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Structural Phase Transition in Polyphenyls.
IV. Double-Well Potential in the Disordered Phase of p-Terphenyl from Neutron (200 K) and X-ray (Room-Temperature) Diffraction data

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New neutron-diffraction data collected at 200 K with deuterated p-terphenyl, and published X-ray data collected at room temperature with protonated p-terphenyl, have been used to determine the characteristics of the double-well potential for the librations of the central ring about the long molecular axis, in the disordered phase. A picture of the double well is obtained simply by halving the atoms outside the molecular axis and imposing constraints on their geometries and thermal parameters. The R values compared with that obtained with the simple-well model, are significantly improved. The deuterated benzene rings, compared to the protonated ones, show a systematic and hard-to-explain distortion: all the internuclear C—C bond lengths parallel to the long axis are shortened and the others lengthened, the mean bond lengths being the same in the two compounds. The double-well potential-barrier height is found to be about 0.6 kcal mol^{-1} at 200 K and at room temperature. This value is in good agreement with that given by potential-energy calculations. The rotation angle between the two wells is about $26°$. Only for the internal g mode is the thermal energy kT sufficient to bring the rings near the top of the barrier. For the central-ring librations the doubly peaked distribution function is an argument for an order–disorder regime. However, the smallness of the double-well barrier height suggests that the p-terphenyl structural phase transition is near the boundary between the order–disorder and displacive regimes.

Introduction

The structure of p-terphenyl in the low-temperature ordered phase has recently been solved (Baudour, Delugeard & Cailleau, 1976). The ordering results from the stabilization of the central ring of each molecule in one of the two bottoms of a double-well potential, at an average angle of $16°$ from the mean planar configur-

ation seen by diffraction at room temperature. The external rings are stabilized at about $5°$ from the mean configuration, but in the opposite sense of the central rings. The conformations of the four independent non-planar molecules in the unit cell, given by X-ray diffraction at 110 K (space group $P\bar{1}$), have been confirmed by recent potential energy calculations (Ramdas & Thomas, 1976).

Phase transitions are often referred to as either the displacive or order–disorder type. The borderline between the two types is not sharp, however, as they

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can be described on the same footing by a simple change of the input parameters in a classical model of linearly coupled anharmonic oscillators (Aubry & Pick, 1974; Aubry, 1975). In any case the very existence of a transition is connected with the fact that each particle (or molecule) feels some double-well potential. Molecular-dynamics calculations have revealed some differences between the so-called order–disorder and displacive regimes. In order–disorder transitions the single-particle distribution function is doubly peaked, even above T_c (Schneider & Stoll, 1973). In a displacive transition the single-particle distribution is singly peaked near T_c. Diffraction data can give some information about this distribution.

Indeed, in the treatment of these data, the smearing function $P(\theta)$ for the libration θ of a molecule about an axis is generally considered as Gaussian, which corresponds to the harmonic approximation. With good data, deviations from a Gaussian distribution can be detected and related to a non-parabolic potential function by Boltzmann's formula. For p-terphenyl an evaluation of this potential, based on van der Waals interactions and orbital alignment energy, has been given (Rietveld, Maslen & Clews, 1970). To compare with these calculations we have tried to specify the potential curve for the central-ring librations, directly from diffraction data.

To test the sensitivity of the method we have used two independent sets of data: new neutron diffraction data collected at 200 K, *i.e.* 22 K above the transition temperature ($T_c = 178$ K); and published X-ray diffraction data (Dejace, 1969) collected at room temperature. In this way it was also possible to see if a temperature variation had an effect on the depth of the double potential well.

Experimental

The single crystal used for neutron diffraction was deuterated (99.2%) and grown from the melt by the Bridgman technique. It had dimensions $4.5 \times 3 \times 1.5$ mm. The experiment was performed on the D10 four-circle neutron diffractometer located on the thermal-neutron guide H-24 at the Institute Laue Langevin. A Cu (111) monochromator was used at an incident wavelength $\lambda = 1.445$ Å. Collimation was provided by the guide and diaphragms between sample and monochromator. Data were collected with the ω scan mode. The intensities of two standard reflexions recorded after every 25 measurements remained constant throughout the data collection. The sample was mounted in a He cryostat and the temperature was controlled to within 0.1 K. A detailed description of the cryostat and the general equipment has already been given (Jost, Rees & Yelon, 1975; Claudet, Tippe & Yelon, 1976). The cell dimensions for the deuterated p-terphenyl at

200 K are $a = 8.00$ (1), $b = 5.56$ (1), $c = 13.55$ (2) Å, $\beta = 92.3$ (0.2) (°); and for the protonated p-terphenyl at room temperature, $a = 8.119$ (5), $b = 5.615$ (3), $c = 13.618$ (8) Å, $\beta = 92.07$ (3) (°). The space group is $P2_1/a$ and $Z = 2$.

