

An X-ray and Neutron Diffraction Refinement of the Structure of *p*-Terphenyl

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(Received 3 December 1968 and in revised form 5 May 1969)

The crystal structure of *p*-terphenyl has been refined using two sets of X-ray data and two projections of neutron data. The lengths of the carbon-carbon bonds, which have been determined to an accuracy of ± 0.005 Å, differ from those in benzene in a manner which is difficult to explain simply in terms of bond environment. The molecule departs slightly from planarity, apparently as a result of packing forces. The neutron analysis has shown that there are in-plane steric deformations of the *ortho* hydrogen atoms which are nevertheless 0.3 Å closer together than the sum of their van der Waals radii. The central ring oscillates more strongly about the long axis of the molecule than do the two end rings. The thermal librations are generally consistent with potential energy functions calculated for rotation about the symmetry axes of the molecule. The final X-ray difference synthesis shows features resulting from the aspherical distribution of the bonding electrons, but there is evidence of strong interaction between the bonding electron distribution and the X-ray thermal parameters. Because of this effect the difference synthesis cannot be interpreted solely in terms of the electron redistribution due to bonding, and the thermal parameters may be considerably in error.

Introduction

The structure of *p*-terphenyl is of interest in the relation which it bears to those of other aromatic hydrocarbons, particularly benzene (Cox, Cruickshank & Smith, 1958), naphthalene and anthracene (Cruickshank & Sparks, 1960), biphenyl (Almenningen & Bastiansen, 1958; Robertson, 1961; Trotter, 1961), and benzo[*c*]phenanthrene (Hirshfeld, Sandler & Schmidt, 1963). It has, in common with biphenyl, an sp^2 - sp^2 bond between benzene rings which is of particular importance in assessing the effects of hybridization, conjugation and hyperconjugation on bond energies. *p*-Terphenyl serves also as an example of an overcrowded molecule. The distance between the undistorted positions of the *ortho* hydrogen atoms of two adjacent rings is less than the sum of their van der Waals radii, resulting in steric interaction between these atoms. This could lead to in-plane and out-of-plane deviations of the molecule. The theoretical aspects of this situation have been studied recently by Haigh (1963). He found that in-plane deviations are more frequent than out-of-plane deviations, and established the conditions under which the latter do not occur. From a comparison of calculated and experimental results for some conjugated hydrocarbons he concluded that the distance between overcrowded hydrogen atoms is significantly less than the sum of their van der Waals radii. This was attributed to the transfer of small charges from the hydrogen atoms to the molecule as a whole, and also to the fact that the potential energy for displacement from the van der Waals separation is less than has generally been supposed.

The crystal structure of *p*-terphenyl was first determined by Pickett (1933), but the analysis is not sufficiently accurate to permit a detailed study of the molecular geometry, and the positions of the hydrogen atoms were not determined. A three-dimensional X-ray refinement was therefore undertaken in order to obtain accurate bond lengths, and to study any distortions in the carbon atom configuration resulting from the steric hindrance.

Projection neutron diffraction data were also collected, since the relatively higher contribution of the hydrogen atoms to the total scattering enables their positions to be determined more accurately than by X-ray analysis. Preliminary results have been reported (Clews, Maslen, Rietveld & Sabine, 1961).

Crystal data

p-Terphenyl C₁₈H₁₄

Monoclinic platy crystals {001} faces

$a = 8.106(4)$, $b = 5.613(2)$, $c = 13.613(6)$ Å

$\beta = 92^\circ 1'(2)$

$Z = 2$

Space group $P2_1/a$ from absences

In order to provide a check on the reliability of the structure refinement two sets of diffraction data were collected using crystals *A* and *B*, grown from solution and from the melt respectively. The specimens were mounted about the *b* axis, and multiple-film equi-inclination Weissenberg photographs were recorded using Cu $K\alpha$ radiation. These photographs contained more than 95% of the independent reflexions within the reflecting sphere. A third crystal, *C*, grown from solution was mounted about the *a* axis and a similar series of photographs was recorded for scaling purposes.

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The intensity data were corrected for Lorentz and polarization factors. No absorption corrections were necessary. The layer scaling factors for crystal *A* were found by comparing the relative intensities of reflexions which were also recorded for crystal *C*. This procedure could not be followed with the data from crystal *B* because it was found that these had a somewhat lower temperature factor. Since both sets of data were collected at room temperature this discrepancy cannot correspond to a real difference in thermal motion. If it can be assumed that the temperature factor is a measure not only of thermal motion but also of disorder it can be inferred that the crystal from the melt is somewhat more perfect. For a reflexion common to both sets one may write

$$F_a^2 = KF_b^2 \exp(-2\Delta B \sin^2 \theta/\lambda^2),$$

where F_a^2 and F_b^2 are intensities from the *a* and *b* axes data after correction for Lorentz and polarization factors respectively, *K* is a scale factor and ΔB is the difference in the temperature factor coefficient. Values for *K* and ΔB were obtained by plotting

$$\log \frac{F_a}{F_b} \text{ versus } \sin^2 \theta/\lambda^2$$

for each common row line. The various *K* were found to give a consistent set of inter-layer scale factors, and the ΔB were generally uniform showing that the temperature factor difference between the two sets of data was isotropic. The mean value of ΔB was 0.88 \AA^2 .

The first set of intensity data, set I, contained the intensities from crystal *A* plus the few intensities from crystal *C* which were not recorded in the *b* axis data.

908 independent reflexions, out of a total of 1413 in the Cu $K\alpha$ sphere, were observed. The second set of intensity data, set II, contained the intensities from crystal *B* plus the extra group of reflexions from crystal *C* corrected for the difference in temperature factor. 861 independent reflexions were observed.

Neutron diffraction intensity data were collected on single-crystal spectrometers installed at the research establishment of the Australian Atomic Energy Commission at Lucas Heights, New South Wales. There are two spectrometers, 4H₂ and 2 Tan,* both of which are of the moving crystal and counter type. During measurement the crystal drive was geared to the counter in the ratio 1:2. The primary beam was monochromatized by reflexion from the (002) face of a copper crystal for 4H₂ and of a lead crystal for 2 Tan. The reflexions for the *h*0*l* and 0*kl* zones were recorded on the 4H₂ and 2 Tan spectrometers respectively. The specimens, which were grown from the melt were approximately rectangular, with dimensions $5 \times 3 \times 2 \text{ mm}^3$ (*h*0*l*) and $2 \times 2 \times 10 \text{ mm}^3$ (0*kl*), the longest edge being parallel to the rotation axis in each case. The neutron wavelengths were determined from the Bragg angles of the reflexions 40.12 and 0.24 , giving mean values of $1.0015(2)$ (*h*0*l*) and $0.942(2)$ \AA (0*kl*). The half widths of the peaks were considerable, amounting to 1° even for the inner reflexions. This effect, which indicated a large mosaic spread in the crystals, prevented the measurement of reflexions with $2\theta > 100^\circ$ because of overlap in that

* 4H₂ and 2 Tan refer to the experimental holes of the HIFAR reactor which contain the collimators for the spectrometers.

