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# On the Isomorphism of *p*-Terphenyl and Phenyl Isocyanate Dimer

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The crystal structure of the phenyl isocyanate dimer has been refined with three-dimensional X-ray intensity data. The final $R$ value is 0·082. Contrary to a previous determination, the C–N bonds in the centre ring are found to be equivalent. The phenyl isocyanate dimer and *p*-terphenyl being isostructural, a comparison is made of their thermal vibrations. The agreement between translational and librational tensors is good except for librational terms about the long molecular axis for which *p*-terphenyl exhibits notably larger values: 260(°)$^2$ in contrast to 31(°)$^2$ for the centre ring, 69(°)$^2$ in contrast to 27(°)$^2$ for the end rings. The large librational amplitudes of *p*-terphenyl cannot be interpreted solely from low-frequency internal modes given by spectroscopic measurements. It is concluded that in this case the planar configuration given by X-ray diffraction is only an average which does not correspond to a stable equilibrium in the crystal. This conclusion confirms earlier potential energy calculations. New equilibrium positions for benzene rings, measured from the planar configuration are determined in agreement with these earlier calculations.

## Introduction

Brown (1955) in determining the crystal structure of the phenyl isocyanate dimer found it to be isostructural with *p*-terphenyl. For the latter, X-ray analysis gives unusual librational tensors about the long axis: about 70(°)$^2$ for the outer ring and 270(°)$^2$ for the centre ring (Dejace, 1969; Rietveld, Maslen & Clews, 1970). This value, probably the most important found for a phenyl ring, may arise from very low frequency internal modes. Another possibility, supported by calculations of potential (Rietveld *et al.*, 1970) is that the planar configuration given by X-rays is only an average which does not correspond to a stable equilibrium, phenyl rings rotating in a double minimum potential. It was considered of interest to compare the thermal motions (or apparent thermal motions) determined from X-ray data for the two isostructural crystals of *p*-terphenyl and phenyl isocyanate dimer. The latter structure (Brown, 1955) apparently presents some inaccuracy: for example, the two pairs of C–N bonds in the central four-membered ring, which might be expected to be equivalent, are different by 0·07 Å. Therefore, before any discussion, we found it worth while to carry out a refinement based on new data collected on a diffractometer.

## Reinvestigation of the structure of the phenyl isocyanate dimer

Crystals of the dimer were prepared by treating phenyl isocyanate with tributylphosphine.

They are monoclinic, space group $P2_1/c$, $Z=2$, $a=12{\cdot}75$ (2), $b=5{\cdot}52$ (1), $c=8{\cdot}08$ (1) Å, $\beta=92{\cdot}3°$ (1), $\lambda(\text{Mo } K\alpha)=0{\cdot}70926$ Å, m.p. 186 °C.

A crystal of approximate dimensions $0{\cdot}2\times0{\cdot}3\times0{\cdot}5$ mm was used in the collection of three-dimensional data on a Nonius automated diffractometer, using the $\theta$–$2\theta$ scan technique. 815 independent reflexions were collected, of which 210 were judged to have zero intensity. No absorption correction was performed. The structure was refined from Brown's (1955) positional parameters, using full matrix least-squares methods (Busing, Martin & Levy, 1963), with isotropic vibrational parameters for H atoms and anisotropic ones for all other atoms. The atomic scattering factors were

Table 1. *Final fractional atomic positional* ($\times 10^4$) *and vibrational parameters for the phenyl isocyanate dimer*

The estimated standard deviations are in parentheses.