Refinement with the harmonic model (simple well)

Neutron diffraction data at 200 K (deuterated p-terphenyl)

The refinement has been performed with a data set of 653 independent reflexions. The main calculations were done with the program *WAGG* (Baudour, 1972). This program allows for the phase shift in the temperature factor expression, as a result of the curvilinear atomic displacements in librations. So no libration correction is needed for bond lengths. In addition it directly refines the translation and libration molecular tensors. The function used for minimization was $\Sigma w(|F_o| - |F_c|)^2$. During the last stage of the refinement, the weighting scheme used was $w^{-1} = \sigma^2 = \sigma_c^2 + (0.02|F_o|)^2$, where σ_c^2 refers to the counting statistics.

The neutron scattering lengths were $b_C = 0.665$ and $b_D = 0.667 \times 10^{-12}$ cm. No absorption correction was performed.

Since deuterium atoms are well localized by neutron diffraction, it was necessary to include in the model the main internal vibrations of these atoms. However, the large librational amplitudes of the benzene rings made an accurate estimation of the riding motions of the deuterium atoms difficult. Therefore, for each atom only the two main vibrations, perpendicular to the bond C–D, have been considered; the radial vibration along C–D has been neglected. The number of adjustable parameters was 74: one scale factor, one isotropic secondary-extinction parameter (negligible), 48 atomic positional parameters, a translation tensor for the whole molecule (6 terms), a libration tensor diagonalized along the axes of inertia, with one additional term for the internal degree of freedom about the long molecular axis (4 terms), and for each deuterium atom two vibrational terms perpendicular to the bond C–D, one in the ring plane and the other perpendicular to it (14 terms in all). During the refinement three reflexions were rejected, one (211) which was expected to be most affected by secondary extinction, and two (020 and 201) because of a possibility of superposition by twinning of the crystal.

The following final R values were obtained: $R = 0.132$ ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) and $R_w = 0.120$ $[R_w = |\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2|^{1/2}]$.

X-ray diffraction data at room temperature (protonated p-terphenyl)

The refinement had been performed (Baudour, 1972) with a data set of 1145 independent reflexions pub-

lished by Dejace (1969) with a weighting scheme essentially based on unit weights. The parameters adjusted were the same as those with neutron data except that the extinction was not considered and that the temperature factors of the H atoms were isotropic. The final value of R was 0·103 for all reflexions (0·086 for observed only).

Discussion

Molecular geometry. The final atomic coordinates are given in Table 1. Bond distances and angles are compared in Fig. 1. A rather surprising result is that with neutron data the endocyclic angles of the deuterated compound, about the long molecular axis, are systematically smaller by two or three degrees than those of the protonated compound (X-ray data). In addition, in the rings the bond lengths parallel to the long axis are systematically shorter when neutron data are used, the shortening varying between 0·030 and 0·053 Å. But the other bond lengths, on the other hand, are longer; the average C—C bond lengths are almost identical from neutron and X-ray data (respectively 1·396 and 1·399 Å).

Table 1. *Fractional atomic coordinates* ($\times 10^5$, for H $\times 10^4$)

The estimated standard deviations are given in parentheses. The atoms C(i') and C(i'') in the double-well model are obtained by undoubling the atom C(i) in the simple-well model.