Table 1. Parameters from set I data refinement*

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>b</i> ₁₁	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₂	<i>b</i> ₂₃	<i>b</i> ₃₃
C(1)	0.0514	0.1747	0.0629	0.0337	-0.0406	0.0066	0.0464	-0.0090	0.0065
C(2)	-0.0464	0.0001	0.0997	0.0133	0.0014	-0.0010	0.0292	0.0007	0.0053
C(3)	-0.0979	-0.1742	0.0346	0.0354	-0.0434	0.0072	0.0454	-0.0073	0.0066
C(4)	-0.0952	0.0006	0.2048	0.0140	0.0046	-0.0013	0.0298	0.0011	0.0054
C(5)	-0.0407	0.1757	0.2698	0.0213	-0.0088	0.0023	0.0380	-0.0051	0.0062
C(6)	-0.0846	0.1722	0.3676	0.0233	-0.0060	0.0019	0.0440	-0.0055	0.0061
C(7)	-0.1837	-0.0039	0.4014	0.0225	0.0048	0.0020	0.0460	-0.0006	0.0060
C(8)	-0.2428	-0.1794	0.3380	0.0236	-0.0136	0.0029	0.0455	0.0029	0.0063
C(9)	-0.1974	-0.1771	0.2398	0.0217	-0.0157	0.0001	0.0418	0.0013	0.0056

* The temperature factors are expressed in the form:

$$\exp[-(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)].$$

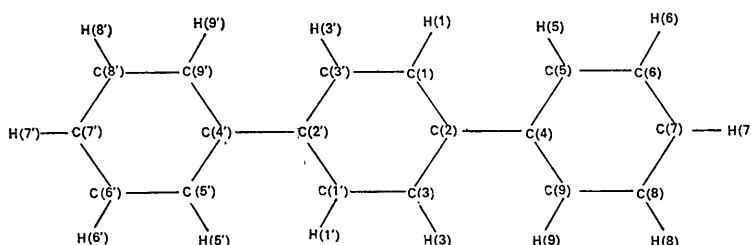


Fig. 1. Numbering of the atoms in the molecule of *p*-terphenyl.

region. Intensities for 126 $h0l$ and 86 $0kl$ reflexions were determined for $d_{h0l} > 0.54 \text{ \AA}$ and $d_{0kl} > 0.62 \text{ \AA}$. The intensities were corrected for background and for the Lorentz factor.

Structure analysis

The set I data were analysed by the least-squares method using the block-diagonal approximation to the least-squares matrix which has a 3×3 and 6×6 unit for the positional and thermal parameters respectively of each atom in the asymmetric unit. The C-H bond lengths were kept constant and each hydrogen atom was given an isotropic temperature factor coefficient equal to the mean for the carbon atom to which it was bonded. The scattering factor of Freeman (1959) was used for carbon and that of McWeeny (1951) for hydrogen.

In the refinement each of the terms corresponding to an observed reflexion was given a weight W , where

$$W = 1 \text{ for } |F_o| < F^* \\ W = |F^*/F_o| \text{ for } |F_o| > F^*$$

where F^* , the magnitude of the most reliable structure factor, is 7σ . The quantity minimized is $\sum W(F_o - F_c)^2$. The properties of this weighting function are discussed by Mills & Rollett (1961). The R value† was 0.123 for the final structure factors. The parameters are given in Table 1, and the numbering of the atoms is given in Fig. 1.

For the set II refinement the weighting scheme, whose properties are also described by Mills & Rollett (1961), was

$$W = |F_o|/F^* \text{ for } |F_o| < F^* \\ W = F^*/|F_o| \text{ for } |F_o| > F^*$$

† Defined as $\sum |F_o| - |F_c| / \sum |F_o|$ for the observed reflexions.

with F^* equal to 3.0σ . An examination of the data at an intermediate stage of refinement showed that the $|F_o|$ for the stronger reflexions were all consistently less than the corresponding $|F_c|$ values, indicating data errors due to extinction. The five largest and hence most strongly affected terms were excluded and the remainder were rescaled, the omitted terms being 003, 110, 111, 201 and 211. After further refinement of the parameters for the carbon atoms only the R value was 0.097. A list of these parameters and their standard deviations is given in Tables 2 and 3. The structural parameters for the hydrogen atoms were then refined, holding the parameters of the carbon atoms constant. Only the coordinates and mean isotropic temperature factor coefficients of the hydrogen atoms were varied.

The final parameters are listed in Table 4. The positions of the hydrogen atoms for a C-H bond length of 1.08 \AA with the bonds radiating directly outwards from the centre of the benzene ring are given for comparison. The agreement of the isotropic temperature factors of chemically equivalent hydrogen atoms is good, except perhaps between H(6) and H(8). Their values indicate that the hydrogen atoms execute relatively the same vibrations as the carbon atoms to which they are bonded. The standard deviations in the positions are rather large, so that any physical interpretation is of doubtful value.

An attempt was made to refine the structure by the use of the scattering factors developed by McWeeny (1954) for bonded carbon atoms, but this was not successful. Rae & Maslen (1965) have shown that McWeeny's calculations are in error in that they ignore the imaginary contribution to the scattering factor. However, a further attempt at refining the structure including the imaginary component was also unsuccessful. It was concluded that McWeeny's bonded atom

Table 2. Atomic positions from set II refinement

	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$
C(1)	0.0519	0.0006	0.1739	0.0009	0.0623	0.0003
C(2)	-0.0466	0.0004	0.0001	0.0006	0.0998	0.0002
C(3)	-0.0970	0.0006	-0.1729	0.0008	0.0350	0.0003
C(4)	-0.0953	0.0003	-0.0023	0.0006	0.2047	0.0002
C(5)	-0.0404	0.0005	0.1756	0.0008	0.2695	0.0003
C(6)	-0.0854	0.0005	0.1734	0.0008	0.3679	0.0003
C(7)	-0.1842	0.0005	-0.0060	0.0009	0.4016	0.0002
C(8)	-0.2419	0.0006	-0.1794	0.0008	0.3379	0.0003
C(9)	-0.1979	0.0005	-0.1774	0.0007	0.2403	0.0002

