In spite of its simplicity, the model developed in previous sections makes it possible to scale some parameters (force constants, potential barrier heights, shape of the intramolecular potential) which must usually be introduced and adjusted to reproduce experimental frequencies in more elaborate models. As we shall see this simple model gives a plausible response to the difficult question of whether the molecules are really planar in the crystal at room temperature; it confirms the displacive nature of the biphenyl phase transition, explains the extremely high amplitude of libration about the long molecular axis, gives an estimation of the increase in intermolecular interactions when the temperature is lowered, and permits estimation of competing forces in the incommensurate phase.

Intramolecular interactions between two adjacent phenyl rings can reasonably be considered to be the same in all polyphenyls. However, we must make sure that the parameters associated with intermolecular forces in *p*-terphenyl and *p*-quaterphenyl can also be used in the case of biphenyl. A first argument is that the high-temperature crystal structures are isomorphous (space group $P2_1/a$) showing similar molecular packing and almost identical *a* and *b* cell parameters ($a = 8{\cdot}12$, $8{\cdot}11$, $8{\cdot}11$ Å; $b = 5{\cdot}63$, $5{\cdot}61$, $5{\cdot}61$ Å for biphenyl, *p*-terphenyl and *p*-quaterphenyl, respectively), the *c* parameter being approximately parallel to the major molecular axis and increasing regularly when new phenyl rings are added to the molecule ($c = 9{\cdot}51$, $13{\cdot}61$, $17{\cdot}91$ Å). Thus, we can infer that the external restoring forces for rotation about the long molecular axes are very similar in all polyphenyls.

This is corroborated by a lattice-dynamical calculation (Bonadeo & Burgos, 1982), which shows that the biphenyl torsional mode calculated for a planar equilibrium conformation in the crystal becomes unstable when the frequency associated with this motion in the free molecule reaches $\omega_t = -62\ \text{cm}^{-1}$. (This frequency is negative since the planar configuration corresponds to a maximum of the internal energy.) The instability arising when $\omega_e + \omega_t = 0$, the value $\omega_e = 62\ \text{cm}^{-1}$ obtained in biphenyl, is similar to the frequency $\omega_e = (C_e/I)^{1/2} = 70\ \text{cm}^{-1}$ calculated for the external libration mode of *p*-terphenyl.

The main results obtained from the model are summarized in Table 1 and illustrated in Figs. 6 and 7. With the modified non-sinusoidal intramolecular potential, the crystalline potential exhibits two minima corresponding to a twist angle $\theta_t = 13{\cdot}3°$, each phenyl ring being rotated by $6{\cdot}65°$ from the average planar configuration. However, contrary to what is observed in *p*-terphenyl and *p*-quaterphenyl, the biphenyl potential barrier height $V = 1{\cdot}25\ \text{kJ mol}^{-1}$ is found to be much less than the thermal energy $kT \simeq 2{\cdot}49\ \text{kJ mol}^{-1}$ at room temperature, in agreement with the displacive nature of the phase transition driven by a soft mode. Although the torsional crystalline potential exhibits a double minimum, the biphenyl probability density function $P(\varphi)$ associated with the rotation φ of a phenyl ring and calculated by a classical Boltzmann averaging of all possible conformations, is not doubly peaked but only flattens on top as shown in Fig. 9. Thus to give a response to the question concerning the planarity of molecules we can say that at room temperature the average configuration is planar, the most probable configuration is also planar but the equilibrium configuration is slightly distorted. However, at high *T* the twist mode is sufficiently excited over the whole double well, so that anharmonic effects are weak and the lattice-dynamical calculation can be treated by introducing an effective harmonic torsional frequency (Plakida *et al.*, 1983).

The mean-square amplitude of libration about the long molecular axis calculated by applying the Boltzmann formula to the model is $\langle\varphi^2\rangle = 95{\cdot}2\ \text{deg}^2$ in reasonably good agreement with the value determined from X-ray diffraction experiments: $\langle\varphi^2\rangle = 109{\cdot}2\ \text{deg}^2$ ($\sigma = 2{\cdot}8\ \text{deg}^2$) (Charbonneau & Délugeard, 1977). Although complete agreement between these two values must not be anticipated since diffraction data treatment based on the harmonic approximation implies a Gaussian probability density function which is not produced by the anharmonic model, this agreement can be obtained by slightly decreasing the external force constant C_e from 0·259 to 0·229 mdyn Å rad^{-2}.