(*a*) Deuterated *p*-terphenyl (200 K)

Harmonic-well model for the central-ring librations

	x	y	z
C(1)	−9664	−18428	3410
C(2)	−4692	90	10126
C(3)	5240	18233	6146
C(4)	−9510	−151	20475
C(5)	−19836	−18424	24169
C(6)	−24162	−18641	33860
C(7)	−18561	−825	40483
C(8)	−8415	17964	36712
C(9)	−4241	18203	27124
D(10)	−17416	−33887	6097
D(11)	9921	32655	11191
D(12)	−24573	−32823	19074
D(13)	−32832	−32666	36466
D(14)	−21885	−721	48253
D(15)	−3553	31863	42045
D(16)	4203	32617	24678

(*b*) Protonated *p*-terphenyl (room temperature)

Harmonic-well model for the central-ring librations

	x	y	z
C(1)	−9994 (63)	−18036 (81)	3484 (28)
C(2)	−4613 (37)	63 (56)	9968 (21)
C(3)	5413 (62)	18005 (81)	6376 (28)
C(4)	−9590 (40)	−94 (60)	20492 (22)
C(5)	−19784 (49)	−17982 (72)	23999 (25)
C(6)	−24298 (54)	−18147 (80)	33836 (27)
C(7)	−18439 (50)	−429 (76)	40178 (26)
C(8)	−8457 (53)	17530 (78)	36865 (26)
C(9)	−3929 (49)	17958 (72)	26990 (25)
H(10)	−1326 (92)	−3473 (116)	601 (38)
H(11)	783 (93)	3393 (117)	1035 (39)
H(12)	−2321 (63)	−3333 (89)	2000 (32)
H(13)	−3118 (67)	−3156 (97)	3605 (33)
H(14)	−2186 (58)	−31 (88)	4709 (30)
H(15)	−509 (68)	3328 (97)	4159 (33)
H(16)	137 (63)	3344 (89)	2438 (32)

Double-well model for the central ring librations

	x	y	z
C(1′)	−6860	−20441	3935
C(1″)	−12296	−15505	2940
C(2)	−4651	97	10140
C(3′)	2185	20483	5645
C(3″)	8007	15170	6711
C(4)	−9538	−135	20478
C(5)	−19853	−18395	24169
C(6)	−24165	−18590	33866
C(7)	−18602	−824	40478
C(8)	−8435	17909	36704
C(9)	−4224	18225	27137
D(10′)	−12142	−37237	6965
D(10″)	−21995	−28496	5160
D(11′)	3782	36981	9998
D(11″)	14394	27439	11941
D(12)	−24553	−32804	19071
D(13)	−32791	−32607	36474
D(14)	−21915	−762	48223
D(15)	−3581	31881	42040
D(16)	4218	32644	24661

