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Structural Phase Transition in Polyphenyls. VIII. The Modulated Structure of Phase III of Biphenyl ($T \simeq 20$ K) from Neutron Diffraction Data

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(*Received* 15 *March* 1982; *accepted* 14 *June* 1982)

Abstract

Starting from the approximation of the superstructure [Cailleau, Baudour & Zeyen (1979). *Acta Cryst.* B**35**, 426–432] the modulated structure of deuterated biphenyl (phase III, $T \simeq 20$ K) has been determined by taking into account 265 main reflections and 273 first-order satellites. The de Wolff–Janssen–Janner (3 + 1)-dimensional superspace group is the noncentrosymmetric $P^{Pa}_{\bar{1}}$, although the symmetry of the centrosymmetric group $P^{P2_1/a}_{1\,\bar{1}}$ is almost respected. The refinement based on a harmonic displacive modulation has been performed with a very limited number of variable parameters: four positional parameters, phenyl rings being described by rigid blocks, 11 thermal parameters (individual isotropic Debye–Waller factors), and six modulation parameters: three amplitudes and three phases. The final value of R is 0·106 (0·088 for main reflections, 0·176 for satellites. The main features of the modulation are (*a*) a torsion around the long molecular axis with a maximum deformation of 11°, (*b*) a rotation around the normal to the mean molecular plane with an amplitude of 1·0°, 90° out of phase with the torsion, and (*c*) a translation along the long molecular axis with an amplitude of 0·035 Å, in phase with the torsion.

Introduction

At about 40 K biphenyl undergoes a structural phase transition induced by a so-called soft phonon observed with Raman spectroscopy (Bree & Edelson, 1977). In a first neutron diffraction study (Cailleau, Baudour & Zeyen, 1979) this structural phase transition had been interpreted as resulting from the appearance of superlattice reflections at the B $(0,\frac{1}{2},0)$ point of reciprocal space, corresponding to a doubling of the b parameter only and not to the doubling of a and b as found for other polyphenyls: *p*-terphenyl (Baudour, Delugeard & Cailleau, 1976) and *p*-quaterphenyl (Baudour, Delugeard & Rivet, 1978).

The space group of biphenyl at room temperature is $P2_1/a$ with two planar molecules on inversion sites (Hargreaves & Rizvi, 1962; Trotter, 1961; Robertson, 1961) and the essential structural modifications in the low-temperature phase result, as in other polyphenyls, from a torsion angle between the planes of phenyl groups. In biphenyl this angle was estimated from the first study (Cailleau, Baudour & Zeyen, 1979) to be about 10° and was in opposite senses for two neighbouring molecules along **b**.

More recent elastic neutron scattering measurements (Cailleau, Moussa & Mons, 1979) performed on a cold-source triple-axis spectrometer (with $\lambda = 4 \cdot 1$ Å instead of $\lambda = 1 \cdot 26$ Å in the first study) gave a higher resolution and showed clearly that each 'pseudo superlattice reflection' could be resolved into four or two (this number depending upon the temperature) satellite reflections typical for a modulated structure (Fig. 1). So, in fact, the new reflections appearing at low temperature were not characterized by the commensurate wavevector $\mathbf{q}^* =$

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$\frac{1}{2}\mathbf{b}^*$, but by the incommensurate one $\mathbf{q}^* = \pm k_1\mathbf{a}^* + k_2\mathbf{b}^*$, k_1 and k_2 changing with temperature. Between $T_{\rm I} = 38$ K and $T_{\rm II} = 21$ K, $k_1 \simeq 0{\cdot}05$ and $k_2 \simeq 0{\cdot}46$, for deuterated biphenyl. These values define an intermediate phase called phase II. For this phase it is not fully established whether the modulation must be described with two wavevectors $\mathbf{q}_1^* = k_1\mathbf{a}^* + k_2\mathbf{b}^*$ and $\mathbf{q}_2^* = -k_1\mathbf{a}^* + k_2\mathbf{b}^*$ or with one wavevector. Indeed the splitting of each pseudo superlattice reflection into four satellites (instead of two in phase III) may result from the existence of symmetry-related domains such as those found in *p*-terphenyl (Baudour *et al.*, 1976) and *p*-quaterphenyl (Baudour *et al.*, 1978). Below $T_{\rm II} = 21$ K, $k_1 = 0$, $k_2 \simeq 0{\cdot}46$ for phase III, which is a one-dimensional modulated structure. Second-order satellites located near main reflections because $2\mathbf{q}^* \simeq 0{\cdot}92\mathbf{b}^*$ are not seen in an ordinary diffraction experiment. High-resolution elastic neutron scattering measurements reveal some of them, showing that they are very weak (Cailleau, Baudour, Meinnel, Dvorkin, Moussa & Zeyen, 1980). These new neutron scattering results have confirmed the existence of two low-temperature phases already observed by Cullick & Gerkin (1977) in an EPR experiment and by Bree & Edelson (1978) from birefringence measurements.

In this paper we study only the modulated phase III of biphenyl at $T \simeq 20$ K. Firstly we discuss the former results obtained in the approximation of the superstructure. In this case refinements gave very different scale factors for main reflections and for pseudo superlattice reflections. This can now be interpreted as resulting from the modulation. Then we have re-examined the intensity profiles of each pseudo superlattice reflection, integrated in the first study. In many cases it has been possible to distinguish two peaks more or less well resolved, and to measure their magnitudes.

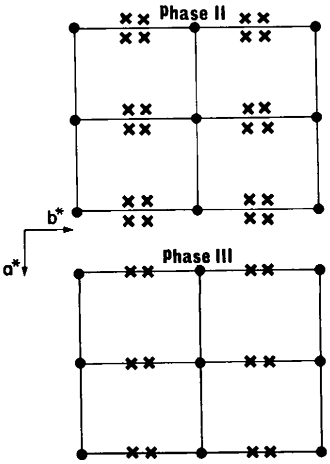

Fig. 1. (001) zone scattering plane in the reciprocal lattice of biphenyl. Full circles indicate the reciprocal-lattice points in the high-temperature phase and crosses locate the satellite reflections found between 38 and 21 K (phase II) and below 21 K (phase III) (for deuterated biphenyl).