Table 3. Thermal parameters from set II refinement

	b_{11}	$\sigma(b_{11})$	b_{12}	$\sigma(b_{12})$	b_{13}	$\sigma(b_{13})$	b_{22}	$\sigma(b_{22})$	b_{23}	$\sigma(b_{23})$	b_{33}	$\sigma(b_{33})$
C(1)	0.0339	0.0011	-0.0445	0.0024	0.0076	0.0007	0.0468	0.0019	-0.0102	0.0011	0.0052	0.0002
C(2)	0.0124	0.0004	-0.0012	0.0012	-0.0007	0.0004	0.0197	0.0009	0.0006	0.0007	0.0046	0.0002
C(3)	0.0337	0.0011	-0.0452	0.0022	-0.0099	0.0007	0.0395	0.0017	-0.0064	0.0010	0.0057	0.0002
C(4)	0.0128	0.0005	-0.0059	0.0013	-0.0002	0.0004	0.0245	0.0011	0.0004	0.0008	0.0043	0.0002
C(5)	0.0194	0.0007	-0.0104	0.0016	0.0025	0.0006	0.0340	0.0014	-0.0045	0.0009	0.0056	0.0002
C(6)	0.0218	0.0007	-0.0056	0.0017	0.0028	0.0006	0.0378	0.0015	-0.0066	0.0010	0.0051	0.0002
C(7)	0.0206	0.0007	-0.0053	0.0018	0.0031	0.0006	0.0409	0.0015	0.0011	0.0010	0.0051	0.0002
C(8)	0.0224	0.0007	-0.0168	0.0019	0.0026	0.0006	0.0393	0.0016	0.0042	0.0010	0.0056	0.0002
C(9)	0.0193	0.0006	-0.0174	0.0016	0.0017	0.0005	0.0319	0.0014	0.0005	0.0009	0.0050	0.0002

Table 4. *Hydrogen atom parameters from X-ray refinement**

	<i>x/a</i>		<i>y/b</i>		<i>z/c</i>		<i>B</i>
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
H(1)	0.0848	0.0929	0.3062	0.3133	0.1042	0.1125	7.98
H(3)	-0.1779	-0.1754	-0.2997	-0.3124	0.0601	0.0626	7.13
H(5)	0.0281	0.0380	0.3002	0.3152	0.2472	0.2431	3.70
H(6)	-0.0444	-0.0413	0.3071	0.3098	0.4147	0.4180	4.13
H(7)	-0.2097	-0.2175	-0.0123	-0.0071	0.4754	0.4775	5.94
H(8)	-0.3233	-0.3217	-0.3119	-0.3177	0.3650	0.3648	2.79
H(9)	-0.2270	-0.2423	-0.3047	-0.3145	0.1934	0.1903	3.99

* The temperature factors are expressed in the form $\exp[-(B \sin 2\theta/\lambda^2)]$.

Table 5. *Positional parameters from neutron refinement*

	<i>x/a</i>	$\sigma(x/a)$	<i>y/b</i>	$\sigma(y/b)$	<i>h0l</i>		<i>0kl</i>	
					<i>z/c</i>	$\sigma(z/c)$	<i>z/c</i>	$\sigma(z/c)$
C(1)	0.0571	0.0021	0.1688	0.0071	0.0643	0.0014	0.0623	0.0025
C(2)	-0.0457	0.0014	-0.0117	0.0056	0.1015	0.0014	0.1000	0.0018
C(3)	-0.1031	0.0025	-0.1770	0.0062	0.0334	0.0014	0.0332	0.0025
C(4)	-0.0958	0.0014	0.0016	0.0056	0.2043	0.0014	0.2034	0.0018
C(5)	-0.0362	0.0015	0.1745	0.0051	0.2707	0.0014	0.2710	0.0018
C(6)	-0.0833	0.0015	0.1786	0.0056	0.3674	0.0014	0.3686	0.0025
C(7)	-0.1857	0.0015	0.0029	0.0091	0.4028	0.0014	0.4023	0.0025
C(8)	-0.2408	0.0015	-0.1852	0.0056	0.3373	0.0014	0.3391	0.0018
C(9)	-0.2002	0.0015	-0.1817	0.0056	0.2375	0.0014	0.2390	0.0018
H(1)	0.1026	0.0060	0.3180	0.0184	0.1068	0.0026	0.1078	0.0060
H(3)	-0.1753	0.0051	-0.3280	0.0156	0.0505	0.0021	0.0536	0.0060
H(5)	0.0368	0.0051	0.3159	0.0110	0.2446	0.0021	0.2443	0.0049
H(6)	-0.0455	0.0060	0.3078	0.0194	0.4197	0.0026	0.4194	0.0049
H(7)	-0.2212	0.0036	-0.0157	0.0256	0.4794	0.0016	0.4786	0.0060
H(8)	-0.3208	0.0055	-0.3095	0.0177	0.3632	0.0026	0.3565	0.0055
H(9)	-0.2392	0.0053	-0.3146	0.0192	0.1993	0.0040	0.1967	0.0074

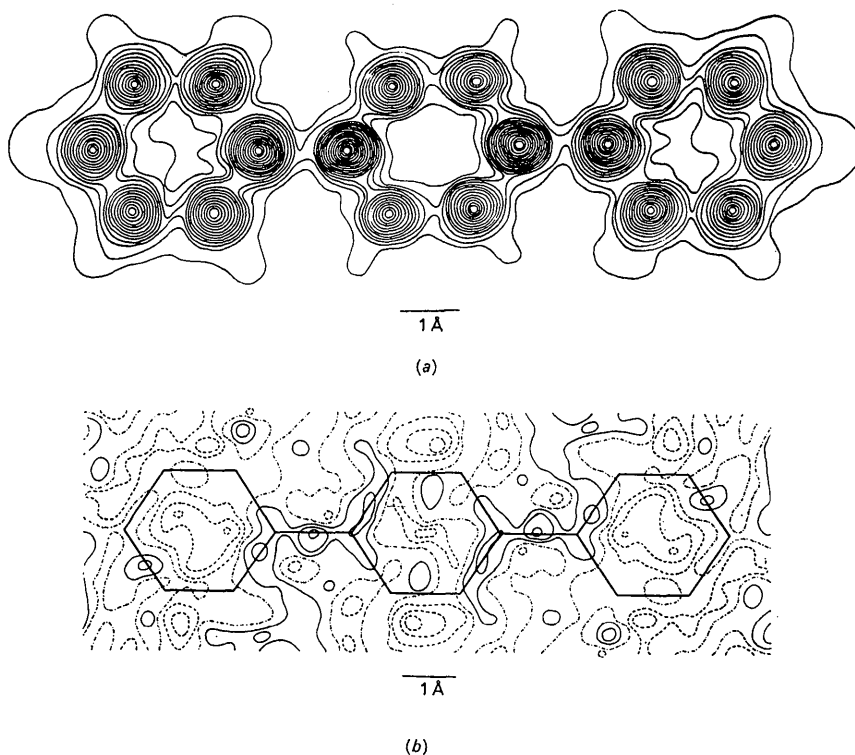


Fig. 2. (a) Electron density in the mean molecular plane of *p*-terphenyl. Contour interval: 0.5 e. \AA^{-3} (zero contour omitted). (b) Section of the difference synthesis in the mean molecular plane after correcting for extinction. Contour interval: 0.05 e. \AA^{-3} . — positive contour, - - - zero contour, ····· negative contour.