Double-well model for the central-ring librations

|	x	y	z
C(1′)	−7060 (77)	−20222 (116)	4038 (43)
C(1″)	−12524 (76)	−14930 (116)	3005 (42)
C(2)	−4610 (35)	35 (50)	9960 (20)
C(3′)	2600 (77)	20083 (116)	5829 (43)
C(3″)	7946 (78)	14926 (115)	6840 (42)
C(4)	−9592 (37)	−102 (54)	20495 (21)
C(5)	−19793 (45)	−17976 (64)	23990 (23)
C(6)	−24320 (51)	−18112 (71)	33838 (24)
C(7)	−18439 (47)	−439 (69)	40189 (23)
C(8)	−8421 (51)	17539 (71)	36874 (24)
C(9)	−3904 (46)	17967 (64)	26984 (23)
H(10′)	−972 (105)	−3676 (133)	712 (45)
H(10″)	−1992 (105)	−2906 (130)	519 (44)
H(11′)	268 (107)	3671 (135)	987 (46)
H(11″)	1269 (109)	2865 (135)	1176 (45)
H(12)	−2350 (65)	−3343 (92)	2008 (33)
H(13)	−3067 (66)	−3119 (96)	3604 (32)
H(14)	−2189 (60)	−6 (88)	4727 (31)
H(15)	−558 (66)	3372 (95)	4170 (34)
H(16)	80 (63)	3399 (90)	2427 (33)
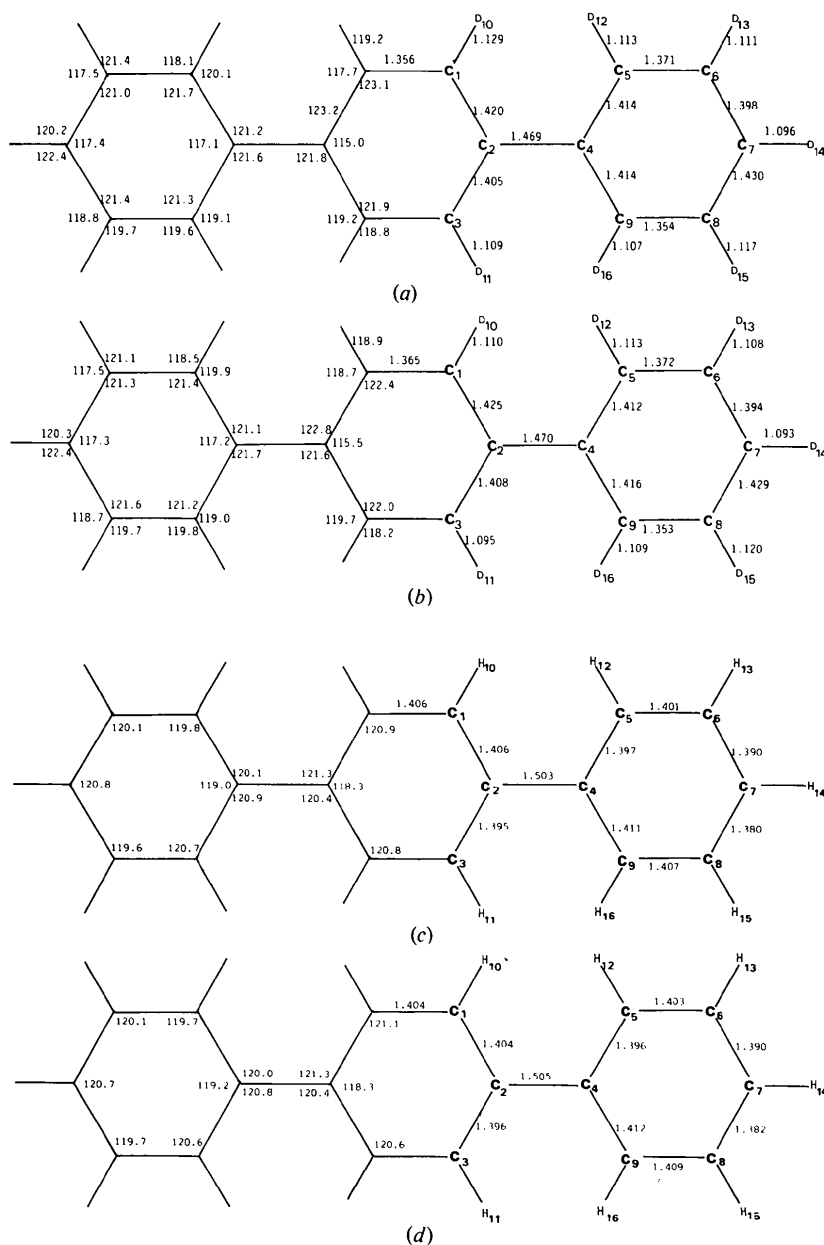
Fig. 1. Bond distances (Å) and angles (°) in the p-terphenyl molecule. (a) Neutron data (200 K) with a simple-harmonic-well model for the central-ring librations. (b) The same as (a) but with a double-well model. (c) X-ray data (room temperature) with a simple-harmonic-well model. (d) The same as (c) but with a double-well model. Mean standard deviations: 0·005 Å, 0·3°.

These systematic differences cannot be attributed to the thermal model since the two refinements were performed with the same program and almost the same adjustable parameters. The R values are similar and rather high, as is usual in disordered structures. It is also difficult to seek a reason for the present results in the disorder, since both compounds are disordered. Besides, the seven C—D bond lengths are quite acceptable with a mean value of 1·112 Å and a range of 0·033 Å (against 0·076 Å for the C—C bond lengths).

However, diffuse scattering in the proximity of the phase transition might systematically alter the intensities and account for the serious distortion of the deuterated benzene rings. Nevertheless, each remains planar to within 0·01 Å.*

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* A recent neutron-diffraction study of the 1:1 molecular complex of TCNQ with p-terphenyl (Lisensky, Johnson & Levy, 1976) does not yield such a large deformation in the molecular dimensions for p-terphenyl.

Thermal motion. The translation tensors are given in Table 2. The terms T_{11} (along the normal to the benzene rings) and T_{22} (about the long molecular axis) are surprisingly smaller at high temperature. This result is similar to that obtained in the disordered phase of solid methane CD_4 (Press, 1973), where a deviation from

spherical symmetry for the probability density function of the deuterium atoms disappears on lowering the temperature. This is equivalent to an increase of thermal motion in the disordered phase, when the transition is approached.