These double-peaked profiles indicated that data corresponded to phase III (and certainly near phase II). Using these data we have determined the symmetry of the modulated structure in (3 + 1) dimensions following the method developed by de Wolff (1974). Then we have used the structure factor formula for incommensurate phases established by the same author, adapted in order to perform a constrained refinement of the different components of the modulation: the same phase will be attributed to each phenyl ring in a torsional motion and to each molecule in a librational or translational motion.

The approximation of the superstructure

In the diffraction pattern of biphenyl at $T \simeq 20$ K a large number of reflections, generally the most intense, can be assigned to a normal monoclinic reciprocal lattice with basis vectors $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, with $\mathbf{b}^*$ perpendicular to $\mathbf{a}^*$ and $\mathbf{c}^*$. Each of these reflections, called main reflections, is accompanied by 'satellites' which can be described by introducing a fourth index m and an extra basis vector $\mathbf{q}^* = k_2\mathbf{b}^*$ ($k_2 \simeq 0{\cdot}46$) in an extended form of the diffraction vector $\mathbf{H} = h_1\mathbf{a}^* + h_2\mathbf{b}^* + h_3\mathbf{c}^* + m\mathbf{q}^*$ (h_1, h_2, h_3, m integers). These extra reflections result from a displacive one-dimensional modulation which does not respect the symmetry of translation along the binary axis b. However, as shown by de Wolff (1974), a modulated structure can approximately be described as a superstructure by substituting rational numbers for the irrational components of $\mathbf{q}^*$ in the basic lattice $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$. In the particular case of phase III of biphenyl one takes $\mathbf{q}^* = \mathbf{b}^*/2$ instead of the true value $\mathbf{q}^* \simeq 0{\cdot}46\mathbf{b}^*$. The diffraction vectors $\mathbf{H} = h_1\mathbf{a}^* + h_2\mathbf{b}^* + h_3\mathbf{c}^* + m\mathbf{q}^*$ of first-order satellites h_1, h_2, h_3, 1 and h_1, $h_2 + 1$, h_3, -1 are very near in reciprocal space because the vectors $h_2\mathbf{b}^* + \mathbf{q}^* = (h_2 + 0{\cdot}46)\mathbf{b}^*$ and $(h_2 + 1)\mathbf{b}^* - \mathbf{q}^* = (h_2 + 0{\cdot}54)\mathbf{b}^*$ are rather similar (Fig. 1), resulting in more or less severe overlap of the diffraction peaks, particularly when a short wavelength is used ($\lambda = 1{\cdot}26$ Å). In the approximation of the superstructure (Cailleau, Baudour & Zeyen, 1979) the separation between these two neighbouring satellites was overlooked and one integrated pseudo superlattice reflection was considered.

With this approximate model the cell parameter **b** doubles in the low-temperature phase. The space group *Pa* is in good agreement with spectroscopic results which indicate two inequivalent molecules and the structure is noncentrosymmetric as imposed by spectroscopic selection rules (Villermain-Lecollier, Wyncke & Hadni, 1971; Brenner, Hutchison & Kemple, 1974; Friedman, Kopelman & Prasad, 1974; Hochstrasser, Scott, Zewail & Fuess, 1975). The torsion angles for the two independent molecules are found to be very similar: 10·2° and for two neighbouring molecules, in opposite directions for each translation **b**/2.

A rather puzzling feature was that at the end of the refinement the ratio between the scale factors for superlattice and lattice reflections was 0·674 (all reflections being measured in the same conditions on a diffractometer). A trial refinement of the structure with the same scale factor for all reflections gave a torsion angle of about 6° but in this case the agreement factor becomes sensibly higher.

In the first study the reason for the discrepancy between scale factors was sought in an order–disorder behaviour. It can be postulated that molecules jump between two opposite configurations A and B characterized by the inversion of the torsion angle φ. Main reflections depend only on the mean structure, the average being made on all the high-temperature (in a geometrical sense) unit cells. The fact that below T_c half the molecules are stabilized in configuration A and the other half in configuration B does not change the average structure (on condition that the torsion angle $|\varphi|$ is temperature independent). On the other hand, the structure factor of a superlattice reflection can be written as $F \propto (P_A - P_B)\varphi$, P_A and P_B being the occupancy probabilities of the two opposite configurations for a given particular molecule (Baudour & Meinnel, 1982). So when the order is not completely realized the structure factors of superlattice reflections are multiplied by a factor $|P_A - P_B|$ less than unity, main reflections not being affected. This weakening of superlattice reflections can be taken into account in refinement by attributing a smaller scale factor to them. In fact, although the transition is called displacive as it is accompanied by a soft mode, this behaviour which can be qualified as order–disorder explains the decrease and finally the cancellation of satellite reflections between 20 and 38 K, the modulation amplitude being independent of temperature and the long-range correlated atomic displacements in the incommensurate phase becoming uncorrelated displacements in the high-temperature phase (Baudour, Meinnel & Delugeard, 1983).

However, at 20 K the stabilization of molecules can be considered as completely realized and the discrepancy between scale factors can be interpreted simply from a displacive modulation. Firstly, by anticipating the results of the next section, we note that the torsion angle (10·2°) determined in the approximation of the superstructure is near the actual amplitude of the torsion component of the displacement wave (11·0°). This value of 10·2° for the torsion angle was determined in the first study by main reflections which contain information on the average structure. Indeed, several studies (Depmeier, 1981; de Pater, 1979) show that in the average structure refinement the distortion wave is observed as anisotropic smearing out of the atoms.

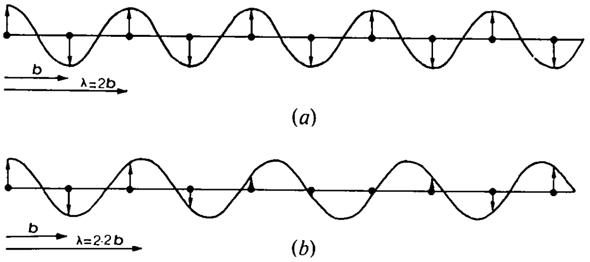

Fig. 2. Schematic representation of the modulation wave in biphenyl. (*a*) In the superstructure model ($\mathbf{q}^* = 0{\cdot}5\mathbf{b}^*$, $\lambda = 2b$) all molecules exhibit the complete distortion. (*b*) With the actual modulated structure ($\mathbf{q}^* = 0{\cdot}46\mathbf{b}^*$, $\lambda = 2{\cdot}2b$) a number of molecules are almost undistorted.