The $b_{ij}$ are defined by $T=\exp\left[-10^{-4}(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)\right]$.

| | $x/a$ | $y/b$ | $z/c$ | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 1841 (5) | − 114 (13) | 711 (7) | 59 (5) | 266 (25) | 92 (8) | − 2 (10) | 12 (5) | − 5 (14) |
| C(2) | 2488 (5) | 1723 (14) | 176 (8) | 66 (5) | 293 (28) | 135 (10) | − 7 (11) | 13 (6) | 26 (15) |
| C(3) | 3517 (6) | 1715 (16) | 702 (9) | 66 (6) | 408 (34) | 191 (13) | −31 (13) | 32 (7) | − 3 (20) |
| C(4) | 3934 (6) | −43 (17) | 1743 (9) | 69 (5) | 474 (37) | 158 (12) | 14 (14) | 4 (6) | −22 (20) |
| C(5) | 3268 (6) | −1850 (16) | 2264 (9) | 85 (6) | 376 (34) | 172 (13) | 19 (13) | 17 (7) | 50 (18) |
| C(6) | 2225 (5) | −1904 (14) | 1743 (8) | 57 (5) | 358 (31) | 138 (10) | 23 (11) | 17 (6) | 39 (16) |
| C(7) | 99 (5) | 1500 (13) | − 703 (7) | 67 (5) | 313 (28) | 81 (8) | 13 (11) | 17 (5) | 3 (16) |
| N | 783 (4) | − 169 (11) | 170 (6) | 71 (4) | 293 (22) | 103 (7) | −14 (9) | 17 (5) | 14 (12) |
| O | 226 (4) | 3240 (10) | −1473 (6) | 81 (4) | 351 (21) | 168 (8) | −17 (8) | 12 (5) | 109 (12) |

Table 1 (*cont.*)

Hydrogen atom parameters

| | *x/a* | *y/b* | *z/c* | *B* (Å²) |
|---|---|---|---|---|
| H(1) | 2196 (50) | 3159 (131) | − 299 (79) | 2·68 (1·56) |
| H(2) | 3935 (60) | 3006 (152) | 638 (92) | 4·88 (1·98) |
| H(3) | 4783 (43) | − 106 (114) | 2060 (66) | 1·39 (1·22) |
| H(4) | 3485 (61) | −3119 (158) | 2580 (96) | 5·48 (2·07) |
| H(5) | 1844 (59) | −3185 (152) | 1857 (90) | 6·01 (1·96) |

taken from *International Tables for X-ray Crystallography* (1968). The final agreement index is $R=0{\cdot}082$ for non-zero reflexions. The final atomic and thermal parameters are given in Table 1.*

### Description of structure

The bond lengths and angles are shown in Fig. 1(*a*). The unexpected difference of 0·07 Å found by Brown between the C–N bonds in the centre ring is now reduced to 0·009 Å, namely within the e.s.d. Each individual phenyl ring is planar, the plane being a distance of 0·18 Å from the molecular centre of symmetry. The central block as a whole is approximately planar. Table 2 gives the least-squares planes and atomic deviations. The normals to the centre and outer rings intersect at an angle of 11°26′. The arrangement of the molecules in the crystal will be compared with that of *p*-terphenyl in a later paragraph.

Table 2. *Least-squares planes and deviations (for the phenyl isocyanate dimer)*

The axes are parallel to **a**, **b**, **c***.

The least-squares plane through the carbon atoms in the benzene ring is

$$0{\cdot}2597X-0{\cdot}5531Y-0{\cdot}7916Z=0{\cdot}1855.$$

Deviations from the plane (Å)

| | | | |
|---|---|---|---|
| C(1) | −0·0012 | C(4) | 0·0020 |
| C(2) | −0·0017 | C(5) | −0·0043 |
| C(3) | 0·0012 | C(6) | 0·0037 |

The least-squares plane through C(7), N, O and the symmetric atoms about the origin is

$$0{\cdot}0632X-0{\cdot}5628Y-0{\cdot}8242Z=0{\cdot}0.$$

Deviations from the plane (Å)

| | |
|---|---|
| C(7) | 0·0023 |
| N | 0·0109 |
| O | −0·0051 |

### Translational and librational motions

A segmented-body analysis (Johnson, 1970) allowing for torsional oscillations about the single covalent bonds can be used. A simple model is to consider the librations about the single bond as independent (Baudour & Delugeard, 1971). As site-symmetry is $\bar{1}$, the screw motion tensor introduced by Schomaker & Trueblood (1968) vanishes. Therefore, Cruickshank's (1956*a*) treatment is applicable by adding one librational term for an internal degree of freedom about the long molecular axis. The results of such an analysis are given in Table 3. The r.m.s. deviation of the observed thermal vibration ellipsoids from those calculated is 0·0052 Å². This value and the criteria defined by Burns, Ferrier & McMullan (1968) show that the fit is only moderately good. In particular, the observed