If we use a sinusoidal intramolecular potential (parameter $A = 0$), the resulting crystalline potential is a simple well and molecules are planar in the crystal. In this case, as already observed by Bonadeo & Burgos (1982) from their complete lattice-dynamical calculation, the calculated amplitude of libration remains high: $\langle\varphi^2\rangle = 88{\cdot}8\ \text{deg}^2$ from our model. Thus, the shape (single well or double well) of the effective crystalline torsional potential has little influence on the amplitude of thermal motion at room temperature. This is not surprising since the barrier height in the double well is significantly less than the thermal energy *kT*.

When the temperature is lowered from room temperature to 110 K there is a noticeable contraction in the *a*-axis direction which is nearly perpendicular to the molecular planes. This contraction is three times as large in biphenyl ($\Delta a \simeq 0{\cdot}3$ Å) as in *p*-terphenyl or *p*-quaterphenyl ($\Delta a \simeq 0{\cdot}1$ Å). In consequence marked changes appear in the vibrational spectra, most of

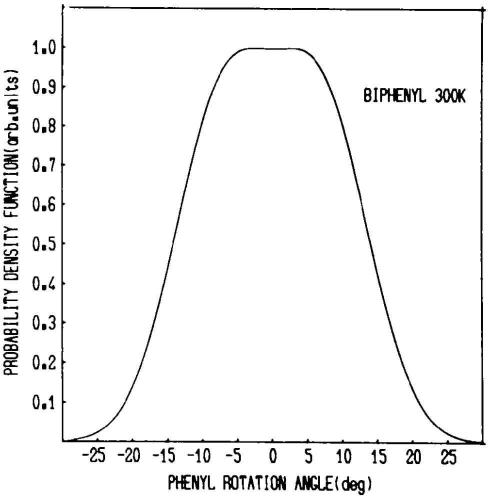

Fig. 9. Singly-peaked probability density function $P(\varphi)$ of crystalline biphenyl calculated from the model, at room temperature.

the bands in the low-frequency region shifting to higher frequencies. Thus we can anticipate an increase of the intermolecular force constant C_e when the temperature is lowered. If we adjust the constant C_e so that the model value $\langle\varphi^2\rangle$ at 110 K agrees with the experimental value $\langle\varphi^2\rangle = 45{\cdot}7\ (2{\cdot}06)\ \mathrm{deg}^2$ (Charbonneau & Délugeard, 1976), we find that C_e increases from 0·259 mdyn Å rad^{-2} at room temperature to 0·327 mdyn Å rad^{-2} at 110 K. In this model, the shape of the probability density function becomes more and more anharmonic when the temperature is lowered, whereas it is Gaussian in the diffraction data treatment. This does not truly permit a quantitative estimation of C_e at 110 K. However the increase in C_e can be roughly estimated from the model. It is worthwhile noting that the same calculation made with the sinusoidal intramolecular potential (parameter $A = 0$) gives no increase of C_e at 110 K, which is incompatible with the contraction in the a-axis direction.

The increase in C_e when the temperature is lowered induces a decrease of the barrier height, which from the model reduces to 0·80 kJ mol^{-1} at 110 K, a value of the same order as kT ($=0{\cdot}9$ kJ mol^{-1}); the minima of the double well is now located at $\varphi = \pm 5{\cdot}3^\circ$. This torsion angle could explain the discrepancy between the value $\langle\varphi^2\rangle = 22{\cdot}7\ \mathrm{deg}^2$ given by a lattice-dynamical calculation (Bonadeo & Burgos, 1982) based on a planar molecular configuration in the harmonic approximation, and the observed value at 110 K $\langle\varphi^2\rangle = 45{\cdot}7\ \mathrm{deg}^2$ from X-ray measurements (Charbonneau & Délugeard, 1976). Indeed the square root of the difference: $(45{\cdot}7 - 22{\cdot}7)^{1/2} = 4{\cdot}8^\circ$ is very near the value of $\varphi = \pm 5{\cdot}3^\circ$ given by our model at the minima of the double-well potential.