Table 2 also gives the libration tensors. The terms L_{11} and L_{33} decrease normally when the temperature is reduced. The r.m.s. libration amplitude $L_{22}^{1/2}$ of the outer ring, about the long axis, decreases slightly: $7.4°$ at 200 K ($8.3°$ at room temperature). For the central ring the variation is very weak: $15.7°$ at 200 K ($16.1°$ at room temperature). This can easily be understood since the apparent motion corresponds to the distance between the two minima of the double-well potential and not to true thermal motion.

Table 3 gives the r.m.s. vibrational amplitudes of the deuterium atoms. As already mentioned, in a refinement it seems difficult to separate these internal riding vibrations from those arising from the ring librations, especially if, as is the case here, the latter have a considerable amplitude. Therefore the radial displacements have been neglected. For the six deuterium atoms outside the long molecular axis, the r.m.s. in-plane displacements vary between 0.118 and 0.175 Å (0.12 Å in a spectroscopic normal-coordinate analysis for benzene, Johnson, 1970). For the same atoms, the out-of-plane displacements in the external ring vary between 0.134 and 0.168 Å (0.15 Å in benzene). However, in the central ring they reach abnormally high values: 0.299 and 0.261 Å. This can be considered to be a consequence of the inadequate thermal model which thus far has not taken into account the double-well potential for the central-ring librations.

Refinement with the double-well model for the central-ring librations

Choice of a model and refinement

The existence of a double-well potential theoretically could be visualized on a difference map, with $(F_o - F_{c,h})$

Table 2. *Translation and libration tensors*

(a) Translation tensors

$\overrightarrow{OX}$ is perpendicular to the mean plane, $\overrightarrow{OY}$ is about the long molecular axis, $\overrightarrow{OZ} = \overrightarrow{OX} \times \overrightarrow{OY}$.

	200 K Harmonic-well model	200 K Double-well model
T_{11}	$48 (2.6) \times 10^{-3}$ Å^2	$45 (1.7) \times 10^{-3}$ Å^2
T_{22}	$65 (1.3)$	$65 (1.2)$
T_{33}	$33 (1.8)$	$35 (1.2)$
T_{12}	$-5 (1)$	$-5 (0.9)$
T_{13}	$-8 (1)$	$-8 (0.9)$
T_{23}	$4 (0.8)$	$4 (0.7)$

	Room temperature Harmonic-well model	Room temperature Double-well model
T_{11}	$33.5 (1.3) \times 10^{-3}$ Å^2	$32.3 (1.2) \times 10^{-3}$ Å^2
T_{22}	$41.6 (0.6)$	$41.9 (0.6)$
T_{33}	$35.6 (1)$	$36.1 (0.9)$
T_{12}	$2 (0.5)$	$2.1 (0.5)$
T_{13}	$0.8 (0.6)$	$0.2 (0.5)$
T_{23}	$-1.2 (0.5)$	$-1.2 (0.5)$

(b) Libration tensors

	200 K Harmonic-well model	200 K Double-well model
L_{11}	$2.2 (0.3) (°)^2$	$1.9 (0.3) (°)^2$
L_{22} (central ring)	$248.0 (11.6)$	$36.2 (4.0)$
L_{22} (external ring)	$55.4 (5.6)$	$52.4 (4.6)$
L_{33}	$0.9 (0.4)$	$1.2 (0.3)$

	Room temperature Harmonic-well model	Room temperature Double-well model
L_{11}	$3.6 (0.2) (°)^2$	$3.4 (0.2) (°)^2$
L_{22} (central ring)	$260.3 (7.5)$	$52.5 (7.8)$
L_{22} (external ring)	$68.9 (3.8)$	$64.4 (3.4)$
L_{33}	$2.7 (0.3)$	$2.9 (0.2)$

Table 3. *R.m.s. vibration amplitudes* (Å) *of the deuterium atoms*

The radial vibrations, along C—D, are not introduced in the model.