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* A table of calculated and observed structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30236 (6 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

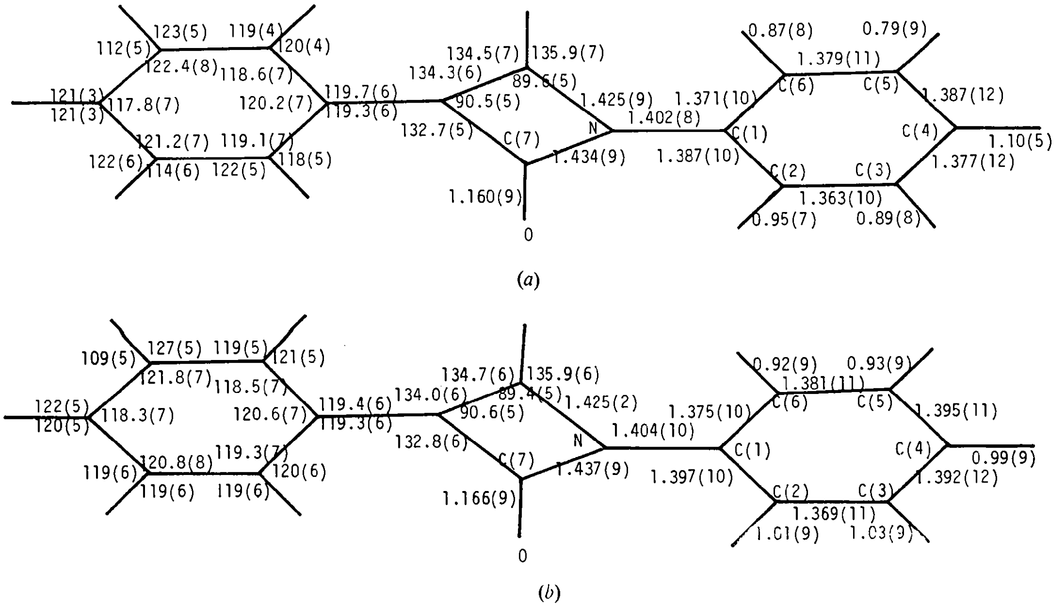

Fig. 1. (*a*) Bond lengths (Å) and angles (°) in the phenyl isocyanate dimer. The corresponding e.s.d.'s given in parentheses refer to the last decimal positions. (*b*) Bond lengths and angles corrected for librations.

ellipsoid is larger for N in the centre ring than for C(1) in the outer ring. So it is concluded that the thermal motion of N is relatively independent. This probably explains the importance of some standard deviations. Nevertheless, since from the preceding criteria, no atom is labelled as 'non-rigid', the calculated tensors can be considered as physically significant.

Moreover, when the torsional oscillations are large it may be important to allow for skewness. In Johnson's (1969) treatment, by addition of higher cumulants to the structure factor, the number of variable parameters increases greatly and requires a large amount of accurate data. Another kind of analysis suggested by Pawley (1964) is to use the rigid-body model from the start, by introducing the molecular tensors in the structure-factor expression. If the model is physically reasonable this method gives tensors having more meaning than those obtained by the standard procedure. Pawley & Willis (1970) have generalized this treatment allowing for higher cumulants. The temperature factor being formulated $\langle \exp i\mathbf{Q}\mathbf{u}(\omega)\rangle$ where $\mathbf{Q}$ is a vector in reciprocal space, $\mathbf{u}(\omega)$ the atomic displacement caused by a rotation $\omega$, and the symbol $\langle \ldots \rangle$ denoting a time and lattice average, they give an expansion correct to the second power of $\langle \omega^2 \rangle$. However for very large librational amplitudes such as those exhibited by the *p*-terphenyl centre ring, this analysis is not the most satisfactory for high-order reflexions (Baudour, 1972). For these, it is better to use the temperature factor expression derived by Kay & Behrendt (1963) based on an expansion of $\mathbf{u}(\omega)$ the to second power of $\omega$ and an exact integration of $\langle \exp i\mathbf{Q}\mathbf{u}(\omega)\rangle$. However for low-order reflexions Pawley & Willis's treatment is better.