Because the true modulation is characterized by the incommensurate wavevector $\mathbf{q}^* = 0{\cdot}46\mathbf{b}^*$ instead of $\mathbf{q}^* = 0{\cdot}5\mathbf{b}^*$, a great number of molecules are actually not or only weakly distorted as schematized on Fig. 2, contrary to the superstructure model in which all molecules exhibit the complete distortion. This superstructure model equivalent to a split-atom approximation for main reflections gives, as already mentioned, a rather good estimate of the maximum torsion angle. However, satellites are much more sensitive to this approximation of the incommensurate harmonic modulation, which requires for them a smaller amplitude. Since the torsion angle is unique in the superstructure model and imposed by main reflections, this is compensated in refinement by a smaller scale factor for satellite reflections.

In order to confirm this hypothesis we have calculated the structure factors F_s of some pseudo superlattice reflections (superstructure model) and that of the two corresponding satellite reflections F_1 and F_2 (modulated structure as developed in the following sections). In the case of a sinusoidal distortion wave including one component (a torsion around the long molecular axis, with an amplitude of 5° for each phenyl ring), we have found that the ratio $(F_1^2 + F_2^2)^{1/2}/F_s$ varied between 0·66 and 0·76 with an average value of 0·72. For a square wave the average ratio is 0·90. The value of 0·674 for the ratio of scale factors found in the refinement based on the approximation of the superstructure means that the actual modulation is certainly much better described by a sinusoidal wave form than by a steeper type of periodic function.

Experimental

The experimental conditions have already been described by Cailleau, Baudour & Zeyen (1979). We recall that the compound was biphenyl-d_{10} of 99·4% nominal isotopic purity. The sample chosen had dimensions 3 × 3 × 2 mm. The experiment was performed on the D10 four-circle neutron diffractometer at the Institut Laue–Langevin. A vertically focusing Cu (200) monochromator was used at an incident wavelength $\lambda = 1{\cdot}26$ Å. Data were collected with the ω-scan mode. The sample was mounted in a He cryostat. The constancy of the temperature was controlled to within 0·1 K but the absolute error was about 1 K. So the indication that the crystal was in phase III and not in phase II was obtained from the double-peaked aspect of intensity profiles.

It must be noted that no new data have been collected. The 265 main reflections are exactly the same as in the first study. However, the intensity profiles of 'pseudo superstructure reflections' have been re-examined visually. The separation between two peaks was extremely variable from one reflection to another. For example, the splitting could be visible for one reflection and invisible for its symmetry-equivalent one. This is probably due to the mosaicity of the crystal which gives an anisotropic resolution, as indicated by the largely variable FWHM (full width at half maximum) of main-reflection Bragg peaks. Even when the existence of two peaks appeared clearly, from separated maxima, the bases generally overlapped more or less severely. So the separation was made visually and graphically by imposing symmetric profiles for each peak. Then each peak was integrated. In this way 273 first-order satellite reflections have been measured. A number were very weak and certainly affected by an important relative error.

Numerical values of parameters defining the so-called basic unit cell at $T \simeq 20$ K are $a = 7{\cdot}77\ (0{\cdot}02)$, $b = 5{\cdot}57\ (0{\cdot}01)$, $c = 9{\cdot}44\ (0{\cdot}02)$ Å, $\beta = 93{\cdot}7\ (0{\cdot}2)°$.

No corrections were applied for absorption ($\mu \simeq 3 \times 10^{-3}\ \mathrm{mm}^{-1}$) or extinction.

The symmetry of the modulated structure in (3 + 1) dimensions

As shown by de Wolff (1974) a structure with a one-dimensional modulation is conveniently described by using a four-dimensional space-group symmetry which restores the characteristics of crystals, *i.e.* a lattice of symmetry translations. The real crystal can be regarded as a three-dimensional section through the four-dimensional periodic 'supercrystal'. These ideas have been extensively developed (Janner & Janssen, 1977; de Wolff, 1977; Janner, Janssen & de Wolff, 1979; Janner & Janssen, 1980*a*,*b*; de Wolff, Janssen & Janner, 1981).

Point group

In terms of the indices $h_1\ h_2\ h_3$ and m, the diffraction pattern of biphenyl at 20 K is invariant under the following point-group operation:

$$m' = \begin{vmatrix} 1 & & & \\ & \bar{1} & & \\ & & 1 & \\ & & & \bar{1} \end{vmatrix}.$$

The prime in m' stands for reversal of the sign of the fourth reciprocal coordinate m. Because of the Friedel law the diffraction pattern also exhibits a centre of symmetry which does not necessarily exist in the actual symmetry.

Space group

The following systematic extinctions or pseudo extinctions occur: main reflections $h_1\ 0\ h_3\ 0$ are absent for h_1 odd; main reflections $0\ h_2\ 0\ 0$ are probably absent (or at least extremely weak) for h_2 odd; satellite reflections $0\ h_2\ 0\ \pm 1$ although weak probably exist for h_2 odd. [This existence is difficult to establish with certainty because each of these satellites with h_2 odd is situated in reciprocal space near a satellite with h_2 even (Fig. 1).]

By admitting the extinction of reflections $0\ h_2\ 0\ 0$ for h_2 odd, the average three-dimensional structure, obtained by disregarding satellites, obeys space group $P2_1/a$ with two planar molecules in the unit cell, the asymmetric unit being one phenyl ring (half a molecule). This average structure is the same as that of the high-temperature phase.

However, if we consider the existence of some weak satellites $0\ h_2\ 0\ \pm 1$ for h_2 odd, the superspace group cannot be centrosymmetric. So the basic space group we choose is not the centrosymmetric $P2_1/a$ but the noncentrosymmetric Pa (these two space groups obeying the point-group symmetry). In this case the basic space group is a subgroup of the space group of the basic structure defined as a zero-order approximation of the actual structure. The asymmetric unit is a complete molecule.