Table 6. Thermal parameters from neutron refinement

	b_{11}	$\sigma(b_{11})$	b_{22}	$\sigma(b_{22})$	b_{33}	$\sigma(b_{33})$	b_{33}	$\sigma(b_{33})$	b_{23}	$\sigma(b_{23})$	b_{13}	$\sigma(b_{13})$
C(1)	0.0274	0.0033	0.0454	0.0130	0.0046	0.0007	0.0050	0.0025	-0.0153	0.0071	0.0080	0.0021
C(2)	0.0083	0.0007	0.0184	0.0056	0.0033	0.0007	0.0041	0.0025	-0.0081	0.0043	0.0003	0.0007
C(3)	0.0303	0.0033	0.0393	0.0123	0.0050	0.0007	0.0055	0.0025	-0.0104	0.0061	0.0100	0.0025
C(4)	0.0097	0.0014	0.0228	0.0066	0.0027	0.0007	0.0040	0.0025	0.0015	0.0050	0.0008	0.0014
C(5)	0.0166	0.0015	0.0239	0.0071	0.0047	0.0007	0.0046	0.0025	-0.0063	0.0043	0.0074	0.0015
C(6)	0.0201	0.0021	0.0323	0.0109	0.0049	0.0007	0.0066	0.0025	0.0022	0.0061	0.0023	0.0021
C(7)	0.0178	0.0021	0.0362	0.0097	0.0048	0.0007	0.0046	0.0025	0.0057	0.0066	0.0005	0.0021
C(8)	0.0197	0.0021	0.0393	0.0142	0.0048	0.0007	0.0047	0.0025	0.0019	0.0061	0.0058	0.0021
C(9)	0.0169	0.0015	0.0362	0.0126	0.0033	0.0007	0.0034	0.0025	0.0013	0.0043	0.0006	0.0015
H(1)	0.0649	0.0121	0.1265	0.0355	0.0149	0.0029	0.0133	0.0043	-0.0333	0.0205	0.0076	0.0076
H(3)	0.0700	0.0059	0.0479	0.0291	0.0050	0.0007	0.0104	0.0056	-0.0227	0.0186	0.0074	0.0072
H(5)	0.0373	0.0080	0.0363	0.0251	0.0058	0.0007	0.0078	0.0035	-0.0150	0.0140	0.0143	0.0055
H(6)	0.0456	0.0103	0.0784	0.0266	0.0051	0.0015	0.0060	0.0035	-0.0175	0.0210	0.0049	0.0066
H(7)	0.0272	0.0053	0.0621	0.0338	0.0022	0.0007	0.0084	0.0075	-0.0075	0.0375	0.0120	0.0029
H(8)	0.0370	0.0083	0.0758	0.0682	0.0069	0.0015	0.0077	0.0043	0.0173	0.0251	0.0142	0.0062
H(9)	0.0283	0.0078	0.0714	0.0704	0.0154	0.0039	0.0125	0.0075	-0.0197	0.0305	0.0066	0.0085

scattering factors are a poorer approximation than Freeman's isotropic values, and the refinement was terminated.

For the neutron data a least-squares refinement using the block-diagonal approximation was carried out, and was terminated when the shifts in parameters were less than 0.1σ . The scattering lengths for all structure factor calculations were those given in *International Tables for X-ray Crystallography* (1962). The final R values were 0.090 ($h0l$) and 0.080 ($0kl$). The final coordinates and thermal parameters are listed in Tables 5 and 6.*

Electron density distribution

Fourier and difference syntheses were calculated using the data and parameters from the set II refinement since this appears to be more accurate than that of set I. The electron density distribution in the molecular plane is shown in Fig. 2(a). The shapes of the atomic peaks are consistent with the thermal motion in the structure. The hydrogen atoms appear as bulges in the $0.5e.\text{\AA}^{-3}$ contour. Fig. 2(b) shows the difference electron density in the molecular plane. All the atomic sites are close to points of zero electron density except C(2) and C(4), which are on slightly positive regions. It is interesting to note that recent theoretical calculations (Roos & Skancke, 1967) predict that these atoms acquire an excess negative charge in the electron redistribution associated with the bonding of the two rings. There are also small peaks on each of the carbon-carbon bonds, suggestive of bonding electrons. Sections perpendicular to the plane of the ring through bonds between carbon atoms with hydrogen atom substituents show the characteristic dumb-bell shape observed for similar bonds in orthonic acid (Hall & Maslen, 1967). At the centres of the benzene rings there are also regions of negative density similar to those reported for related structures by other workers (*e.g.* Cruickshank, 1956b).

The results of the Fourier syntheses for the neutron data are shown in Fig. 3.

Analysis of the thermal motion

The anisotropic motion of a set of atoms can be attributed partly to the independent motion of each atom in the framework of the molecule and partly to the motion of the molecule as a whole. Following Cruickshank (1956a) one may describe the molecular motion by two tensors, one of which, \mathbf{T} , represents the translational motion of the mass centre of the molecule, and the other, ω , describes the librations of the molecule as a whole.

It is convenient to define a set of orthogonal axes as shown in Fig. 4. Axis L passes through the origin and

* A list of the observed and final calculated structure factors for both the X-ray and neutron data has been deposited at the Reid Library, University of Western Australia. Copies are available on request.

C(2), axis *N* is perpendicular to the least-squares plane through the six atoms of the centre ring and axis *M* is the perpendicular to axes *L* and *N*. As has been shown by Pawley (1967) there is no group theoretical reason for the principal axes of vibration and libration to coincide with molecular symmetry axes which are not elements of the space group symmetry. Nevertheless there is close correspondence between the principal axes of libration and the molecular axes in this structure. It is preferable to describe the **T** and **ω** tensors in the coordinate system defined by the latter set of axes,

since this simplifies the treatment of the free rotation about the C(2)–C(4) bond without appreciable loss in validity.

It was thought worth while first to calculate **T** and **ω** for the molecule as a whole, in view of the possibility that the energy associated with the overlap of the π -orbitals of neighbouring rings might be sufficient to hold the molecule coplanar. The results of this calculation are listed in Table 7(a). The standard deviations were obtained from the diagonal elements of the inverse to the normal equations matrix. As indicated