	Harmonic-well model Vibrations in plane	Harmonic-well model Vibrations out of plane	Double-well model Vibrations in plane	Double-well model Vibrations out of plane
Central ring				
D(10)	0.144 (0.023)	0.299 (0.046)	0.166 (0.027)	0.152 (0.036)
D(11)	0.118 (0.025)	0.261 (0.050)	0.144 (0.030)	0.161 (0.037)
External ring				
D(12)	0.153 (0.015)	0.153 (0.033)	0.148 (0.014)	0.183 (0.024)
D(13)	0.175 (0.017)	0.134 (0.039)	0.186 (0.015)	0.120 (0.036)
D(14)	0.098 (0.030)	0.215 (0.017)	0.110 (0.019)	0.209 (0.012)
D(15)	0.147 (0.020)	0.149 (0.035)	0.156 (0.016)	0.152 (0.029)
D(16)	0.136 (0.019)	0.168 (0.031)	0.141 (0.017)	0.167 (0.025)

as Fourier coefficients. F_o is the observed neutron structure factor and $F_{c,h}$ is the neutron structure factor calculated with a harmonic simple well. The use of neutron data here has the advantage of giving pure probability densities, whereas X-ray data give a convolution of a stationary electronic density with the probability density function.

Unfortunately, for p-terphenyl, as for CD_4 and generally for disordered systems, large-amplitude thermal motions strongly reduce the Bragg intensities and the refinements give rather high R values. Under these conditions, interesting features cannot be extracted from background on a difference map. Consequently it is necessary to work not in real space, but in reciprocal space. The method consists of taking into account the distortion from a given model, generally harmonic or spherical, by adapting the structure factor expression and examining whether the new model significantly improves the R value. A new method of data analysis, based on the application of cubic harmonics, has been proposed (Press & Hüller, 1973) to provide a description of the orientational disorder in the high-temperature plastic crystalline phases. This method seems to be particularly well suited for systems with few geometrical parameters (CD_4, ND_4Br, Press, 1973), where no well-defined equilibrium positions exist for the atoms. This treatment is probably more difficult to apply to p-terphenyl, because the minima of the double well are rather well localized, as we shall see. Besides, the molecule is not very symmetric and each deuterium atom moves independently. Thus, the number of adjustable parameters increases considerably in a general treatment.

However, for the p-terphenyl central ring, we can give a rather satisfying picture of the double well by placing half atoms outside the long molecular axis on either side of the mean plane. The pseudo-atoms thus obtained have scattering lengths $b_C/2$ or $b_D/2$ (Levy & Peterson, 1952). This somewhat artificial treatment has the advantage of giving no additional parameters in the refinement, if at the end of each cycle we average the geometries of the two pseudo-central rings and the vibration amplitudes of each pair of halved deuterium atoms. The libration term L_{22} about the long molecular axis is constrained to be the same for the two pseudo-central rings. But now it gives the libration amplitude in each well of the double minimum. In these calculations we use the same program adapted to curvilinear displacements in molecular librations.

The double-well model significantly improves the R values, particularly at low temperature. With neutron data at 200 K, the final R was lowered from 0·132 to 0·120 and from 0·105 to 0·093 for observed reflexions $[I > 3\sigma_c(I)$, $\sigma_c(I)$ from counting statistics], and the weighted R_w from 0·120 to 0·108. With X-ray data, at room temperature, the final R value is reduced from 0·103 to 0·095 and from 0·086 to 0·078 for observed

reflexions. The improvement is, as expected, more significant at low temperature; the central rings are more localized in the two bottoms of the double well and the corresponding change of the structure factor amplitudes is more important.*

Positional and thermal parameters

The use of the double-well model for the central-ring librations has little effect upon the overall geometry of the molecules, as can be seen in Fig. 1.

The thermal parameters of the outer ring are almost the same in the two analyses (Table 2). The term $L_{22}^{1/2}$ for the central-ring librations decreases to a normal value in each well of the double minimum: 6° at 200 K (15·7° with the simple-well model), and 7·2° at room temperature (16·1° with the simple-well model). These values are now of the same order as that obtained for the phenyl isocyanate dimer central ring: 5·6° (Baudour, Delugeard & Sanquer, 1974). In the latter structure, an isotype of p-terphenyl, there is no disorder, which explains the relatively small value of L_{22} obtained with a simple-well model.

When the double-well model is used, the out-of-plane vibration amplitudes of deuterium atoms in the central ring decrease to about 0·15 Å. Thus they become similar in central and outer rings (Table 3), whereas they were very different with the simple-well model: about 0·30 and 0·15 Å respectively.