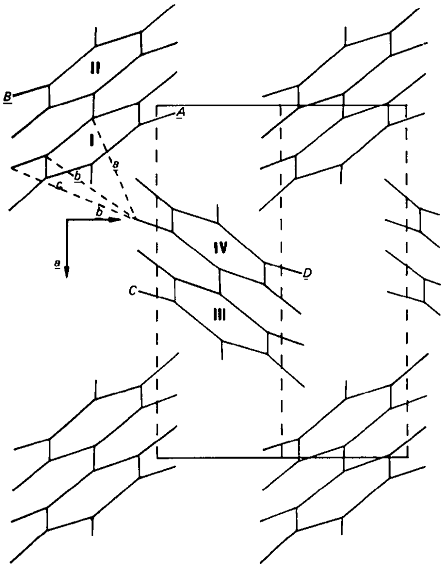

Fig. 3. A projection of the molecular arrangement along the c axis, in the average unit cell (basic structure). Broken lines: intermolecular distances considered in Fig. 6.

The symmetry operation to be considered in four dimensions is: $(x,y,z,\tau) \rightarrow (\frac{1}{2}+x, -y, z, -\tau)$, the centre of the molecule taken as asymmetric unit, being located at (0, −0·25, 0) in the average unit cell (Fig. 3).

In order to facilitate the comparison with the other phases of biphenyl, we use a setting with $\mathbf{q}^* \parallel \mathbf{b}^*$ (**b** binary axis) instead of $\mathbf{q}^* \parallel \mathbf{c}^*$, **c** binary axis in the setting chosen by de Wolff *et al.* (1981). Consequently, using the two-line symbols established by de Wolff *et al.* the superspace group is $P^{Pa}_{\bar{1}}$. In the following sections, however, we will compare results of refinements performed with the two superspace groups ($P^{Pa}_{\bar{1}}$ and $P^{P2_1/a}_{1\ \bar{1}}$) in order to try to confirm, by statistical arguments based on the agreement factor R, the choice of the noncentrosymmetric group.

The structure factor

De Wolff (1974) has shown that the actual structure factor can be calculated by a four-dimensional Fourier transformation of the periodic structure in four-dimensional space: R_4. In R_4 atoms are represented by strings having periodic bends (for a displacive modulation) continuing endlessly in the overall direction ($\mathbf{e}_4$) of the normal to R_3, the usual three-dimensional space. De Wolff establishes the structure factor expression upon summing over the string index μ.

$$F(h_1,h_2,h_3,m) = \sum_{\mu} f_\mu \exp 2i\pi(h_1\bar{x}_1^\mu + h_2\bar{x}_2^\mu + h_3\bar{x}_3^\mu)$$
$$\times \int_0^1 \mathrm{d}\tau \exp 2i\pi\left[\sum_1^3 (h_i + mk_i)\, u_i^\mu(\tau) + m\tau\right]. \qquad (1)$$

$\bar{x}_i^\mu$ are the average coordinates of undisplaced atoms in the basic unit cell. u_i^μ atomic displacements are periodic functions of τ.

$$\tau = t + k_1\bar{x}_1^\mu + k_2\bar{x}_2^\mu + k_3\bar{x}_3^\mu \qquad (2)$$
$$\mathbf{q}^* = k_1\mathbf{a}^* + k_2\mathbf{b}^* + k_3\mathbf{c}^*$$

($\mathbf{q}^*$ being the modulation wavevector). t denotes the phase of this periodic function, varying when moving from one given three-dimensional (3D) unit cell to another.

For sinusoidal displacements

$$u_i^\mu = U_i^\mu \sin(2\pi\tau - \alpha), \qquad (3)$$

the integral in (1) is

$$\exp[im(\alpha + \pi)]\, J_m\left|2\pi\sum_1^3 (h_i + mk_i)\, U_i^\mu\right|,$$

J_m being the Bessel function of order m.

Now the relations derived by van Aalst, den Hollander, Peterse & de Wolff (1976) give the expression of t in 3D space. An atom is located in the reference structure at $\mathbf{r}'$ (the index μ is omitted for simplicity). Primed symbols are used for quantities depending on the unit cell in which the atom is located.

$$\tau = \mathbf{q}^*\, \mathbf{r}'$$
$$\mathbf{r}' = \bar{x}_1\mathbf{a} + \bar{x}_2\mathbf{b} + \bar{x}_3\mathbf{c} + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}.$$

$\bar{x}_1, \bar{x}_2, \bar{x}_3$ define the undisplaced atomic position in the unit cell where the atom is effectively located and (n_1, n_2, n_3) which are integers define this particular unit cell in the reference structure.

The above relations give:

$$\tau = n_1k_1 + n_2k_2 + n_3k_3 + k_1\bar{x}_1 + k_2\bar{x}_2 + k_3\bar{x}_3.$$

A comparison with (2) shows that

$$t = n_1k_1 + n_2k_2 + n_3k_3.$$

The refinements of the low-temperature structures of other polyphenyls (*p*-terphenyl, *p*-quaterphenyl) had shown that, because of the relatively small number of data, it was necessary to impose constraints on molecular geometries (phenyl rings being considered as rigid blocks) and thermal motion. In the case of the modulated structure of biphenyl, additional constraints must be imposed on amplitudes and phases of the modulation. Indeed, in a phenyl ring considered as a rigid block all atoms must be in phase in the same unit cell (defined by t) for a particular component of the modulation (libration or translation). Besides, amplitudes U_i for each atom are completely determined from the amplitude of the modulation of the phenyl ring, when the libration or translation axes have been chosen (in principle the axes of inertia).

So instead of expression (3): $u_i = U_i \sin(2\pi\tau - \alpha)$, in which the argument τ depends on the particular atomic coordinates, we use $u_i = U_i \sin(2\pi t - \varphi)$ in which φ has the same value for all atoms of a given phenyl ring.

