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Structural Phase Transition in Polyphenyls.
VII. A Neutron Diffraction Study of the Structural Phase Transition in Biphenyl-d10

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Abstract

Recently a soft mode has been observed in biphenyl-h10 (hydrogenated) by Raman spectroscopy below $T_c = 40$ K. The structural phase transition in biphenyl-d10 (deuterated) has been investigated by neutron diffraction. Surprisingly, superlattice reflections appeared below 40 K, corresponding to a doubling of the *b* parameter only, and not to the doubling of *a* and *b*, as was found for *p*-terphenyl and *p*-quaterphenyl. The torsion angle between the planes of the phenyl groups is about 10°, and is in opposite directions for two neighbouring molecules along **b**. The intensity of the superlattice reflections shows a linear behaviour with temperature, in agreement with Landau theory.

Introduction

The field of structural phase transitions in solids is the subject of many experimental and theoretical investigations, especially *via* the study of the soft-mode mechanism in ionic and inorganic materials, as for the well known example of $SrTiO_3$ (Shapiro, Axe, Shirane & Riste, 1972). In comparison, molecular crystals have not been studied so exhaustively, and the first soft mode has been observed only recently in chloranil (Terauchi, Sakai & Chihara, 1975; Hanson, 1975; Ellenson & Kjems, 1977). For biphenyl, a recent Raman spectroscopy study has found a soft mode associated with a structural phase transition around 40 K (Bree & Edelson, 1977). In *p*-terphenyl, an 'order–disorder' phase transition takes place around 180 K (Baudour, Delugeard & Cailleau, 1976; Baudour, Cailleau & Yelon, 1977; Cailleau, Baudour, Girard & Yelon, 1976) and shows critical scattering similar to that of methane (Hüller & Press, 1972; Press & Hüller, 1973; Press, Hüller, Stiller, Stirling & Currat, 1974).

The polyphenyl molecules are not planar either in the gaseous state or in solution (Bastiansen, 1949; Barrett & Steele, 1972; Suzuki, 1959; Schmid & Brosa, 1972). There is a double-well intramolecular potential for the torsion angle between the phenyl rings. In the crystal, molecules are coupled by intermolecular forces. Thus, polyphenyls are good examples for the models of coupled double-wells in the theoretical investigation of structural phase transition in solids (Aubry, 1975; Shneider & Stoll, 1974). For these models, the type of the phase transition, 'displacive' or 'order–disorder', depends on the strength of the coupling compared to the barrier height. A comparison between the properties of biphenyl and *p*-terphenyl is therefore very instructive.

It is well known that the biphenyl molecules are considered planar in the crystal at room temperature (Robertson, 1961; Trotter, 1961; Hargreaves & Rizvi, 1962). This crystal is isostructural with *p*-terphenyl (Dejace, 1969; Rietveld, Maslen & Clews, 1970) and *p*-quaterphenyl (Delugeard, Desuche & Baudour, 1976) (space group $P2_1/a$, $Z = 2$). Recent X-ray diffraction studies at room temperature (Charbonneau & Delugeard, 1977) and at 110 K (Charbonneau & Delugeard, 1976) outline the unusual librational amplitude of the phenyl rings about the long molecular axis. This amplitude is, however, smaller than those for *p*-terphenyl (Baudour *et al.*, 1977) and *p*-quaterphenyl (Delugeard *et al.*, 1976) (Table 1). Electron paramagnetic resonance and electron nuclear double resonance studies, at 1·9 K, show that the molecule of biphenyl does not have the idealized symmetry *mmm* (Brenner, Hutchison & Kemple, 1974; Cullick & Gerkin, 1977). The fluorescence spectra indicate that biphenyl crystals may undergo a structural modification upon cooling to 4·2 K (Hochstrasser, McAlpine & Whiteman, 1973). Elsewhere, a Raman spectroscopy study (Friedman, Kopelman & Prasad, 1974) reveals the appearance of internal and external infrared active modes (Villermain-Lecollier, Wyncke & Hadni, 1971) as the temperature is lowered from about 75 K to 15 K. The structure at low temperature is therefore

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Table 1. *Root-mean-square librational amplitudes of the phenyl rings about the long molecular axis with a harmonic model*