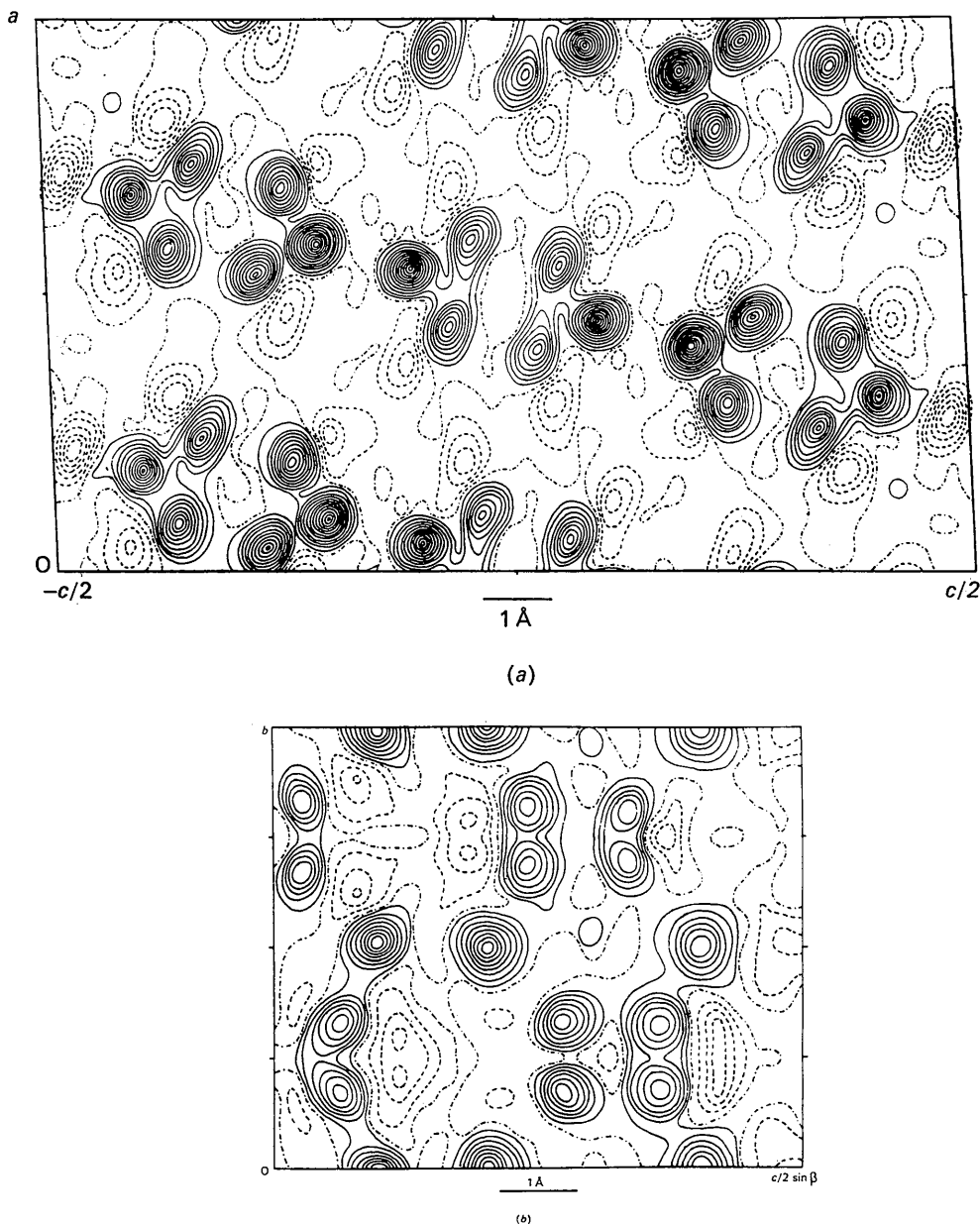


Fig. 3. (a) Fourier synthesis using $h0l$ neutron data. Contour interval: $2.0 \times 10^{-5} \text{ \AA}^{-1}$; (b) Fourier synthesis using $0kl$ neutron data. Contour interval: $2.5 \times 10^{-5} \text{ \AA}^{-1}$.

above the off-diagonal terms, which differ from zero by amounts of the same order as their standard deviations, are consistent with the librations of the molecule being almost entirely about the molecular axes. The term ω_{22} seems to be significant with a value of 3σ . It is however, physically meaningless, as it has a negative value. The anomaly largely disappears when \mathbf{T} and ω are evaluated for the centre and outer ring independently. The large difference in the ω_{11} values indicates an appreciable amount of free rotation about the C(2)–C(4) bond [Table 7(b) and (c)]. The ω_{22} value for the inner ring is still negative, but is less than one standard deviation, which is not significant. It can be seen, on comparing the value for set I and set II, that the ω tensors agree within the limits set by the standard deviations. The \mathbf{T} tensors on the other hand differ markedly, the diagonal elements for set I being in all cases larger than those for set II. As explained earlier this result may be accounted for if we assume that \mathbf{T} represents not only the translational vibrations of the molecule, but also disorder.

Although the ω tensors for sets I and II agree closely, the amplitudes of oscillation about the axes L and M for the centre ring differ considerably from those for the outer ring. The differences for the M axis oscillations are at the 3σ level of significance, and are very much greater than expected from the general consistency of the results corresponding to the two sets of data. The reason for the anomaly became obvious when the observed vibrational parameters relative to the molecular axes were compared with those calculated from \mathbf{T} and ω . For the atoms C(2) and C(4) the observed parameters were generally too low.

As is noted above, these two atoms are predicted by recent molecular orbital calculations to have acquired a net excess of electrons. The calculations of Roos & Skancke (1967) indicate that, in a hydrocarbon of this kind, an sp^2 carbon atom which has three carbon atoms as neighbours acquires an electron excess corresponding to a charge of $-0.023e$; an atom similar except for having one hydrogen substituent has a net deficiency of electrons, corresponding to a charge of $+0.015e$. This

contrasts with simpler molecular orbital theories (e.g. Coulson, 1961) where the formal charges for all the carbon atoms in an alternant hydrocarbon are predicted to be zero. It is clear, however, that the small charge movements indicated by the more exact calculations have interacted with the thermal parameters, which are therefore in error. A low temperature factor for C(2) has given a spurious decrease in ω_{22} for the central ring, whereas that for C(4) has increased ω_{22} for the outer ring. This is shown by repeating the calculation of \mathbf{T} and ω for the outer ring excluding the parameters of C(4). All the remaining atoms have the same formal charge, and temperature factor errors resulting from the electron deficiencies are expected to affect \mathbf{T} rather than ω . The results of the calculation are given in Table 7(d). The ω_{22} values, as expected, have decreased from 3.2 and 3.1 to 1.2 and 1.6 degrees² for the set I and set II data respectively. A similar calculation for the centre ring is not possible because, if the C(2) parameters are excluded, the problem is not sufficiently overdetermined. An estimate of the errors in the temperature factors of C(1), C(3) and C(2) was made using a procedure developed by Stewart & Coppens (1968) and is of the magnitude necessary to give an ω_{22} value for the centre ring equal to those in Table 7(d), within the limits of accuracy indicated by the standard deviations. The size of the errors in temperature factors resulting from the small formal charges in this structure supports the recent assertion by Coppens (1968) that large errors in temperature factors result from the use of inadequate form factors in the analysis of light atom structures by X-ray methods.

Notwithstanding this fact, the differences in the thermal oscillations of the rings about the L axis are so large that they must be regarded as real. A quasi rigid-body model for the structure is therefore inappropriate and for this type of oscillation each of the rings must be considered separately. The change in alignment of the atomic orbitals for relative rotation of the rings will give rise to a torque towards the coplanar configuration, but this will be opposed by the effect of the relaxation of the steric hindrance between the *ortho* hydro-

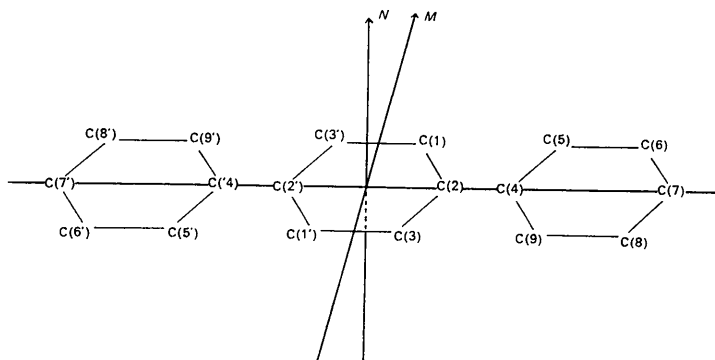


Fig. 4. Molecular axes for *p*-terphenyl.

gen atoms. This results in a low energy differential for rotation of the rings and consequently in a large degree of independence for their thermal motions.