The integral in (1) becomes:

$$\exp 2i\pi m \sum_1^3 k_i\bar{x}_i \int_0^1 \mathrm{d}t \exp 2i\pi\left[\sum_1^3 (h_i + mk_i)\, u_i^\mu(t) + mt\right].$$

Then the structure factor is expressed as:

$$F(h_1,h_2,h_3,m) = \sum_\mu f_\mu \exp 2i\pi\left[\sum_1^3 (h_i + mk_i)\, \bar{x}_i^\mu\right]$$
$$\times \int_0^1 \mathrm{d}t \exp 2i\pi\left[\sum_1^3 (h_i + mk_i)\, u_i^\mu(t) + mt\right],$$

obtained from the de Wolff expression (1) by replacing h_i by $(h_i + mk_i)$ outside the integral and τ by t inside the integral.

For two symmetry-related atoms having, respectively, the coordinates (x_1, x_2, x_3) and $(\frac{1}{2} + x_1, -x_2,$

x_3) in the basic unit cell, the modulated displacements are given, from the superspace group $P^{Pa}_{\bar{1}}$, by

$$u_1^2(t) = u_1^1(-t-\varphi); \quad u_2^2(t) = -u_2^1(-t-\varphi);$$

$$u_3^2(t) = u_3^1(-t-\varphi),$$

the phase change φ being unrestricted by symmetry conditions.

Determination and refinement of the modulated structure

In order to carry out a constrained refinement, bond lengths and angles of phenyl rings were imposed (Fig. 4) by averaging the values obtained at 110 K and room temperature by Charbonneau & Delugeard (1976, 1977), values taking account of libration corrections. The C—D bond lengths have been set to 1·105 Å.

Biphenyl has two molecules in the unit cell of the basic phase. However, as explained in a preceding section, the asymmetric unit in the space group of the supercrystal consists of one complete molecule, each of the two phenyl rings exhibiting a periodic distortion as a function of t. As 0 h_2 0 0 reflections apparently vanish, the average molecular configuration is probably centrosymmetric and planar. However, the existence of some weak 0 h_2 0 0 reflections cannot be discarded and so the possibility of a weak torsion angle for the average molecule has not been rejected. By adding to this internal geometrical parameter the three Eulerian angles to allow the molecule to take up any arbitrary orientation in the crystal, the total number of variable geometrical parameters is four.

Firstly only individual isotropic temperature factors were considered and atoms related by the probable centre of symmetry of the average structure were given the same temperature factors. So the number of thermal parameters was eleven.

The refinement realized in the approximation of the superstructure had shown that the essential feature of the modulation was a torsion in which the two phenyl rings of a molecule rotate around the long molecular axis, in opposite senses, with the same amplitude. In the expression of atomic displacements assumed to be sinusoidal for simplicity $u_i = U_i \sin(2\pi t - \varphi)$, torsion was taken into account by considering a phase $\varphi = 0°$ for the first phenyl ring and $\varphi = 180°$ for the second of the reference molecule. For the second molecule situated in the basic unit cell the phase change was adjusted to obtain the best R factor. The curvilinear atomic displacements resulting from the torsion modulation were approximated by rectilinear displacements. The amplitude of each atom was calculated from the libration amplitude of phenyl rings. In this purely torsional model, modulation was characterized by only two variable parameters: the torsion amplitude and the phase change between the second and the first molecule of the basic unit cell.

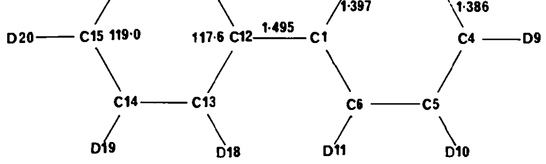

Fig. 4. A molecule of biphenyl showing the numbering of the atoms. Bond lengths (Å) and angles (°) were imposed in the constrained refinement.

A full-matrix least-squares program was written. The integral appearing in the structure factor formula was calculated from Bessel functions. Derivatives on geometrical parameters and amplitude of modulation were computed numerically. Derivatives on thermal parameters were calculated analytically. As mentioned in *Experimental*, the data set included 538 independent reflections of which 273 were satellite reflections.

The neutron scattering lengths were $b_C = 6{\cdot}63$ and $b_D = 6{\cdot}67$ fm. The function minimized was $\sum w(|F_o| - |F_c|)^2$. All reflections were given unit weights.

From a geometrical point of view all refinements indicated that the average molecular configuration should be considered as planar (Table 1). As regards modulation, satellite reflections are much more sensitive than main reflections to its characteristics. So they are the better test to estimate the validity of the model. For these 'satellites' the final reliability factor was 0·305 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) obtained for an amplitude of modulation converging very quickly to 5·5° and a phase change of approximately 100° between the two molecules of the basic unit cell. At this stage two important features could be noted. Firstly, in refinements permitting independent scale factors, the same values, within standard deviations, were obtained for main and satellite reflections. So the anomaly observed with the superstructure model had disappeared. Secondly, by considering satellites only, the ratio $\sum |F_o| / \sum |F_c|$ converged to 1·13. In particular, for several satellites the observed structure factor was notably larger than the calculated one. This was an indication that the actual modulation was more complex than a simple torsion and that it was probably necessary to introduce additional components.

It must be noted that by superposing several motions of a rigid body, librations and translations, around or along different axes, each with a particular phase, the individual atomic motions become elliptic in R_3, as already shown in Na_2CO_3 (van Aalst *et al.*, 1976). In these conditions the integral appearing in the structure factor formula was calculated numerically.

Many attempts were made combining different components for the overall modulation and consuming

Table 1. *Positional parameters, isotropic temperature factors and final modulation parameters*

(*a*) Final positional parameters ($\times 10^4$) and isotropic temperature factors (Å^2)

The phenyl rings are considered as rigid blocks with an imposed geometry in the refinement (Fig. 4). The e.s.d.'s on the Euler angles positioning the molecule are about 0·05°. The second half of the average molecule is deduced by considering a centre of inversion at (0, −0·25, 0). Standard deviations of the temperature factors are in parentheses.

	x	y	z	B (Å^2)
C(1)	351	−2518	756	0·92 (0·10)
C(2)	−52	−708	1704	1·30 (0·11)
C(3)	602	−746	3109	1·26 (0·11)
C(4)	1674	−2594	3604	0·79 (0·10)
C(5)	2087	−4404	2677	0·85 (0·11)
C(6)	1433	−4368	1271	0·70 (0·11)
D(7)	−905	770	1319	2·10 (0·13)
D(8)	266	702	3842	1·88 (0·14)
D(9)	2194	−2624	4721	1·34 (0·11)
D(10)	2941	−5884	3061	1·99 (0·13)
D(11)	1769	−5818	538	1·72 (0·13)

(*b*) Final modulation parameters

L and *N* are respectively the long molecular axis and the axis normal to the mean molecular plane.