Temperature	Biphenyl ($T_c \simeq 40$ K)	*p*-Terphenyl (central ring) ($T_c \simeq 180$ K)	*p*-Quaterphenyl (central rings)
300 K	105·9 (deg^2)	260·3 (deg^2)	178·3 (deg^2)
200		248·0	
110	45·7	19·3	

noncentrosymmetric. This structural change is confirmed by the recent observation of a soft mode. A low-temperature structure of biphenyl has therefore been postulated (Bree & Edelson, 1977) with a doubling of parameters *a* and *b* [by analogy with *p*-terphenyl (Baudour *et al.*, 1976)]. This hypothetical structure is therefore quite similar to that obtained for *p*-quaterphenyl at 110 K (Baudour, Delugeard & Rivet, 1978). The torsion of the rings results in the loss of the centre of symmetry for each molecule. However, the proposed structure can maintain a centre of symmetry between the molecules if the torsion amplitude is the same for each molecule. Elsewhere, a neutron diffraction study of deuterated biphenyl powder (Hochstrasser, Scott, Zewail & Fuess, 1975) has not shown superlattice reflections and has suggested that the room-temperature space group persists in the low-temperature phase. But, the phase transition being 'displacive', the superlattice reflections must be weak, and a single crystal is more suitable for a structural diffraction study.

The purpose of this paper is to report the results of a neutron diffraction study of the structural phase transition in a single crystal of deuterated biphenyl.

Experimental

Biphenyl-d10 of 99·4% nominal isotopic purity was obtained from Merck, Sharp & Dohme, Ltd. The compound was purified by zone refining and a single crystal was grown from the melt by the Bridgman technique. The sample chosen had dimensions 3 × 3 × 2 mm.

The experiment was performed on the D10 four-circle neutron diffractometer located on the thermal neutron guide at the Institut Laue–Langevin. A vertically focusing Cu(200) monochromator was used at an incident wavelength $\lambda = 1{\cdot}26$ Å. Collimation was provided by the guide and diaphragms between sample and monochromator or detector. Data were collected with the ω scan mode. The intensities of two standard reflections recorded after every 25 measurements remained constant throughout the data collection. The sample was mounted in a He cryostat. A detailed description of the cryostat and the general equipment has already been given (Claudet, Tippe & Yelon, 1976). Because of a temporary technical fault, it was not possible to obtain a stable temperature below 22 K. At 22 K the temperature was controlled to within 0·1 K.

Low-temperature unit cell

The biphenyl (Robertson, 1961; Trotter, 1961; Hargreaves & Rizvi, 1962), *p*-terphenyl (Dejace, 1969; Rietveld *et al.*, 1970) and *p*-quaterphenyl (Delugeard *et al.*, 1976) crystals are isostructural at room temperature. Their space group is $P2_1/a$ with two pseudo-planar molecules per unit cell. The *a* and *b* parameters are similar for these compounds; only the *c* parameter is proportional to the molecular length.

For *p*-terphenyl at 110 K (Baudour *et al.*, 1976), the molecules are non-planar. The low-temperature phase is characterized by ($\pi\pi0$)-type antiparallel ordering of each molecule in one of the two bottoms of the double-well potential. Thus, the central rings of neighbouring molecules rotate in opposite senses along the *a* and *b* crystal axes. There is a doubling of these parameters and the superlattice reflections correspond to $(h + \frac{1}{2}, k + \frac{1}{2}, l)$ points of the high-temperature reciprocal space. The low-temperature space group is $P\bar{1}$ with four molecules per unit cell.