The thermal motions about the three axes can be correlated with simple theoretical calculations of the potential energy functions for rotation of the molecule as a whole about axes *M* and *N*, and for each of the rings separately about axis *L*. The contribution to the potential functions from intermolecular interactions were evaluated using the generalized potential proposed by Kitajgorodskii* (1965). For the rotations of the

rings about axis *L* similar terms must be included for the intramolecular interactions, and to this is added the change in energy with the relative orientations of the atomic orbitals in neighbouring ring systems. For the end ring the latter term will be very close to the corresponding term for biphenyl which, along with that for the central ring, has been evaluated by Polansky (1963). In order to reduce the computation it was necessary to regard the whole system, apart from the molecule or ring being rotated, as at rest. All intermolecular interactions within three coordination spheres, which contribute more than 99% of the total interaction potential, were included. The results of the calculations, which for convenience have been adjusted by a constant to give zero at the origin are shown in Fig. 5(a) to (d). The curves are generally consistent with

* In the formula for the interaction potential

$$U = U_{2/3} \left(\frac{1}{Z^6} - \frac{6}{\alpha} \exp \alpha \exp(-\alpha Z) \right) / \left(11.4 - \frac{6}{\alpha} \exp \alpha / 3 \right)$$

given in that paper, a quotient sign has been omitted.

Table 7. *Vibration and oscillation tensors*

(a) Vibration tensors T_{ij} in Å ² and oscillation tensors ω_{ij} in degrees ² for the whole molecule												
T_{ij}			$\sigma(T_{ij})$			ω_{ij}			$\sigma(\omega_{ij})$			
Set I												
0.0549	0.0012	0.0025	0.0041	0.0040	0.0042	124.8	-0.5	-1.0	20.2	1.9	3.7	
	0.0408	0.0000		0.0061	0.0061		-3.3	0.2		1.1	1.1	
		0.0662			0.0086			3.3			1.1	
Set II												
0.0451	0.0000	0.0020	0.0044	0.0044	0.0046	131.1	-0.5	-0.6	22.1	2.1	4.0	
	0.0321	0.0023		0.0067	0.0067		-3.9	0.2		1.3	1.2	
		0.0628			0.0094			3.3			1.2	
(b) Vibration tensors T_{ij} in Å ² and oscillation tensors ω_{ij} in degrees ² for the centre ring												
T_{ij}			$\sigma(T_{ij})$			ω_{ij}			$\sigma(\omega_{ij})$			
Set I												
0.0537	0.0009	0.0030	0.0008	0.0008	0.0010	265.0	-5.3	1.1	5.5	2.3	2.9	
	0.0411	-0.0005		0.0010	0.0010		-0.8	-0.3		1.1	0.8	
		0.0422			0.0021			4.5			0.8	
Set II												
0.0425	0.0003	0.0030	0.0014	0.0014	0.0018	286.1	1.1	5.9	10.0	4.1	5.3	
	0.0333	0.0010		0.0018	0.0019		-0.6	-1.2		2.0	1.4	
		0.0361			0.0038			4.8			1.3	
(c) Vibration tensors T_{ij} in Å ² and oscillation tensors ω_{ij} in degrees ² for the outer ring												
T_{ij}			$\sigma(T_{ij})$			ω_{ij}			$\sigma(\omega_{ij})$			
Set I												
0.0552	0.0014	0.0025	0.0014	0.0014	0.0015	70.7	-0.5	-1.0	7.0	0.5	1.1	
	0.0387	0.0012		0.0032	0.0033		3.2	0.3		0.5	0.5	
		0.0351			0.0042			3.6			0.5	
Set II												
0.0459	0.0003	0.0020	0.0018	0.0018	0.0018	73.5	-0.6	-0.8	8.6	0.7	1.3	
	0.0278	0.0039		0.0040	0.0040		3.1	0.4		0.7	0.6	
		0.0291			0.0052			3.9			0.6	
(d) Vibration tensors T_{ij} in Å ² and oscillation tensors ω_{ij} in degrees ² for the outer ring, excluding atom C(4)												
T_{ij}			$\sigma(T_{ij})$			ω_{ij}			$\sigma(\omega_{ij})$			
Set I												
0.0553	0.0014	0.0025	0.0015	0.0015	0.0015	46.2	-0.6	-1.1	12.1	0.5	1.0	
	0.0353	0.0013		0.0039	0.0039		1.4	0.3		0.9	0.5	
		0.0562			0.0096			4.0			0.5	
Set II												
0.0466	-0.0003	0.0020	0.0017	0.0017	0.0018	53.4	-0.7	-0.8	14.2	0.6	1.2	
	0.0208	0.0037		0.0046	0.0046		1.6	0.4		1.1	0.6	
		0.0465			0.0112			4.7			0.6	

the degree of rotation observed for the four types of oscillation. Those which describe the librations of the molecule about axes M and N [Fig. 5(c)] are nearly symmetrical about the origin, and approximate quite closely to simple harmonic potentials. The function for M axis rotation increases more rapidly than that for the N axis, in accordance with the observed librational amplitudes.

The potential energy curves for the intramolecular interactions associated with the L axis rotations, which must be closely symmetrical because of the molecular geometry, resemble fairly closely those given in Polansky's (1963) earlier calculation. The sums of the intramolecular interactions and orbital contributions, which represent the potential energy function for the molecule in the gaseous state, have minima at $\phi_L = 37\frac{1}{2}^\circ$.