The displacement wave $\mathbf{u}'(t)$ of the second molecule situated in the basic unit cell is obtained from that of the first molecule $\mathbf{u}(t)$ by $\mathbf{u}'(t) = S\,\mathbf{u}(-t - 100°)$, S being the point-group operation of the basic space group *Pa*. Standard deviations are in parentheses.

	Amplitude	Phase
Torsion around *L*	11·0 (0·2)°	First phenyl ring 0° Second phenyl ring 180
Libration around *N*	1·0 (0·1)	90
Translation along *L*	0·035 (0·005) Å	0

much calculation time because of the integration in the structure factor formula. At each refinement cycle atomic displacements were calculated by summing over the v components $u_i(t) = \sum_v U_i^v \sin(2\pi t - \varphi v)$. The following general remarks can be made. Refinements give a good estimate of the amplitudes of the different components of the modulation. Indeed, almost the same values are obtained with a limited number of data: 70 'satellites' and 20 main reflections are sufficient to obtain reliable results. This is a consequence of the very small number of variable parameters and is important to save computer time.

As regards phase angles, they were not refined (the *R* factor is only slightly sensitive to a slight variation of 3 or 4°) but adjusted to minimize the *R* factor.

Description of the modulated structure

Starting from the basic structure, which is essentially the structure at room temperature, with planar molecules, the modulated structure of biphenyl at $T \simeq 20$ K can be described as resulting from the combination of three motions:

(1) A torsion around the long molecular axis ($\varphi_1 = 0°$, $\varphi_2 = 180°$ for the two phenyl rings) with an amplitude of 5·5° for each phenyl ring (the maximum deformation angle being 11°). This torsion is the essential feature of the modulation.

(2) A rotation around the normal to the mean molecular plane, with an amplitude of 1·0°, approximately 90° out of phase with the torsion modulation.

(3) A translation along the long molecular axis with an amplitude of 0·035 Å approximately in phase with the torsion modulation.

The other possible modulations of the molecule's position and of its Eulerian angles are found too weak in our analysis to be significant.

If for a particular component (torsion, rotation or translation) the displacement of an atom of the reference molecule is given by $\mathbf{u}(t) = \mathbf{U}\sin(2\pi t - \varphi_0)$, for the symmetry-related atom of the second molecule situated in the basic unit cell, it is expressed as $\mathbf{u}'(t) = S\mathbf{U}\sin(-2\pi t - \varphi_0 - \varphi)$, S being the point-group operator associated with the glide plane. The best *R* factor is obtained for $\varphi \simeq 100°$.

Table 2 shows that the introduction of each new component of the modulation improves sensibly the *R* factor for satellite reflections and simultaneously makes their ratio $\sum F_o/\sum F_c$ tend to unity. On the other hand, the *R* factor for main reflections is not improved by adding new components to torsion. This means that these main reflections do not allow detailed characteristics of modulation to be specified. The final *R* was 0·106 for all reflections, 0·087 for main reflections and 0·176 for satellite reflections (0·165 for observed satellite reflections).* A calculation of the intensities of the second-order satellites confirms that they are very weak. Indeed, considering the average calculated

Table 2. *Evolution of* $R = \sum|F_o - F_c|/\sum F_o$ *for satellite and main reflections when new components are added in the modulation wave*

L and *N* are, respectively, the long molecular axis and the normal to the mean molecular plane.

Modulation components	Torsion-*L*-(11°)	Torsion-*L*-(11°) and libration-*N*-(1°)	Torsion-*L*-(11°), libration-*N*-(1°) and translation-*L*-(0·035 Å)
R (satellites only)	0·305	0·195	0·176
R (main reflections only)	0·088	0·088	0·088
SF_o/SF_c (satellites only)	1·127	1·026	1·007

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36997 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

intensities, the ratio between main reflections and second-order satellites is found to be 860; *cf.* the ratio of 17 between main reflections and first-order satellites.

Our results showing that the torsional and translational components (both antisymmetric for the inversion) are in phase and that the rotational component (symmetric for the inversion) is 90° out of phase with the former have been confirmed by a recent theoretical analysis using the rigid-phenyl approximation, inversion at high temperature and time-reversal symmetry (Vettier, 1982). From a crystallographic point of view, one can say that a phase change between torsion–translation and rotation, different from 90°, give, for two atoms related by the average centre of symmetry, elliptical trajectories not related by inversion. In this case, our structure factor calculations in $P^{Pa}_{\bar{1}}$ show that main reflections $0\ h_2\ 0\ 0$ with h_2 odd are no longer absent, in agreement with an average structure having lost its centre of symmetry.

Fig. 5 shows for a particular deuterium atom (No. 8, Fig. 4), and for the symmetry-related one of the second molecule in the unit cell, the projections on x_1, x_2 of atomic displacements when t varies between 0 and 1. The atomic trajectories are elliptical, involving a maximum displacement of about 0·2 Å from the mean position. It can be noted that when the distortion is maximum for one molecule it is almost minimum for the other. Fig. 6 is a plot of the behaviour of some intermolecular contact distances.

In the last stages, anisotropic temperature factors of the usual type were introduced, in the way described by van Aalst *et al.* (1976). In order to restrain the number of variable parameters, atoms were distributed between six groups: (1, 4, 12, 15); (2, 5, 13, 16); (3, 6, 14, 17); (9, 20); (7, 10, 18, 21); (8, 11, 19, 22) (see Fig. 4 for the numbering of atoms). Thermal parameters were the same for all atoms of each group. This resulted in an insignificant improvement on R (Hamilton, 1965) for main reflections: 0·084 instead of 0·087 and no improvement at all for satellites. Attempts with the formalism proposed by Yamamoto (1980) always in the approximation of anisotropic temperature factors independent of t, *i.e.* independent of the location of the unit cell in the crystal, gave no better results.