For biphenyl, surprisingly, results are different from those of *p*-terphenyl. At the beginning of data collection many superlattice reflections indicated a doubling of parameter *b* and some reflections a doubling of parameter *a*. However, it soon appeared that the data collection was perturbed by various factors: twinning and the existence of two or more single crystals in the sample. A distinction between true and false reflections was tried on the basis of several criteria: an unusual displacement of the profile maximum and a large difference between the intensities I_{hkl} and $I_{\bar{h}kl}$ were indications of false or overestimated reflections. Unhappily lack of time did not permit measurements to be made below and above the transition temperature in order to obtain unambiguously a good selection of superlattice reflections. However, recent neutron film measurements (Cailleau, Baudour, Toupet & Wright, 1978) indicated that weak reflections corresponding to a doubling of parameter *a* exist at high temperature. Also, it became evident that the true superlattice reflections corresponded to a doubling of the *b* parameter only and not to the doubling of both *a* and *b* parameters as for *p*-terphenyl and *p*-quaterphenyl. The structure is noncentrosymmetric, as imposed by spectroscopic selection rules. The observation of some weak reflections ($h0l$ with $h \neq 2n$), which would have imposed the triclinic space group $P1$, has been attributed to the twinning of the crystal. Indeed the neutron film study has revealed that these reflections also existed above the transition temperature, and were not superlattice reflections. Thus the space group is *Pa* (monoclinic, with the systematic conditions for the appearance of $h0l$ reflections being $h = 2n$). This choice is statistically confirmed by the structure refinement. The refinement in space group $P1$, although doubling the number of independent atoms, gives no improvement on the agreement factor between observed and calculated structure factors and leads to a structural arrangement identical (in the limit of standard deviations) to that obtained in *Pa*.

The space group *Pa* is in good agreement with spectroscopic results which indicate two inequivalent molecules at low temperature (Brenner *et al.*, 1974; Hochstrasser *et al.*, 1973; Friedman *et al.*, 1974). However, our choice of space group *Pa* remains based on statistical arguments and space group $P1$ may not be completely remote.

The cell dimensions for deuterated biphenyl at 22 K are: $a = 7{\cdot}77$ (0·02), $b = 11{\cdot}14$ (0·02), $c = 9{\cdot}44$ (0·02) Å, $\beta = 93{\cdot}7$ (0·2)°.

Long-range order

The long-range-order parameter η may be defined by the mean value $\langle\varphi\rangle$ of the torsion angle between the phenyl rings. In antiferrodistortive structural phase transitions (Gränicher & Müller, 1971), the intensity of the superlattice reflections is proportional to the square of the order parameter. The integrated intensity of the $\bar{6}72$ reflection, referred to the low-temperature cell, was monitored. The behaviour of the intensity is linear (Fig. 1).

The linear behaviour for the intensity of the superlattice reflections is in agreement with Landau's theory of structural phase transition: $\eta \propto (T_c - T)^{1/2}$. It is interesting to note the difference from the phase transitions of *p*-terphenyl (Cailleau *et al.*, 1976) where $I \propto (T_c - T)^{0\cdot3}$ and chloranil where the result is consistent with a 3D Ising model (Ellenson & Kjems, 1977) and not with mean field theory, since $I \propto (T_c - T)^{0.66}$. This behaviour is similar to that of the intensity of a Raman line which disappears in the high-temperature phase (Bree & Edelson, 1977).

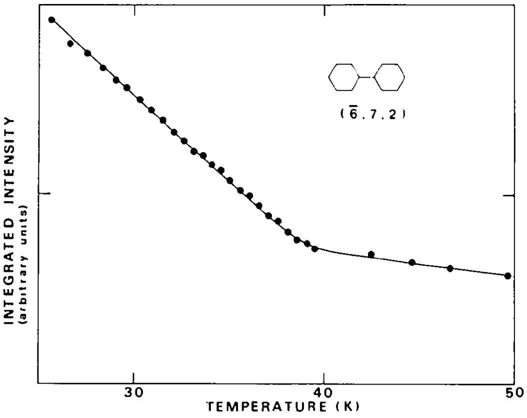

Fig. 1. Temperature dependence of the intensity of the reflection 672. The estimated errors are smaller than the size of the dots.

In the hydrogenated compound, from Raman spectroscopy Bree & Edelson (1977) considered that the nature of the phase transition is second order, and the transition temperature obtained is $T_c = 40{\cdot}0$ K. However, by electron paramagnetic resonance, Cullick & Gerkin (1977) came to the conclusion that a first-order phase transition was present with $\Delta H \simeq 292{\cdot}6$ J mol^{-1} and $T_c = 42{\cdot}4$ (0·3) K. In the deuterated compound, we observed a strong diffuse critical scattering close to 40 K which was broadening at high temperature. It was not possible to obtain the Bragg contribution only and so the transition temperature cannot be determined precisely.