As high-order reflexions are very important in the determination of thermal tensors, a refinement has been performed for the phenyl isocyanate dimer with the program *Anhar* used for *p*-terphenyl (Baudour, 1972). This program is based on Kay & Behrendt's formula and includes translational and librational tensors in the structure-factor expression. It also accounts for the internal degree of freedom about the single bond. The results are given in Table 4 for positional parameters. The bond lengths and angles are shown in Fig. 1(*b*). Table 5 gives thermal parameters. They are close to those obtained by the standard procedure. The agreement factor $R=0{\cdot}088$ for observed reflexions is significantly poorer in the constrained refinement than in the unconstrained one ($R=0{\cdot}082$). This means that the mechanistic model is not as simple as for *p*-terphenyl. For the N atom, the difference $U^o-U^c$ given in Table 3 results mainly from an important out-of-plane motion which can be attributed to an internal mode where the central ring librates about its axis of least inertia OCCO. For the phenyl ring atoms, the differences $U^o-U^c$ cannot be interpreted simply and it seems difficult to extract more thermal-motion information from our data.

Table 4. *Fractional atomic positional parameters* ($\times 10^4$) *corrected for librations* (*program Anhar*) (*phenyl isocyanate dimer*)

| | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|
| C(1) | 1842 (5) | − 113 (13) | 716 (9) |
| C(2) | 2489 (6) | 1738 (14) | 165 (10) |
| C(3) | 3523 (6) | 1740 (15) | 687 (11) |
| C(4) | 3939 (6) | −36 (14) | 1747 (11) |
| C(5) | 3274 (6) | −1867 (15) | 2266 (11) |
| C(6) | 2229 (6) | −1913 (14) | 1745 (10) |
| C(7) | 100 (5) | 1505 (13) | − 704 (8) |
| N | 782 (4) | − 172 (10) | 174 (7) |
| O | 227 (4) | 3255 (9) | −1478 (6) |
| H(1) | 2177 (70) | 3252 (153) | − 370 (113) |
| H(2) | 4043 (74) | 3180 (161) | 673 (124) |
| H(3) | 4684 (71) | −30 (164) | 2120 (124) |
| H(4) | 3570 (76) | −3266 (163) | 2727 (125) |
| H(5) | 1838 (70) | −3269 (156) | 1928 (115) |

Table 3. *Rigid-body thermal parameters and estimated standard deviations* (*for the phenyl isocyanate dimer*)

The two rings have independent librational amplitudes about the long molecular axis.

The parameters are calculated from $b_{ij}$

$OX \perp$ N–C(1)–C(6) $OY \parallel$ C(1)–N $OZ \parallel OX \wedge OY$

| Tensor | 11 | 22 | 33 | 12 | 13 | 23 |
|---|---|---|---|---|---|---|
| **T** ($10^{-4}$ Å$^2$) | 292 (34) | 576 (17) | 327 (25) | 9 (18) | 74 (25) | − 1 (17) |
| **Ω** [$10^{-2}$ (°)$^2$] | 433 (60) | 3248 (460) centre ring<br>2959 (920) outer ring | 300 (72) | −263 (178) | 20 (59) | 65 (95) |

$\langle \Delta U^2 \rangle^{1/2} = 0{\cdot}0052$ Å$^2$ (corrected for the number of the degrees of freedom).