Interactions in the low-temperature incommensurate phase III *of biphenyl*

The simple model developed previously also permits the estimation of some interesting parameters in the low-temperature incommensurate phase III at $T < 21$ K. In the solid, neighbouring molecules form a cage around a given molecule (Fig. 10). Assuming a purely sinusoidal modulation of the phenyl-ring twist angle with a wavevector $q_b\mathbf{b}^*$ where $q_b = 0{\cdot}46$, the volume of the cage varies slowly between two extrema: this volume is a minimum when the cage is formed by distorted neighbouring molecules; in this case the molecule at the centre of the cage is planar and the intermolecular force constant $C_e^{\max}$ is a maximum. Conversely, when the cage is formed by planar molecules its volume is a maximum, the molecule at the center exhibits a maximum torsion angle $\theta_t = 11^\circ$ (Baudour & Sanquer, 1983) and the intermolecular force constant $C_e^{\min}$ is a minimum. As shown in Fig. 11, $C_e^{\max}$ is equal to the slope of the intramolecular couple at $\theta = 0$ (θ denoting the twist of one phenyl ring from the planar configuration of the molecule, the torsion angle being $\theta_t = 2\theta$): $C_e^{\max} = (\mathrm{d}\Gamma_i/\mathrm{d}\theta)_{\theta=0} = 0{\cdot}966$ mdyn Å rad^{-2}; $C_e^{\min}$ is such that $C_e^{\min}\theta$ intersects the intramolecular couple at $\theta = 5{\cdot}5^\circ$ (Fig. 11), which gives $C_e^{\min} = 0{\cdot}316$ mdyn Å rad^{-2}.

It is interesting to compare these results based only on the interpretation of diffraction results with those given by the much more sophisticated and complete models developed by Heine & Price (1985), Benkert, Heine & Simmons (1987) and Benkert & Heine (1987) to explain the origin of the incommensurate phase III of biphenyl. Benkert, Heine & Simmons

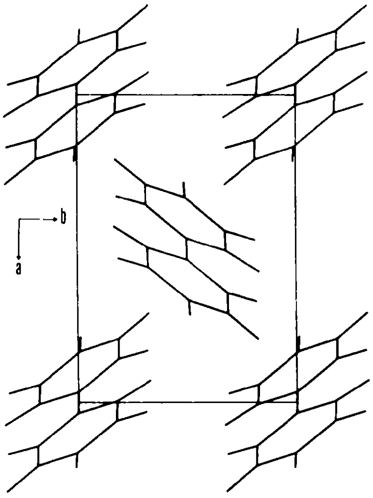

Fig. 10. A projection of the molecular arrangement along the c axis, in solid biphenyl, at room temperature.

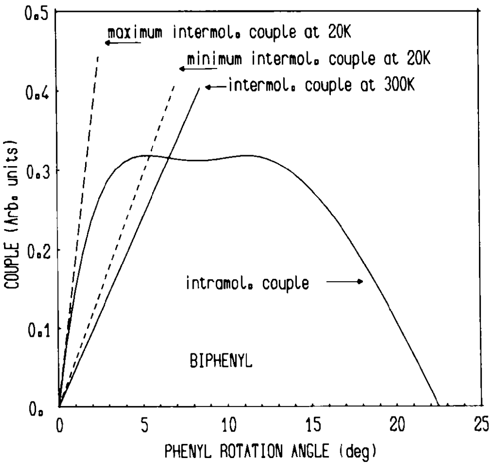

Fig. 11. In the low-temperature incommensurate phase III of biphenyl intermolecular interactions are modulated between two extrema (dashed lines). They are always larger than intermolecular interactions at room temperature (staight solid line).