Refinement of the structure at 22 K

The refinement has been performed with data monitored at 22 K. Owing to the limited neutron-beam time available to us, data collection was extended to $\sin\theta/\lambda$ values of 0·51 Å^{-1} only. No corrections were applied for absorption ($\mu \simeq 3 \times 10^{-3}$ mm^{-1}) or extinction. A model must be chosen to start the refinement. A comparison between the librational amplitudes (Table 1) about the long molecular axis of *p*-quaterphenyl (Delugeard *et al.*, 1976), *p*-terphenyl (Badour *et al.*, 1977) and biphenyl (Charbonneau & Delugeard, 1977) at room temperature permits the torsion angle to be estimated at about 10° for biphenyl. So, for each molecule, the two rings were each rotated 5°, but in opposite directions. Since there is a doubling of only the *b* parameter, the *a* and *c* parameters being unchanged apart from thermal contraction, neighbouring molecules along **b** must have this torsion in an opposite sense, whereas neighbouring molecules along **a** and **c** have this torsion in the same sense.

In the low-temperature ordered phase the number of independent atoms is 44 (two independent complete molecules) instead of 11 (half a molecule) at room temperature, but the number of measured reflections having a significant intensity is approximately the same. So it is necessary to carry out a constrained refinement. Bond lengths and angles have been imposed (Fig. 2) by averaging the values obtained at 110 K and room temperature by Charbonneau & Delugeard (1976, 1977) in their refinements, taking account of librational corrections. The C—D bond lengths have been set to 1·105 Å, as found for the same bond in the 1:1 molecular complex between TCNQ and deuterated *p*-terphenyl (Lisensky, Johnson & Levy, 1976).

For each molecule the variable geometrical parameters are the torsion angle between the phenyl rings and the three Eulerian angles to allow the molecule to take up any arbitrary orientation in the crystal. Therefore, the total number of geometrical parameters is eight for the two independent molecules. In addition, the same isotropic temperature factor is attributed to atoms which were symmetry related in the high-temperature phase, giving 11 thermal parameters.

During the refinement it appeared necessary to introduce two independent scale factors: one for the high-temperature lattice reflections which are almost unchanged by the transition, and the other for the superlattice reflections. Indeed, at 22 K, as indicated by the temperature variation of the order parameter, the structure is far from being completely ordered and the superlattice reflections have not attained their maximum intensity. The data set included 463 independent reflections of which 198 were superlattice reflections.

It should be noted that because of the glide plane, the proposed structure of biphenyl, unlike those of *p*-terphenyl and *p*-quaterphenyl, respects the experimental condition $I_{hkl} = I_{h\bar{k}l}$. Thus, unlike the other polyphenyls, it is not necessary to consider the two sorts of domains in the crystal which are related by a glide plane, and the intensities of which must be added.

However, as for *p*-terphenyl and *p*-quaterphenyl, two structures can be obtained for biphenyl, each deduced from the other, for example, by inverting the directions of rotation for molecules *C* and *D* (Fig. 2), molecules *A* and *B* being unchanged. As explained in Fig. 2, because the torsion angles are very similar these two structures are almost related by a centre of symmetry and give very similar structure factor amplitudes. Therefore, they cannot be distinguished experimentally from diffraction data.