Size, shape and orientation parameters for thermal ellipsoids

| | $U^o$ (Å$^2$.10$^4$) | $U^o-U^c$ (Å$^2$.10$^4$) | $\sigma$ | $S$ | $\theta$ | Conclusion |
|---|---|---|---|---|---|---|
| C(1) | 1197 | −122 | 60 | 19 | 14° | ? |
| C(2) | 1440 | −96 | 70 | 1 | 19 | *R* |
| C(3) | 1788 | 41 | 84 | 187 | 11 | ? |
| C(4) | 1816 | 38 | 82 | 39 | 19 | *R* |
| C(5) | 1847 | 54 | 86 | 46 | 31* | *R* |
| C(6) | 1473 | −87 | 72 | 138 | 36* | *R* |
| C(7) | 1296 | −14 | 64 | 17 | 29* | *R* |
| N | 1367 | 149 | 55 | 30 | 22 | ? |
| O | 1761 | 38 | 54 | 23 | 12 | *R* |

## Discussion of the analogy between structural and thermal parameters

The arrangement of the phenyl isocyanate dimer molecules in the cell is shown in Figs. 2 and 3. The packing for *p*-terphenyl is superposed in dashed lines, on the same scale. As the cell dimensions are not exactly the same, a shift appears. However, for the two overlapped molecules at the origin (on the centre of symmetry) the immediate environments are very similar.

But the most remarkable point concerns thermal parameters. In Table 5, translational and librational tensors are found to compare reasonably well, except for the librational terms about the single covalent bonds, for which *p*-terphenyl presents notably larger values: $69(°)^2$ in contrast to $27(°)^2$ for the outer ring; $260(°)^2$ in contrast to $31(°)^2$ for the centre ring. The similarity of thermal parameters not involving the internal degree of freedom means that the molecular interactions are almost identical in the two structures. This agrees well with the similar molecular dimensions and arrangements in the cell. But in order to explain the larger librational amplitude about the single bond, shown by *p*-terphenyl, there are two possibilities: the phenyl isocyanate dimer molecule is almost completely rigid, without any internal rotations; or the tensors encountered in *p*-terphenyl are not purely dynamic but include a static term; in other words the planar configuration given by X-rays does not correspond to a stable equilibrium. The spectroscopic data give some indication on the problem.

## Use of spectroscopic data of *p*-terphenyl

For *p*-terphenyl, we shall follow the assignments proposed by Reynolds & White (1972), using incoherent inelastic neutron scattering. The molecular axes are shown in Fig. 4. For librations about $X$ and $Z$, Cruickshank's (1956*b*) treatment is straightforward. Neglecting the $A$–$B$ splitting (there are two molecules in the unit cell) and supposing the modes undispersed, the high-temperature approximation gives $\omega^2=kT/I\Omega$ with $\omega=2\pi\nu$, $k$ being Boltzmann's constant, $T$ the absolute temperature, $\nu$ the frequency, $I$ the moment of inertia and $\Omega$ the librational tensor. These frequencies have been calculated by Rietveld *et al.* (1970). They find $\nu_x=39\pm4$ cm$^{-1}$, $\nu_z=73\pm10$ cm$^{-1}$. From tensors given in Table 5 we find $\nu_x=44\pm3$ cm$^{-1}$, $\nu_z=53\pm3$ cm$^{-1}$. These values agree moderately well with Raman assignments: $\nu_x=35{,}5$ cm$^{-1}$, $\nu_z=41$ cm$^{-1}$ (Marqueton & Décamps, 1970).

For librations about the single covalent bond, always neglecting the $A$–$B$ splitting and dispersion, we can expect one external 'lattice' mode and two internal modes. So, with the experimental frequencies it is possible to calculate an order of magnitude for librational tensors. We use the very simplified model shown in Fig. 5. Using respectively $C_1$ and $C$ for external and internal couple constants, the moments of inertia of the three components being the same, the equations of motion are straightforward:

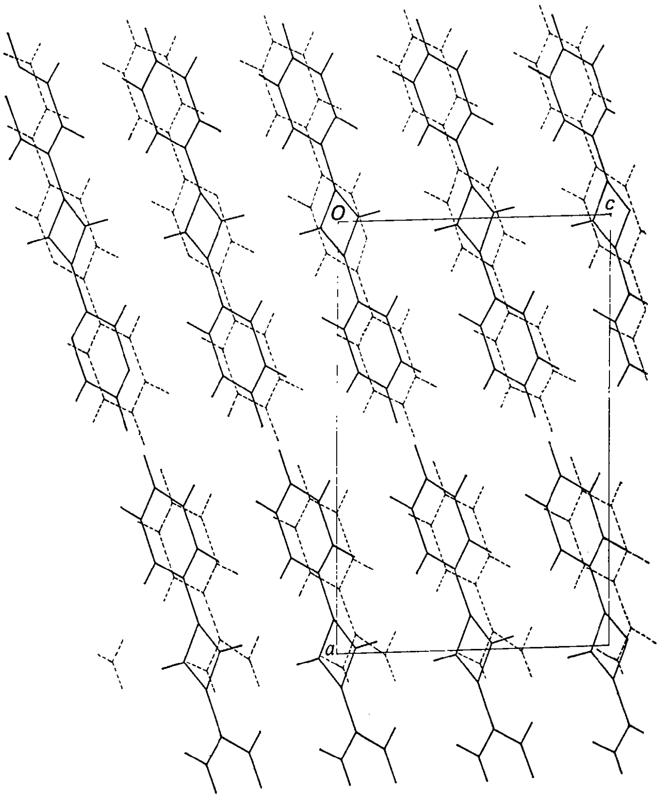

Fig. 2. Projection along the *b* axis. The arrangement of *p*-terphenyl molecules is superposed in broken lines.

Table 5. *Comparison of molecular tensors* (*program Anhar*)

The axes are shown in Fig. 4 for *p*-terphenyl. For the phenyl isocyanate dimer, the axes are the same as those in Table 3.

| | *p*-Terphenyl | | Phenyl isocyanate dimer |
|---|---|---|---|
| $T_{11}$ | 335 (13) × $10^{-4}$ Å$^2$ | $T_{11}$ | 336 (21) × $10^{-4}$ Å$^2$ |
| $T_{22}$ | 416 (6) | $T_{22}$ | 600 (14) |
| $T_{33}$ | 356 (10) | $T_{33}$ | 346 (15) |
| $T_{12}$ | 20 (5) | $T_{12}$ | 8 (11) |
| $T_{13}$ | 8 (6) | $T_{13}$ | 75 (10) |
| $T_{23}$ | − 12 (5) | $T_{23}$ | −4 (12) |
| $\Omega_{11}$ | 3·58 (0·20) $(°)^2$ | $\Omega_{11}$ | 4·16 (0·45) $(°)^2$ |
| $\Omega_{22}$ | 260·29 (7·46) (centre ring) | $\Omega_{22}$ | 31·25 (2·68) (centre ring) |
| $\Omega_{22}$ | 68·89 (3·81) (outer ring) | $\Omega_{22}$ | 27·04 (6·19) (outer ring) |
| $\Omega_{33}$ | 2·74 (0·27) | $\Omega_{33}$ | 2·82 (0·54) |