(1987) model the intramolecular part of the potential as a double well

$$V_{\text{intra free}} = -(A_1/2)\varphi^2 + (B_1/4)\varphi^4, \tag{16}$$

where φ is the rotation of a phenyl ring, the total twist between the rings being 2φ.

The intermolecular potential is described using intermeshed rotations of the phenyl rings (Heine & Price, 1985), which gives the form

$$V_{\text{inter}} = \sum_{\mu\nu} L'\varphi_\mu^2 + \tfrac{1}{2}\sum_{\mu\nu}(J_{\mu\nu} - K_{\mu\nu})\varphi_\mu\varphi_\nu, \tag{17}$$

where the summation is made over all molecules in the crystal. The first term shows the cage effect which in the crystal reduces the average twist from $\varphi = 21°$ in the vapour phase to approximately $\varphi = 5°$ in the solid phase. The second term describes the coupling between the molecules in which the parameters $K_{\mu\nu}$ and $J_{\mu\nu}$ favour twist in the same and opposite directions respectively.

Thus, Benkert & Heine (1987) define an effective intramolecular potential

$$V_{\text{intra crystal}} = -(A'/2)\varphi^2 + (B_1/4)\varphi^4, \tag{18}$$

such that

$$A' = A_1 - 2L'. \tag{19}$$

This effective intramolecular potential can either be a double well or a single well depending on the sign of A'.

The first part of (17), $L'\varphi^2$, gives the average intermolecular potential per molecule, and $\frac{1}{2}C_e\varphi^2$ is the intermolecular energy associated with one phenyl ring in our model; L' is to be identified with C_e. Indeed, modelling the intermolecular interactions by the sum of atom–atom potentials including electrostatic energy, Heine & Price (1985) find $L' = 0{\cdot}706$ mdyn Å rad^{-2}, an estimate similar to the average of the extreme values found in our model: $(C_e^{\max} + C_e^{\min})/2 = 0{\cdot}64$ mdyn Å rad^{-2}.

As regards intramolecular interactions the parameter $A_1 = |(\mathrm{d}^2V_{\text{free}}/\mathrm{d}\varphi^2)_{\varphi=0}|$ is to be identified with $2(\mathrm{d}\Gamma_i/\mathrm{d}\varphi)_{\varphi=0} = 2C_e^{\max}$ in our model, as $\Gamma_i = \mathrm{d}V_{\text{free}}/\mathrm{d}\theta_t = \mathrm{d}V_{\text{free}}/2\mathrm{d}\varphi$ (with the torsion angle $\theta_t = 2\varphi$). The double-well potential condition, *i.e.* the condition for having a twisted molecule, is $A_1 > 2L'$ from (19). This condition becomes $(\mathrm{d}\Gamma_i/\mathrm{d}\varphi)_{\varphi=0} > C_e$ with our notation, as clearly illustrated in Fig. 11. Benkert, Heine & Simmons (1987) estimate A_1 to be equal to 1·26 mdyn Å rad^{-2}, a value smaller than the equivalent term in our model: $2(\mathrm{d}\Gamma_i/\mathrm{d}\varphi)_{\varphi=0} = 1{\cdot}93$ mdyn Å rad^{-2}. This means that the intramolecular potential we consider is more repulsive than theirs near the planar configuration.

From the estimates of $L' = 0{\cdot}706$ mdyn Å rad^{-2} and $A_1 = 1{\cdot}26$, $A' = -0{\cdot}15$ mdyn Å rad^{-2}. This negative value of A' implies that the double well vanishes and the minimum of the effective intramolecular potential (18) lies at $\varphi = 0$.

However, when they introduce the modulated structure of phase III into (17), the form of the potential changes again and becomes (Benkert & Heine, 1987):

$$V = -(A''/2)\varphi_0^2 + (B_1/4)\varphi_0^4, \tag{20}$$

where φ_0 is the amplitude of the modulated twist angle and

$$A'' = A' + C(q), \tag{21}$$

$C(q)$ being the Fourier transform of the intermolecular coupling in (17), with minimum energy at q_b, $q_b\mathbf{b}^*$ being the incommensurate wavevector. $C(q_b)$ is positive and nearly three times as large as $|A'|$ making the sign of A'' positive and giving a shallow double well in potential (20). Thus $A'' \simeq 2|A'| = 0{\cdot}32$ mdyn Å rad^{-2}.