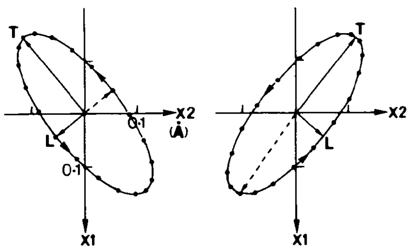

Fig. 5. Projection on x_1, x_2 of atomic displacements for deuterium atom No. 8 (see Fig. 4) and for the symmetry-related one of the second molecule in the unit cell. **T** represents the component of the modulation due to torsion and translation, **L** the component due to libration around the normal to the mean molecular plane. Full circles separate intervals Δt = 0·05. Arrows in dotted lines give the atomic displacements at t = 0.

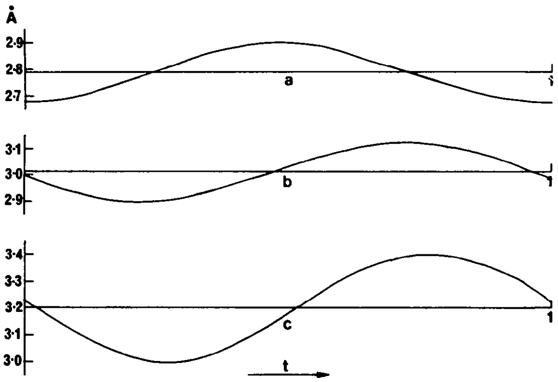

Fig. 6. Some intermolecular distance functions; *cf.* Fig. 3 for the significance of the letters.

A refinement has also been performed in the centrosymmetric superspace group $P^{P2_1/a}_{1\,\bar{1}}$. In this case the phase change φ between the two molecules in the basic unit cell, which is a free parameter found equal to 100° in $P^{Pa}_{\bar{1}}$, now has an imposed value: 360 ($\mathbf{q}^*.\Delta\mathbf{r}$) = 83·25°, $\mathbf{q}^*$ being the wavevector and $\Delta\mathbf{r} = \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b}$ the translation vector between the two molecules (Fig. 3). With $\varphi = 83{\cdot}25°$ the calculated structure factors of satellites $0\ h_2\ 0\ \pm 1$ for h_2 odd are strictly equal to zero, but with $\varphi = 100°$ they are only extremely weak. The R factor on satellite reflections, which are the only reflections sensitive to a phase change, equal to 0·176 in $P^{Pa}_{\bar{1}}$ becomes 0·182 in $P^{P2_1/a}_{1\,\bar{1}}$. The value of the R-factor ratio is 1·034. In the statistical F test (Hamilton, 1965) this value has to be compared to $\mathscr{R}_{1,254,\,0\cdot005} = 1{\cdot}017$. Hence the choice of the noncentrosymmetric superspace group is confirmed with a more than 99·5% probability. Although this test demands the assumption of random errors in the data and that systematic errors (particularly multiple scattering) can be feared, it remains highly significant. In any case, because of the weakness of satellite reflections $0\ h_2\ 0\ \pm 1$ with h_2 odd, it is probably the best method for choosing between a centrosymmetric and a noncentrosymmetric superspace group. Indeed, although the mutual exclusion rule between Raman active modes and infrared active modes characterizing an ordinary centrosymmetric structure is no longer observed in the low-temperature phases of biphenyl, it is an open question as to whether these selection rules still apply to superspace groups of incommensurate structures.

Symmetry of the soft mode in the high-temperature phase

It is clear that the incommensurate phase we have described at $T \simeq 20$ K arises from the basic high-temperature phase ($T > 38$ K) through condensation of a particular soft mode with a fractional wavevector $\mathbf{q}^* \simeq 0{\cdot}46\mathbf{b}^*$ (Cailleau, Moussa & Mons, 1979). So the determination of the characteristics of the modulation in the low-temperature phase can give a response for the fundamental problem in dynamics concerning the symmetry of the soft mode in the high-temperature phase. In this phase the space group is $P2_1/a$ and the soft mode can be symmetric or antisymmetric with respect to the twofold screw axis parallel to **b** which leaves invariant the wavevector $\mathbf{q}^*$. Recent lattice-dynamics calculations (Takeuchi, Suzuki, Dianoux & Allen, 1981) performed in the rigid-phenyl and harmonic approximation and taking into account the coupling between the intramolecular C—C torsion and the translational lattice vibrations have shown clearly the existence of a minimum of the lowest-frequency branch away from the zone boundary at $\mathbf{q} \simeq 0{\cdot}41\mathbf{b}^*$ (instead of $0{\cdot}46\mathbf{b}^*$ for the experimental value). The calculated frequency-dispersion curves indicate that the soft mode is symmetric with respect to the screw axis. These calculations had again not received an experimental confirmation because the determination by neutron scattering of dispersion curves along $\mathbf{b}^*$ was not complete in the whole first Brillouin zone, on account of the difficulty of separating the symmetric and the antisymmetric modes in the region where their dispersion curves cross each other (Cailleau, Moussa, Zeyen & Bouillot, 1981).