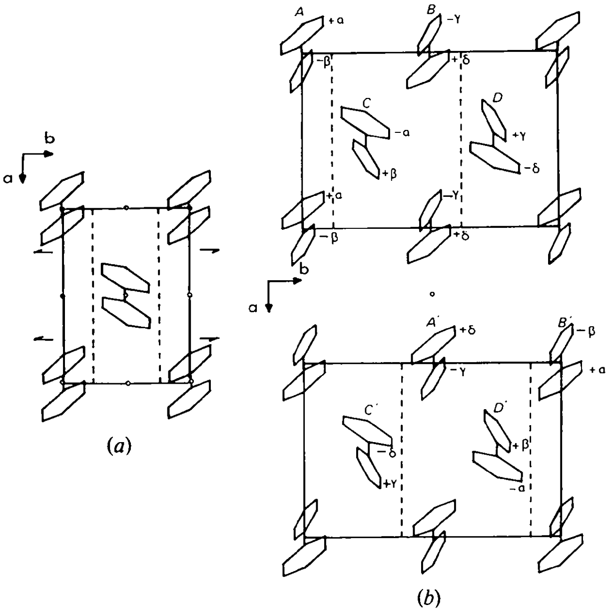

Fig. 2. (*a*) Schematic representation of the room-temperature structure of biphenyl (space group $P2_1/a$, $Z = 2$). (*b*) Construction of two possible low-temperature structures, each without a centre of symmetry or a screw diad axis. However, because all the rotation angles with respect to the planar high-temperature structure α, β, γ, δ are almost 5° (which is not a condition imposed by symmetry) these two structures are almost related by a centre of symmetry and cannot be revealed experimentally from diffraction data.

The neutron scattering lengths were $b_C = 0{\cdot}665$ and $b_D = 0{\cdot}667 \times 10^{-11}$ mm.

The function minimized was $\sum w(|F_o| - |F_c|)^2$. During the last stage of the refinement the weighting scheme used was $w^{-1} = \sigma_c^2$ where σ_c^2 refers to counting statistics. In fact, in such a constrained refinement with few variable parameters, the weighting scheme has practically no influence on the final results.

The following final R and R_w values $[R = \sum(||F_o| - |F_c||)/\sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}]$ were obtained: $R = 0{\cdot}097$, $R_w = 0{\cdot}083$ for all 463 reflections and $R = 0{\cdot}153$, $R_w = 0{\cdot}130$ for the 198 superlattice reflections. The value of the agreement factor is of the same order as those previously obtained for *p*-terphenyl and *p*-quaterphenyl.*

At this stage, attempts were made to refine the structure in the space group $P1$, with four independent molecules in the asymmetric unit, instead of two in Pa. This refinement did not result in a significant variation of the torsion and orientational angles previously obtained in Pa. The maximum variation is 0·2°, of the same order as the estimated standard deviation. The important point is that the refinement in $P1$ although doubling the number of variable geometrical parameters, gives absolutely no improvement on the agreement factors R and R_w. From these statistical arguments we concluded, as previously mentioned, that the space group is Pa.

Also, an attempt to refine the position of the molecular centre, as permitted by space group Pa, did not result in a significant displacement.

Description of the structure

The atoms are numbered in accordance with Fig. 3. The atomic coordinates and isotropic temperature factors are listed in Table 2. A projection of the molecular arrangement along the *c* axis is given in Fig. 4. The torsion angles for the two independent molecules are very similar: 10·2°.

In the low-temperature phase, all the long molecular axes conserve the same orientation as in the high-temperature phase: the largest variation is 0·15°, of the same order as the estimated standard deviation.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34009 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters*

Standard deviations of the temperature factors are in parentheses. Standard deviations of torsion and orientational angles are about 0·1° in the constrained refinement.

	Molecule 1			Molecule 2			
	x	y	z	x	y	z	B (Å^2)
C(1)	351	−1259	756	350	3739	756	0·90 (0·10)
C(2)	60	−308	1675	−158	4591	1731	1·17 (0·10)
C(3)	714	−327	3080	492	4572	3137	1·07 (0·10)
C(4)	1674	−1297	3604	1670	3701	3605	0·97 (0·10)
C(5)	1975	−2248	2706	2189	2849	2650	0·62 (0·10)
C(6)	1321	−2230	1300	1538	2868	1244	0·47 (0·09)
D(7)	−703	468	1266	−1097	5288	1367	1·56 (0·12)
D(8)	468	434	3789	72	5255	3891	1·35 (0·12)
D(9)	2194	−1312	4721	2188	3686	4723	1·48 (0·10)
D(10)	2739	−3025	3114	3128	2152	3014	1·63 (0·12)
D(11)	1567	−2992	591	1958	2186	490	1·17 (0·11)
C(12)	−351	−1240	−756	−350	3760	−756	0·90 (0·10)
C(13)	157	−2091	−1731	−59	2809	−1675	1·17 (0·10)
C(14)	−495	−2073	−3137	−710	2828	−3081	1·07 (0·10)
C(15)	−1674	−1202	−3604	−1670	3798	−3605	0·97 (0·10)
C(16)	−2193	−350	−2649	−1971	4749	−2707	0·62 (0·10)
C(17)	−1540	−369	−1243	−1320	4730	−1301	0·47 (0·09)
D(18)	1097	−2788	−1368	705	2032	−1266	1·56 (0·12)
D(19)	−75	−2755	−3891	−464	2066	−3790	1·35 (0·12)
D(20)	−2194	−1187	−4721	−2188	3813	−4723	1·48 (0·10)
D(21)	−3133	346	−3012	−2735	5526	−3116	1·63 (0·12)
D(22)	−1960	312	−489	−1566	5492	−592	1·17 (0·11)