With this estimate of A'', taking $\mathrm{d}V/\mathrm{d}\varphi_0 = 0$ for $\varphi_0 = 5{\cdot}5°$, equation (20) gives an average potential barrier height equal to 0·44 kJ mol^{-1} for the double well associated with the incommensurate structure. In our model the energy necessary to make a molecule planar when it exhibits the maximum twist is $2\int_0^{\varphi_0}|\Gamma_i - C_e^{\min}\varphi|\,\mathrm{d}\varphi = 0{\cdot}86$ kJ mol^{-1} (the factor two before the integral is associated with the two phenyl rings of a biphenyl molecule). Now considering that the torsion angles $\theta_t = 2\varphi$ in the incommensurate phase are distributed between $2\varphi_0 = 11$ and 0°, the average energy to make all the molecules planar in the crystal is about $0{\cdot}86/2 = 0{\cdot}43$ kJ mol^{-1}, in fair agreement with the above estimates.

Benkert, Heine & Simmons (1987) have also studied the condition under which their model can give an incommensurate structure as the ground state at $T = 0$ K and at low pressure ($P < 0{\cdot}6$ kbar). They find that this can happen only for a limited range of the parameter A_1:

$$0{\cdot}98 < A_1 < 1{\cdot}04 \text{ mdyn Å rad}^{-2}. \tag{22}$$

As their estimate of A_1 is 1·26 mdyn Å rad^{-2} they conclude that the observed incommensurate phase III is a metastable state, the equilibrium phase being the commensurate twofold superlattice (cell $2b$). Our own estimate of A_1 (or $2C_e^{\max}$) from the analysis of diffraction results is 1·93 mdyn Å rad^{-2}. It is also situated above the highest value of the calculated permitted range corresponding to a stable incommensurate phase.

Concluding remarks

One of the most striking features of crystalline polyphenyls is the diversity of phase-transition mechanisms involved: order–disorder for *p*-terphenyl and *p*-quaterphenyl, displacive for biphenyl. With a view to understanding these mechanisms, the thermal motion of the *p*-terphenyl central ring as regards librations around the long molecular axis is the only one, in the whole family of polyphenyls, which can be completely and accurately analyzed from diffraction data. This analysis gives key information on two essential interactions which can be considered to be constant in all polyphenyls: the intermolecular field experienced by a phenyl ring at room temperature and the intramolecular potential between two adjacent phenyl rings, the shape of which has been specified. Thus the information extracted from the *p*-terphenyl diffraction data has permitted us to use a simple model to calculate the potential barrier heights in crystalline *p*-quaterphenyl ($V > kT$) and in crystalline biphenyl ($V < kT$), in fair agreement with NMR results and confirming the difference between the nature of the transitions. The model has also given a value for the torsional potential in gaseous biphenyl in agreement with gaseous electron diffraction results. When the structural characteristics of the biphenyl low-temperature incommensurate phase ($T \simeq 20$ K) are introduced into the model, without changing the intramolecular potential, a large increase in the average intermolecular forces can be deduced. This is well accounted for by the strong crystal contraction in the *a*-axis direction almost perpendicular to the mean molecular planes. The model also gives the energy difference between the incommensurate phase, with a modulated torsion angle, and a structure exhibiting planar molecules, in fair agreement with models based on atom–atom potential-energy calculations.

Thus X-ray and neutron diffraction gives an overall, coherent and accurate estimate of the competing inter- and intramolecular interactions which govern the surprisingly varied behaviour observed in the family of polyphenyls. Even in this case, with the complications of the mixing of torsional and librational modes, it appears to offer a useful complement to other experimental as well as theoretical methods used to estimate dynamic parameters associated with intramolecular motions.