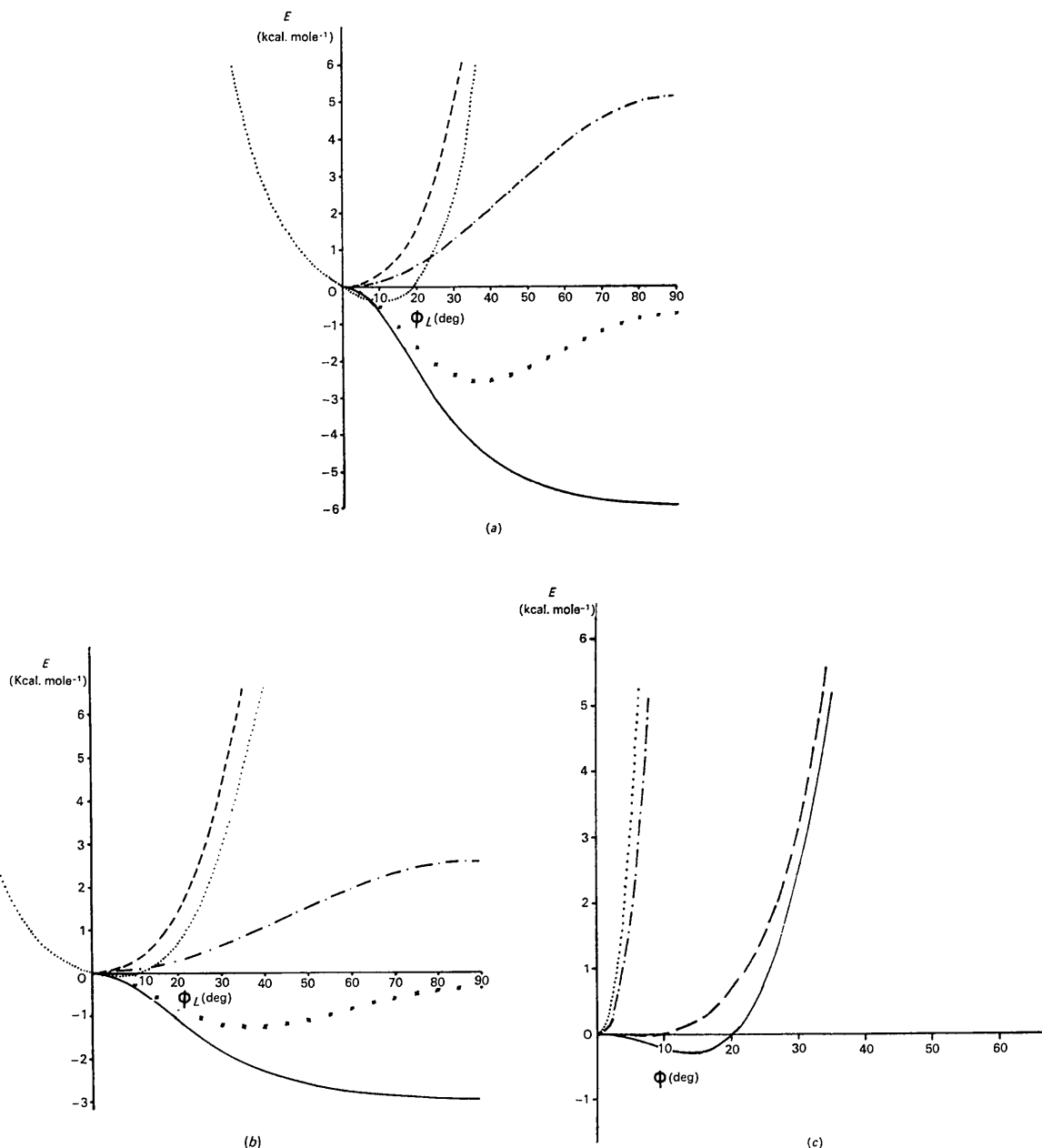


Fig. 5. (a) Contributions to the potential function for centre ring libration about the L axis. intermolecular interactions, ----- averaged intermolecular interactions, ——— intramolecular interactions, - · - · - orbital alignment, × × × sum of intramolecular interactions and orbital contribution. (b) Contributions to the potential function for outer ring libration about the L axis. Contours as for (a). (c) Total potential function. ——— libration of centre ring about the L axis, ----- libration of end ring about the L axis, libration of molecule about the M axis, - · - · - libration of molecule about the N axis.

This is within the range of results quoted by Bastiansen (1949) from his gas electron diffraction study of biphenyl, which is an essentially similar system. The results also support Polansky's observation that the potential energy for $\varphi_L=90^\circ$ is lower than that for $\varphi_L=0^\circ$ in the vapour phase. Both contributions for the central ring have almost exactly double the magnitude of those for the outer ring. This is expected since the effects of π -electron delocalization and the repulsive terms in the potential, which dominate the intramolecular interactions, are effectively double ended for the central ring.

The curves representing the intermolecular interactions have their minima at approximately ten and five degrees from the observed equilibrium positions for the centre and outer rings respectively. The curve for the centre ring is appreciably asymmetric, but not sufficiently so to compensate for the effect of the displacement of the minimum from the equilibrium position. These curves are much more sensitive to the equilibrium separation parameters in the Kitajgorodskii expression than those for the rotations of the molecule as a whole, and may be quite appreciably in error. However, the mean curves about a φ value near to the minimum are less sensitive to these parameters. The means of the two curves averaged about $\varphi_L=+5^\circ$, which are included in Fig. 5(a) and (b), should thus be a reasonable approximation to the actual intermolecular interaction potential. The sums of these functions and the intramolecular and orbital contributions for the two rings are plotted in Fig. 5(c). The curve for rotation of the centre ring is much broader than that for the outer ring, which explains the relative size of the librational amplitudes observed for both these motions.

If the mean energy per mode of libration is taken as kT , or approximately $0.6 \text{ kcal. mole}^{-1}$, the mean-square amplitudes evaluated numerically, assuming classical statistics, are 2.6, 4.6, 138 and 188 degrees², for the

librations of the molecule about *M* and *N* and of the centre and outer rings about *L* respectively. The agreement with the experimental observations can be brought within the limits of error by small changes to the arbitrary parameters in the empirical expressions for the various potential functions. However, this cannot be done in a unique manner, since a wide range of combinations produce effects which are indistinguishable in the relevant regions of these potential functions. Moreover, the calculations for the *L* axis oscillations cannot be taken too seriously since the energy of $0.6 \text{ kcal. mole}^{-1}$ for each mode of libration is not strictly justified because it ignores the effect of coupling between the motion in neighbouring molecules, and the energy level itself should be measured from the curve minimum, rather than the height at $\varphi_L=0^\circ$. The depths and positions of the minima are very sensitive to any errors in the approximations used.

Although it is difficult to make a quantitative estimate of the vibrations from the theoretical calculations, several general conclusions can be drawn. The *M* and *N* librations are quite close to simple harmonic, and their frequencies will be largely independent of change in temperature. The oscillation of the centre ring about the *L* axis, on the other hand is strongly anharmonic, and the libration frequencies will vary quite considerably with temperature. The same tendency, but to a lesser degree, will be shown by the outer ring.

It is expected that the results for the *M* and *N* axis rotations should correlate with either lines or doublets in the Raman spectrum. A Raman spectrum with lines at 17, 35, 42, 80 and 94 cm^{-1} has been reported by Korshunov, Bondarev & Tustanovskaya (1964). The frequencies for the *M* and *N* axis oscillations may be calculated to be 73 ± 10 and $39 \pm 4 \text{ cm}^{-1}$ respectively, using the procedure described by Cruickshank (1956c), and are as close to the observed doublets as is expected from the standard deviations.