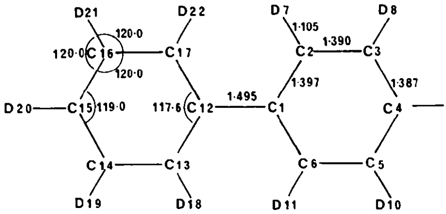

Fig. 3. A molecule of biphenyl showing the numbering of the atoms. Bond lengths (Å) and angles (°) were imposed in the constrained refinement.

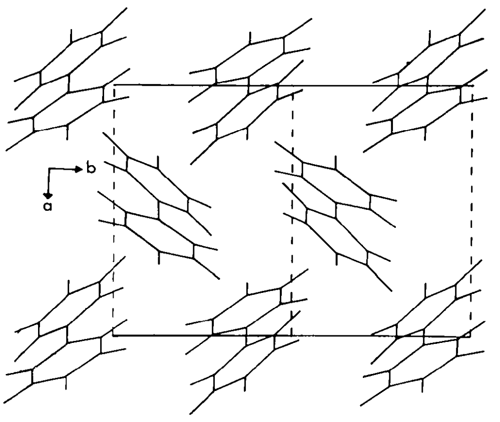

Fig. 4. A projection of the molecular arrangement along the c axis.

When biphenyl undergoes its phase transition, the structural modifications result essentially from rotations of the phenyl rings about the long molecular axes, as in *p*-terphenyl and *p*-quaterphenyl. The torsion angle for two neighbouring molecules is in opposite directions for each translation $b/2$ (with the consequence that the b parameter is doubled), but contrary to *p*-terphenyl and *p*-quaterphenyl this alternation does not exist along **a**.

The isotropic thermal parameters are, as usual, higher for the D atoms than for the C atoms of the phenyl rings. Anisotropic refinements of the atomic thermal motion (Cruickshank, 1956) were not considered here because of the large number of extra parameters introduced.

At the end of refinement the ratio between the scale factors for superlattice and lattice reflections is 0·674. This ratio, which gives the order parameter, means that at 22 K the order is not completely realized. This value of 0·674 is very similar to the value of $[(T_c - T)/T_c]^{1/2} = 0{\cdot}671$ obtained from the linear temperature behaviour for the intensity of the superlattice reflections ($T_c \simeq 40$ K, $T = 22$ K).

A trial refinement of the structure with the same scale factor for all reflections gives a torsion angle of about 6°, smaller than the maximum value of 10°, but in this case the agreement factor becomes very high ($R \simeq 0{\cdot}4$ instead of 0·097 in the refinement with two independent scale factors). These results are discussed in the next section.

General remarks on the phase transition

The mean torsion angle between the phenyl rings is 10°, in agreement with the value proposed by Bree &

Edelson (1977): 9°. However, the model they have used to obtain this value and the barrier height (4·0 mm^{-1}) is too simple. The interaction between the molecules cannot be neglected since it is responsible for the phase transition. It is necessary to consider the theoretical models of coupled double-wells (Aubry, 1975; Shneider & Stoll, 1974) to explain the structural phase transition in polyphenyls.

In these models, the type of the phase transition depends on the strength of the coupling compared to the barrier height. For a weak coupling, the molecule oscillates at the bottom of each well in the high-temperature phase and the phase transition is of the 'order–disorder' type. For a strong coupling, the type is 'displacive'; the molecule may oscillate at the top of the double-well potential in the high-temperature phase, and the dynamical response contains a soft mode contrary to the preceding type.