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APPENDIX

Indirect estimation of the torsion angle θ_0 in gaseous biphenyl from diffraction data

The similarity of the low-temperature structures of *p*-terphenyl (Baudour *et al.*, 1976) and *p*-quaterphenyl (Baudour *et al.*, 1978) suggests a similarity for the high-temperature conformations which can be expressed as $(\varphi, -2\varphi, \varphi)$ for *p*-terphenyl and $(\varphi, -2\varphi, 2\varphi, -\varphi)$ for *p*-quaterphenyl, the angles in brackets giving the rotations of the phenyl rings measured from the average planar configuration. The central ring of *p*-terphenyl and an inner ring of *p*-quaterphenyl exhibiting the same rotation 2φ are submitted to the same intermolecular force $2C_e\varphi$, balanced by the same intramolecular torque which is a sum of two terms, each being associated with an intramolecular bond. If we assume the sinusoidal shape of equation (2) for the intramolecular couple between two adjacent phenyl rings we can write $\sin(\pi 3\varphi/\theta_0) + \sin\pi(3\varphi/\theta_0)$ for the *p*-terphenyl central ring $= \sin(\pi 3\varphi/\theta_0) + \sin(\pi 4\varphi/\theta_0)$ for a *p*-quaterphenyl inner ring, or

$$\sin\left(\pi\frac{3\varphi}{\theta_0}\right) = \sin\left(\pi\frac{4\varphi}{\theta_0}\right). \tag{23}$$

In the range of experimental φ values, the above equation is satisfied if:

$$\theta_0 = 7\varphi. \tag{24}$$

From the similarity of the *p*-terphenyl and *p*-quaterphenyl structures, we can take $2\varphi = 13{\cdot}3^\circ$, the value obtained by resolving the disorder in the high-temperature phase of *p*-terphenyl (Baudour *et al.*, 1977, 1986). Thus we obtain the torsion angle θ_0 between two phenyl rings at equilibrium, when intramolecular interactions only are considered: $\theta_0 = 46{\cdot}55^\circ$. This is an estimate of the torsion angle in gaseous biphenyl.

If we consider the average torsion angles observed in the low-temperature phase of *p*-quaterphenyl (Baudour *et al.*, 1978): $3\varphi = 17{\cdot}1^\circ$ between an outer and an inner ring, $4\varphi = 22{\cdot}6^\circ$ between the inner rings, we obtain $\theta_0 = 39{\cdot}9$ and $39{\cdot}55^\circ$ respectively.

These estimates of the dihedral angle for gaseous biphenyl ($\theta_0 = 46{\cdot}5$, $39{\cdot}9$, $39{\cdot}5^\circ$) obtained indirectly from the similarity of *p*-quaterphenyl and *p*-terphenyl structures, are in reasonably good agreement with results obtained from electron diffraction on gaseous biphenyl: $\theta_0 = 42^\circ$ (Bastiansen, 1949), $\theta_0 = 44{\cdot}4^\circ$ for $C_{12}H_{10}$ and $\theta_0 = 45{\cdot}5^\circ$ for $C_{12}D_{10}$ (Almenningen *et al.*, 1985).

The modifications with regard to the sinusoidal shape of the intramolecular couple Γ_i which are considered in our model are particularly important near the planar conformation. Although these modifications change the potential barrier heights in the crystal substantially, they give only small variations of Γ_i near the equilibrium conformations in *p*-terphenyl and *p*-quaterphenyl in such a way that the equilibrium configurations are very slightly modified (Table 1). Therefore the estimate of θ_0 in the above reasoning based on a sinusoidal shape, is still valid.

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Structure Determination of the Bacteriophage MS2

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Abstract

The structure of the bacterial virus MS2 has been solved at 3·3 Å resolution. Initial phases to 13 Å resolution were obtained from a model based on the known coordinates of the plant virus southern bean mosaic virus. These phases were extended in small steps to a resolution of 3·4 Å. The phases obtained represented essentially the Babinet opposite of the true structure and were not of a sufficiently good quality to allow an interpretation of the electron density contoured at negative levels. Difference Fourier maps of two heavy-atom derivatives based on these phases were interpretable, and these derivatives were used to calculate isomorphous replacement phases at 8·8 Å resolution. Phase extension to 3·3 Å resolution led to maps which could be easily interpreted.

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