$$I\ddot{\theta}_1 = -C_1\theta_1 - C(\theta_1-\theta_2) \quad (1)$$

$$I\ddot{\theta}_2 = -C_1\theta_2 - C(2\theta_2-\theta_1-\theta_3) \quad (2)$$

$$I\ddot{\theta}_3 = -C_1\theta_3 - C(\theta_3-\theta_2)\,. \quad (3)$$

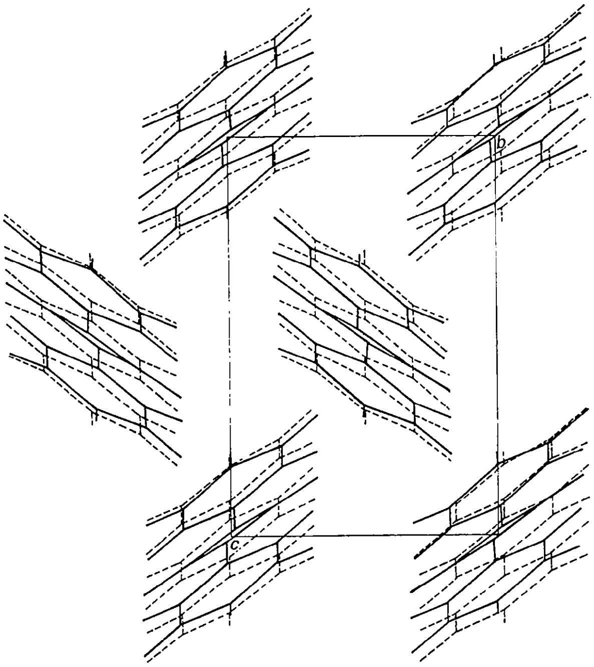

Fig. 3. Projection along the *a* axis.

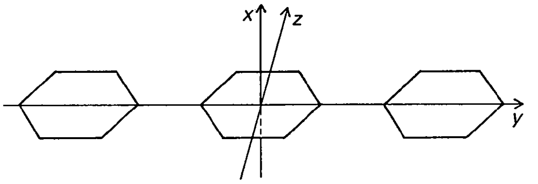

Fig. 4. Molecular axes for *p*-terphenyl.

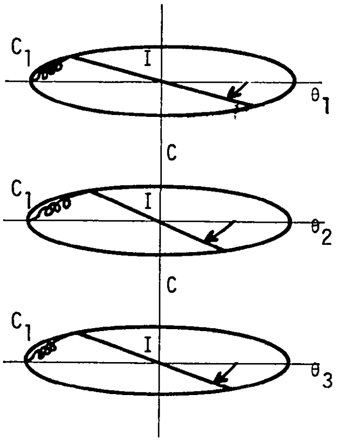

Fig. 5. Simplified dynamical model for *p*-terphenyl.

For a linear oscillator acted on by the restoring force $-C\theta$, the potential energy is clearly $E=C\theta^2/2$.

With the model, the general expression of the potential energy is:

$$E=C_1\theta_1^2/2+C_1\theta_2^2/2+C_1\theta_3^2/2 + C(\theta_1-\theta_2)^2/2+C(\theta_2-\theta_3)^2/2\,. \quad (4)$$

For an external mode

$$\theta_1=\theta_2=\theta_3=a\cos\omega t\,. \quad (5)$$

Substituting (5) into equation (1), (2) or (3):

$$\omega^2=C_1/I\,. \quad (6)$$

Equations (4) and (5) give:

$$E=(\tfrac{3}{2})C_1a^2\,. \quad (7)$$

The librational tensor $\Omega=\langle(a\cos\omega t)^2\rangle=a^2/2$ (the angular parenthesis denoting a time average).

Using (6) and (7):

$\Omega=E/3I\omega^2=kT/3I\omega^2$ ($E=kT$ in the high temperature approximation) which is the usual Cruickshank (1956*b*) formula, $I$ being the moment of inertia of each component.

The total angular momentum for any internal mode must be zero. There are two internal modes involving libration of the rings about the long molecular axis:

$$\text{the } g \text{ mode } \theta_2=-2\theta_1 \quad \theta_1=\theta_3=a\cos\omega t\,, \quad (8)$$

$$\text{the } u \text{ mode } \theta_2=0 \quad \theta_1=-\theta_3=a\cos\omega t\,. \quad (9)$$

For the *g* mode, putting (8) into equation (1), (2) or (3) gives

$$\omega^2=(C_1+3C)/I\,. \quad (10)$$

Equations (4) and (8) give

$$E=3(C_1+3C)a^2\,. \quad (11)$$

From (10) and (11)

$$\Omega_o=a^2/2=E/6I\omega^2=kT/6I\omega^2 \text{ for the outer ring.}$$

From (8)

$$\Omega_c=4\Omega_o \text{ for the centre ring.}$$

For the *u* mode, a similar procedure gives:

$$\omega^2=(C_1+C)/I$$

$$E=(C_1+C)a^2$$

$$\Omega_o=a^2/2=E/2I\omega^2=kT/2I\omega^2 \text{ for the outer ring.}$$

$$\Omega_c=0 \text{ for the centre ring.}$$

With this model, we use the frequencies reported by Reynolds & White (1972) for *p*-terphenyl at 130°K. At room temperature the frequencies would be a little lower. Neglecting this variation, the calculated tensors are given in Table 6. As three frequencies are equal or similar, a permutation in the assignments does not change greatly the total tensor for each ring. For the centre ring $\sum\Omega_c=47{\cdot}1(°)^2$ and for the outer ring $\sum\Omega_o=$

Table 6. *Calculated tensors for the different modes about the long axis* (*for p-terphenyl at room temperature*)

| External mode | First internal mode (*g* mode) | Second internal mode (*u* mode) |
|---|---|---|
| $\theta_1=\theta_2=\theta_3$ | $\theta_1=\theta_3=-\theta_2/2$ | $\theta_1=-\theta_3;\ \theta_2=0$ |
| $\nu=89\ \text{cm}^{-1}$ | $\nu=70\ \text{cm}^{-1}$ | $\nu=89\ \text{cm}^{-1}$ |
| Centre ring $\Omega_c=11{\cdot}1\ (^\circ)^2$ | Centre ring $\Omega_c=36\ (^\circ)^2$ | Centre ring $\Omega_c=0$ |
| Outer ring $\Omega_o=11{,}1\ (^\circ)^2$ | Outer rind $\Omega_o=9\ (^\circ)^2$ | Outer ring $\Omega_o=16{,}6\ (^\circ)^2$ |

Centre ring $\sum\Omega_c=47{,}1\ (^\circ)^2$; outer ring $\sum\Omega_o=36{\cdot}7\ (^\circ)^2$.

$36{\cdot}7(^\circ)^2$. These values are a little larger than those found for the phenyl isocyanate dimer. This can be accounted for by the ratio of the moments of inertia, approximately 3:4. In any case, they do not correspond to those calculated from X-ray data: $\Omega_o=69(^\circ)^2$ and $\Omega_c=260(^\circ)^2$. It is plausible to argue that the differences are due to a static term. In this hypothesis we can determine approximate new equilibrium positions measured from the planar configuration given by X-rays: for the outer ring $\theta_o=\sqrt{(69-36{\cdot}7)}=5{\cdot}7^\circ$, for the centre ring $\theta_c=\sqrt{(260-47{\cdot}1)}=14{\cdot}6^\circ$. These values agree with the positions of the minima on the potential energy curves given by Rietveld *et al.* (1970).

## Conclusion

The comparison of structural and thermal parameters of the phenyl isocyanate dimer and *p*-terphenyl presents some interesting features. First, the analogy between the purely external thermal vibrations, not involving the internal rotations about the single bonds, is well explained by the similarity of molecular configurations and packings in the crystal. It is an argument for the physical meaning of tensors determined from X-ray data. Secondly, the difference between librational terms about the long axis, especially important for the centre rings, illustrates the necessity to interpret these crystallographic results by using other methods, particularly spectroscopy and potential calculations. In the case of *p*-terphenyl, the simplest interpretation would have been to postulate a planar equilibrium configuration for the molecule and the existence of a very low-frequency internal *g* mode ($\theta_1=\theta_3=-\theta_2/2$) at about 30 cm$^{-1}$. This would have explained the ratio approximately 1:4 and the great values of librational tensors about the long axis. But spectroscopic measurements do not give an internal frequency in this range. The non-planar equilibrium configuration of *p*-terphenyl reconciles the crystallographic results, spectroscopic measurements and potential-energy calculations.

For rotation about the long molecular axis, the potential energy function calculated by Rietveld *et al.* (1970) contains an intermolecular term and an intramolecular term. The similarity of the two structures of *p*-terphenyl and the phenyl isocyanate dimer indicates that the intermolecular potentials are similar. The two molecules have however quite different rigidity and consequently behave differently in the crystal field.

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