The π–π interaction, across the C–C inter-ring bond, tends to force the molecules of polyphenyls to be planar, but the existence of H atoms in *ortho* positions introduces repulsive steric forces. Thus, there is a double-well intramolecular potential. Numerous calculations (Casalone, Mariani, Mugnoli & Simonetta, 1968; Dewar & Harget, 1970; Almlöf, 1974) for this potential give a value of the barrier height which is in the range 5·0–18·8 kJ mol^{-1} and a torsion angle in the range 32–40°. The dispersion of values for the barrier height is large, but the torsion angles agree with experimental results (Bastiansen, 1949; Barrett & Steele, 1972; Suzuki, 1959; Schmid & Brosa, 1972). In the crystal, intermolecular interactions tend to force the molecule to be planar in the space group $P2_1/a$. The intermolecular interactions and the barrier heights have the same order of magnitude (Messager, Sanquer, Baudour & Meinnel, 1973). But, since the polyphenyl molecules are not planar at low temperature, the sum of the intramolecular and intermolecular potentials must give a double-well potential, and not a single-minimum potential as considered previously (Burgos, Bonadeo & D'Alesio, 1976). The effect of intermolecular interactions is different according to the wave vector of torsional thermal motion and there is a coupling between the double-wells.

For *p*-terphenyl there are no soft modes in the Raman (Girard, Cailleau, Marqueton & Ecolivet, 1978) and infrared (Wyncke, Brehat & Hadni, 1977) spectra, and the probability density for the central ring, in the high-temperature phase, is double peaked. Also, the type of this phase transition is 'order–disorder'. The barrier height deduced from the thermal-motion analysis in the high-temperature phase is 2·5 kJ mol^{-1} (Baudour *et al.*, 1977) and the mean torsion angle between the rings is about 21° at low temperature.

The barrier height is approximately twice as high for *p*-terphenyl as for biphenyl. Thus, soft modes are observed in the Raman spectra of biphenyl, but the temperature at which these soft modes cancel is higher than the transition temperature. Starting from the mean planar high-temperature configuration, the two rings of a molecule rotate in opposite senses by about 5°. This value is smaller than that for *p*-terphenyl, but it is higher than the tilt angle for chloranil (1·5°). At room temperature the librational thermal motion of the phenyl rings about the long molecular axis is smaller than those for other polyphenyls. It is difficult to decide if there is a double-peaked structure, although the amplitude of this thermal motion is unusual. Thus, if the structural phase transition is clearly 'displacive' for the chloranil (Ellenson & Kjems, 1977), and 'order–disorder' for methane (Press *et al.*, 1974), in polyphenyls it is closer to the intermediary region between the two regimes, on the 'displacive' side for biphenyl, and on the 'order–disorder' side for *p*-terphenyl.

Therefore, the difference between the scale factors for superlattice and lattice reflections can be explained. Indeed, for a 'displacive' phase transition, the torsion angle changes with temperature, and for an 'order–disorder' phase transition, it is the probability of the presence in each one of two positions which changes with temperature.

The investigation of the soft mode in biphenyl using inelastic neutron scattering is currently under way.

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Nitromalonamide. A C—OH Acid with a Very Short Intramolecular O···O Hydrogen Bond

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Abstract

$C_3H_5N_3O_4$, orthorhombic, $P2_12_12_1$, $a = 4{\cdot}8411$ (3), $b = 5{\cdot}0206$ (2), $c = 22{\cdot}582$ (2) Å, $Z = 4$, $D_m = 1{\cdot}78$, $D_x = 1{\cdot}78$ Mg m^{-3}. The molecule has a nearly planar configuration. A part of the molecule forms a six-membered enol-like ring system including the acidic H atom, which is asymmetrically situated between the two amide O atoms. The distance between these two hydrogen-bonded O atoms is only 2·384 (4) Å.

Introduction

This structure determination is part of a study of aliphatic nitro compounds, nitronate salts and tautomeric forms of these compounds.

Nitromalonamide is reported to have an acidity constant $K_a = 10^{3\cdot23}$ (Hantzsch, 1907). Therefore, there might be some doubt about the description of the molecule as a C—H acid. This structure determination was carried out especially to clarify the bonding conditions of the acid function.

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