An important parameter is the rotation angle between the two wells, measured by the angle between the mean planes of the undoubled central rings. The values obtained from X-ray and neutron data, 26·7 and 26·4° respectively, are similar. They are compatible with the extent of non-planarity which appears in the ordered structure at a lower temperature (Baudour et al., 1976).

Potential curve from diffraction data

It is now possible to calculate a potential-energy curve for the librations of the central benzene ring. At the end of the refinement, we have obtained the rotation angle designated by $2\theta_0$, between the two bottoms of the double well (Fig. 2). We have also determined the libration tensor term L_{22} for each half-central ring, with a temperature factor expression assuming the harmonic approximation for each well. To have the total smearing function $P(\theta)$ for the central ring, we must add two functions, each corresponding to one particular well.

With a well-known relation from statistical mechanics, with α^2 equal to L_{22}:

$$P(\theta) = \tfrac{1}{2}(2\pi)^{-1/2} \alpha^{-1} \mid \exp\left[-(\theta - \theta_0)^2/2\,\alpha^2\right]$$
$$+ \exp\left[-(\theta + \theta_0)^2/2\alpha^2\right]\mid, \quad (1)$$

where the coefficient $1/2$ results from the condition

$$\int_{-\infty}^{+\infty} P(\theta)\,d\theta = 1.$$

Thus the probability density function $P(\theta)$ is calculated with the parameters θ_0 and $\alpha = L_{22}^{1/2}$, obtained from diffraction data. $P(\theta)$ is plotted in Fig. 3 at 200 K and at room temperature.

No attempt has been made to evaluate an anharmonic distortion of the potential curve for the end-ring librations. Such a distortion is, in any case, very weak. Indeed, the probability density at $\theta = 0°$ is noticeably larger for the outer rings than for the central one. For the former, a libration amplitude of $5°$ is needed to reach the mean position, $\theta = 0°$, from the equilibrium
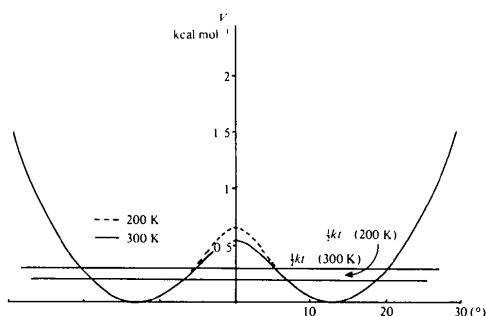

Fig. 2. Potential-energy curves for the p-terphenyl central-ring librations from neutron data (200 K) and X-ray data (room temperature).
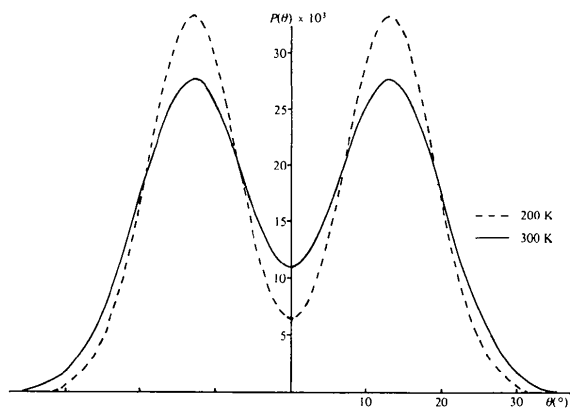

Fig. 3. Probability density function $P(\theta)$ for the p-terphenyl central-ring librations from neutron data (200 K) and X-ray data (room temperature).

position. This can be realized with a not-negligible probability in any mode: the external mode ($\langle\theta^2\rangle \simeq 11\cdot1$ $(°)^2$, Baudour et al., 1974), the internal g mode [$\langle\theta^2\rangle \simeq$ 9 $(°)^2$] or internal u mode [$\langle\theta^2\rangle \simeq 16\cdot6$ $(°)^2$]. On the other hand, for the central ring the probability at $\theta = 0°$ is nil in the internal u mode, and very weak in the external mode since $\theta_0 = 13°$ and $\langle\theta^2\rangle \simeq 11\cdot1$ $(°)^2$. It depends essentially on the internal g mode in which $\langle\theta^2\rangle \simeq 36$ $(°)^2$ for the central ring. So we can consider that for the central ring the probability density at $\theta = 0°$ corresponds to the meeting of the central and external rings in the g mode, and therefore to the passage of the double-well barrier.