Therefore, we have to search in the modulated structure for some relation of symmetry or pseudosymmetry between phenyl rings I and IV (Fig. 3) which in the high-temperature phase are related by a 2_1 axis. However, to illustrate the problem more precisely we consider the particular atoms A and D (Fig. 3). It must be noted that the superspace group $P^{Pa}_{\bar{1}}$ of the modulated structure does not establish any relation of symmetry between atoms A and D but that the glide plane relates atoms A and C on the one part and atoms B and D on the other part (Fig. 3). Table 3 gives for the three components of the modulation: torsion, rotation and translation, the expressions of the modulated displacement waves for atoms A, B, C, D. The point-group symmetry operator associated with the mirror perpendicular to **b**, which transforms a displacement (u,v,w) into $(u,-v,w)$ is designated by S_m and the operator corresponding to the twofold axis parallel to **b** which transforms a displacement (u,v,w) into $(-u,v,-w)$ is designated by S_a. Using relations $S_m(-\mathbf{V}) = -S_m(\mathbf{V}) = S_a(\mathbf{V})$ for any vector **V**, considering that the glide plane of $P^{Pa}_{\bar{1}}$ transforms t into $-t$ and taking account of the phase change φ found equal to 100° in the refinement, the application of simple trigonometric relations shows that for each component of the modulation the motions of atoms A and D are respectively of the form $\mathbf{V}\sin(2\pi t - \varphi_0)$ and $S_a(\mathbf{V}) \times \sin(2\pi t - \varphi_0 + 100°)$. We must remember that going from the first molecule to the second corresponds to an advance of the phase associated with the positional variable t. Consequently, a pattern of atomic displacements symmetric with respect to the twofold screw axis would be obtained by replacing, as already mentioned, the value of 100° obtained from the refinement by $360(\mathbf{q}^*.\Delta\mathbf{r}) = 83{\cdot}25°$, $\Delta\mathbf{r}$ being the translation vector between the two molecules. On the other hand, antisymmetric displacements would be obtained by a simple change of sign for the second molecule, the motion of atom D becoming $-S_a(\mathbf{V}) \times \sin(2\pi t - \varphi_0 + 83{\cdot}25°)$ (with a similarly adapted expression for atom C). One can show (Vettier, 1982) that, in the antisymmetric case, the satellites $0, h_2, 0, \pm 1$ are absent for h_2 even (instead of h_2 odd for the

Table 3. *Modulated displacement waves*

S_m is the point-group symmetry operator corresponding to the mirror perpendicular to **b**; S_a corresponds to the twofold axis parallel to **b**.

$$S_m\begin{pmatrix}u\\v\\w\end{pmatrix}=\begin{pmatrix}u\\-v\\w\end{pmatrix}\qquad S_a\begin{pmatrix}u\\v\\w\end{pmatrix}=\begin{pmatrix}-u\\v\\-w\end{pmatrix}$$

T, **L** and **t** are the displacement vectors generated, respectively, by the intramolecular C—C torsion, the rotation around the normal to the mean molecular plane and the translation along the long molecular axis. Each phenyl ring of the two molecules in the basic unit cell is represented by an atom (Fig. 3). The superspace group $P^{Pa}_{\bar{1}}$ relates atoms A and C on the one part and atoms B and D on the other part. Atoms A and D (and also atoms B and C) which are not symmetry related in $P^{Pa}_{\bar{1}}$ have almost symmetrical displacements with respect to the screw axis. Exactly symmetrical displacements would be obtained by replacing the phase change of 100° obtained from the refinement by $360(\mathbf{q}^*.\Delta\mathbf{r}) = 83{\cdot}25°$.

	Phenyl ring I (atom A)	Phenyl ring II (atom B)	Phenyl ring III (atom C)	Phenyl ring IV (atom D)
Torsion	$\mathbf{T}\sin 2\pi t$	$-\mathbf{T}\sin(2\pi t - 180°)$	$S_m(\mathbf{T})\sin(-2\pi t - 100°)$ $= S_a(-\mathbf{T})\sin(2\pi t - 180° + 100°)$	$S_m(-\mathbf{T})\sin(-2\pi t - 180° - 100°)$ $= S_a(\mathbf{T})\sin(2\pi t + 100°)$
Libration	$\mathbf{L}\sin(2\pi t - 90°)$	$-\mathbf{L}\sin(2\pi t - 90°)$	$S_m(\mathbf{L})\sin(-2\pi t - 90° - 100°)$ $= S_a(-\mathbf{L})\sin(2\pi t - 90° + 100°)$	$S_m(-\mathbf{L})\sin(-2\pi t - 90° - 100°)$ $= S_a(\mathbf{L})\sin(2\pi t - 90° + 100°)$
Translation	$\mathbf{t}\sin 2\pi t$	$\mathbf{t}\sin 2\pi t$	$S_m(\mathbf{t})\sin(-2\pi t - 100°)$ $= S_a(\mathbf{t})\sin(2\pi t + 100°)$	$S_m(\mathbf{t})\sin(-2\pi t - 100°)$ $= S_a(\mathbf{t})\sin(2\pi t + 100°)$

symmetric case). However, practically this extinction rule is not determinant because these satellites with h_2 even are, like those with h_2 odd, extremely weak (at least for the weak indices h_2 considered). Fortunately, the other satellites h_1, h_2, h_3, ± 1 are generally very sensitive to a change from a symmetric to an antisymmetric pattern of atomic displacements. In the latter case, the R factor becomes very high: 0·54. So, although the structure we have described belongs to the superspace group $P^{Pa}_{\bar{1}}$ as it almost obeys the symmetry of $P^{P2_1/a}_{1\,\bar{1}}$ we can conclude that the soft mode in the high-temperature phase is symmetric with respect to the screw axis, in agreement with Takeuchi *et al.* (1981).

The authors are indebted to Professor P. M. de Wolff for critically reading the first version of this paper and particularly for fundamental remarks concerning the choice of the superspace group. They thank Dr Vettier, for private communications, and Drs Currat and Bernard for helpful discussions.

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Molecular Inclusion Phenomena in (2*R*,5*R*,8*R*,11*R*)-1,4,7,10-Tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane

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(*Received* 12 *April* 1982; *accepted* 14 *June* 1982)

Abstract

The title compound, $C_{44}H_{60}N_4$, crystallizes in various different forms including different solvent molecules. The typical form is the tetragonal $P4_3$ with a small aromatic molecule in 1:1 molecular ratio. The X-ray structure analyses reveal that the host molecules in the tetragonal system form a triangular cavity, which is most suitable for the size and shape of the mesitylene molecule. [Crystal data for the mesitylene inclusion complex: $P4_3$, $a = 12{\cdot}110\ (3)$, $c = 32{\cdot}579\ (11)$ Å, $Z = 4$; $R = 6{\cdot}9\%$ for 1203 reflection data.] For a smaller solvent molecule the crystal is metastable, and for a larger solvent molecule a different crystal form appears.

0567-7408/83/010084-06$01.50