With Boltzmann's probability density function, we write:

$$P(\theta) = C \exp\mid - V(\theta)/kT\mid, \quad (2)$$

where C is a constant determined by arbitrarily putting $V = 0$ at $\theta = \theta_0$, $V(\theta)$ is the average potential experienced by the ring as it executes librations about the long molecular axis, k is Boltzmann's constant, and T the absolute temperature.

Knowing $P(\theta)$ from equation (1), $V(\theta)$ is easily calculated from equation (2). Fig. 2 gives the potential-energy curves obtained from neutron (200 K) and X-ray (room-temperature) data. The agreement between the two is good. The potential-barrier height is about $0\cdot6$ kcal mol^{-1}. This value agrees well with that obtained from the potential-energy curves given by Rietveld et al. (1970) by distorting the molecule from its mean planar conformation to its equilibrium position in the crystal, the rotation angles being -5, $+15$ and $-5°$ respectively for the three rings.

It is observed that temperature has little effect on the depth of the potential wells since the difference between the two values ($0\cdot65$ kcal mol^{-1} at 200 K and $0\cdot54$ kcal mol^{-1} at room temperature) is of the same order as the estimated uncertainty.

Conclusion

Our analysis of neutron (200 K) and X-ray diffraction (room-temperature) data of p-terphenyl has allowed us to evaluate the characteristics of the double-well potential seen by the central ring when it librates about the long molecular axis, in the disordered phase. This is a particularly favourable case where the description is obtained simply by halving the atoms outside the libration axis and averaging the geometries and thermal parameters of the two rings obtained from the original one. These constraints have the advantage of introducing no additional parameters in the model and the treatment gives immediately interpretable results for the rotation angle between the two wells and the libration amplitude in each well. Although the method employed is somewhat artificial, it is encouraging to obtain a

significant improvement in the *R* values, to suppress the anomalies concerning the out-of-plane vibrations of the deuterium atoms in the central ring and to find consistent potentials from neutron and X-ray diffraction data. The barrier height, found to be about 0·6 kcal mol^{-1}, is in good agreement with that given by potential-energy calculations. This barrier energy is of the same order as the thermal energy kT of any mode at room temperature, or even at 200 K. But it is only for the internal *g* mode that this energy is sufficient to bring the rings near the barrier top. For the central ring the doubly peaked distribution function is an argument for an order–disorder type of transition. However, the smallness of the double-well barrier height suggests that the *p*-terphenyl structural phase transition is near the boundary between the order–disorder and displacive regimes.

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The Crystal and Molecular Structure of *trans*-1,3,5-Trimethyl-1,3,5-triphenylcyclotrisilthiane: a Stable Twist-Boat Conformation

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The title compound, $C_{21}H_{24}Si_3S_3$, crystallizes in the triclinic system, space group $P\bar{1}$, with unit-cell dimensions $a = 10\cdot941$ (8), $b = 9\cdot423$ (8), $c = 12\cdot252$ (8) Å, $\alpha = 80\cdot02$ (12), $\beta = 75\cdot80$ (12) and $\gamma = 99\cdot40$ (12)°. The structure was solved by the Patterson method and refined by block-diagonal least squares to a final R of 0·059 for 2086 observed reflexions. The structure consists of alternating Si and S atoms in a six-membered ring. A methyl group and a phenyl group are attached to each Si atom. The novelty of this structure is that the Si–S heterocyclic ring is in the twist-boat conformation.

Introduction

In chair–chair equilibrations of various six-membered rings, the boat and twist-boat conformations are postulated as discrete intermediates. The thermodynamic calculations of Beckett, Pitzer & Spitzer (1947) and Howlett (1957) indicate that the boat forms of six-

membered ring carbocycles are of higher energy (3–12 kcal mol^{-1}) than the corresponding chair conformations. This is confirmed by the direct experimental evidence of Johnson, Margrave, Bauer, Frisch, Dreger & Hubbard (1960) and of Jensen & Bushweller (1969). Similarly, reports for other six-membered ring systems such as C–O (Moerman, 1937), C–N (Gutowsky & Temussi, 1967), C–S (Moerman & Wiebenga, 1937; Campaigne, Chamberlain & Edwards, 1962), Si–N (Moedritzer & van Wazer, 1966; Yokoi & Yamasaki,

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