Table 8. Atomic coordinates *X*, *Y*, *Z* in Å relative to molecular axes *L*, *M*, *N*, respectively

	<i>X</i>			<i>Y</i>			<i>Z</i>		
	Set I	Set II	$\sigma(X)$	Set I	Set II	$\sigma(Y)$	Set I	Set II	$\sigma(Z)$
C(1)	0.701	0.693	0.006	1.162	1.160	0.007	-0.004	0.000	0.007
C(2)	1.423	1.423	0.004	0.000	0.000	0.004	0.001	0.000	0.004
C(3)	0.692	0.695	0.005	-1.165	-1.154	0.007	-0.003	0.000	0.007
C(4)	2.921	2.920	0.004	-0.004	-0.010	0.005	0.001	0.009	0.004
C(5)	3.642	3.638	0.005	1.186	1.185	0.006	0.022	0.024	0.006
C(6)	5.033	5.039	0.005	1.176	1.179	0.006	0.049	0.037	0.006
C(7)	5.718	5.720	0.005	-0.004	-0.016	0.007	0.038	0.041	0.006
C(8)	5.027	5.023	0.005	-1.204	-1.200	0.006	-0.008	0.002	0.006
C(9)	3.626	3.638	0.005	-1.195	-1.196	0.006	-0.018	-0.018	0.006
	Neutron analysis			Neutron analysis			Neutron analysis		
H(1)	1.155		0.036	2.139		0.090	0.027		0.069
H(3)	1.088		0.030	-2.184		0.076	0.008		0.058
H(5)	3.124		0.030	2.122		0.056	0.024		0.047
H(6)	5.623		0.036	2.081		0.095	0.046		0.071
H(7)	6.833		0.015	-0.065		0.121	0.066		0.081
H(8)	5.547		0.036	-2.095		0.086	-0.044		0.065
H(9)	3.197		0.052	-2.098		0.093	0.004		0.069

Molecular geometry

Table 8 gives the coordinates of the carbon atoms derived from the X-ray data sets I and II and the hydrogen atoms of the neutron analysis, all referred to the molecular axes L , M , N . The hydrogen coordinates are derived using the z values taken from the $h0l$ refinement, since these are considerably more accurate than those obtained from the $0kl$ data.

The final carbon coordinates agree well within the limits of the experimental errors. The root-mean-square deviation between the two sets is 0.0057 Å compared with the average estimated standard deviation of 0.0056 Å. The maximum discrepancy in a pair of corresponding coordinates is 0.012 Å, which is not significant when compared with the estimated standard deviation of 0.0057 Å.

Neither the centre nor the outer ring carbon skeletons deviate significantly from planarity. However the two rings are not coplanar, a statistical calculation (Weatherburn, 1947) giving a value of $\chi^2=47.1$ for the deviations of the atoms of the outer ring from the mean plane through the centre ring. These deviations are highly significant, although the magnitude of the angular distortion is small, amounting to only 24' for the angle between the normals to the centre and outer rings.

This distortion is not due to any steric interaction within the molecule, and appears to result from intermolecular forces. The distances of closest approach (Fig. 6) are between the carbon and hydrogen atoms of the central molecule and the hydrogen and carbon atoms respectively of the neighbouring molecules.

For the calculation of bond lengths and angles the coordinates of Table 8 must be corrected for the rota-

tional oscillations of the molecule which cause the maxima of the atomic peaks to be moved towards the centre of rotation. Since the molecule lies very nearly in the plane $Z=0$, only the X and Y coordinates are affected.

Correction formulae for simple harmonic motion have been devised by Cruickshank (1961), and these were used to calculate the corrections given in Table 9. The effect of the probable anharmonicity on the magnitudes of the corrections was estimated, and was found to be much less than the standard deviations. It was assumed in the calculations that the hydrogen atoms have the same librations as the rings to which they are attached. Although this may not be strictly true it should be a reasonable approximation, and any errors resulting are also considerably less than the e.s.d.'s. Table 10 shows the carbon-carbon bond lengths calculated from the coordinates of sets I and II, and carbon-hydrogen lengths calculated using the carbon coordinates from the refinement of the set II data and the neutron hydrogen positions. The r.m.s. deviation between the bond lengths from the two sets of X-ray data is approximately equal to the standard deviation, σ , and no individual discrepancy exceeds 2σ . Since the halves of the molecule on either side of the L axis are chemically equivalent one expects equality between corresponding values. Again there is close agreement within the limits set by the standard deviations. The mean bond-lengths for the chemically equivalent pairs are given in Fig. 7, with appropriately reduced standard deviations. The bond angles, treated in a similar manner, are given in Table 11 and Fig. 7.

The results obtained for the carbon skeleton are similar in many respects to those observed in biphenyl by Robertson (1961). The C-C bonds of the benzene

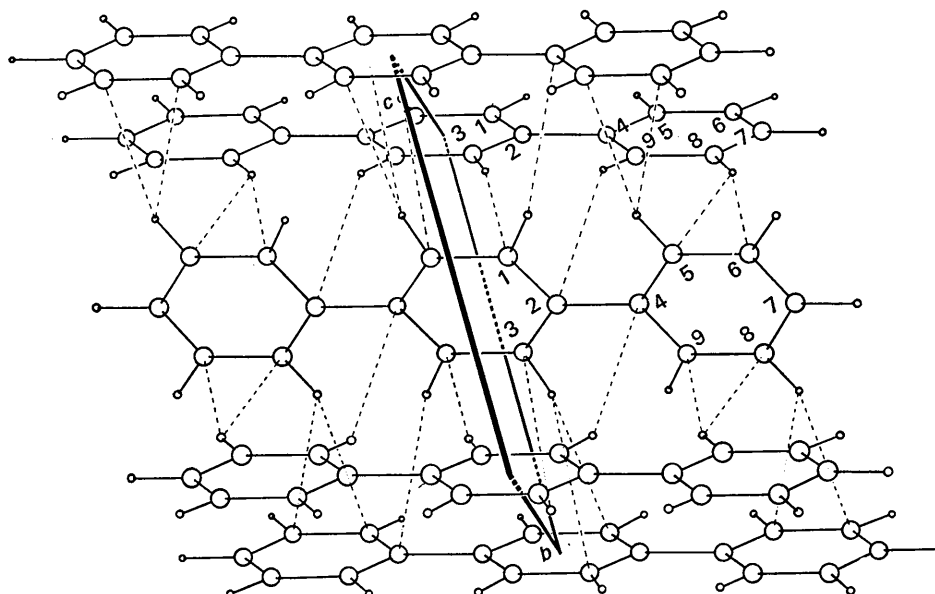


Fig. 6. Intermolecular contacts less than 3.0 Å. The contacts are indicated by dashed lines.

Table 9. Corrections to atomic positions due to libration in Å

	ΔX	ΔY
C(1)	0.008	0.013
C(2)	0.001	0.000
C(3)	0.008	-0.013
C(4)	0.002	-0.000
C(5)	0.003	0.001
C(6)	0.003	0.001
C(7)	0.003	0.000
C(8)	0.003	-0.001
C(9)	0.003	-0.001
H(1)	0.001	0.028
H(3)	0.001	-0.028
H(5)	0.003	0.015
H(6)	0.004	0.014
H(7)	0.006	-0.001
H(8)	0.004	-0.014
H(9)	0.003	-0.015

rings which run parallel to the long axis of the molecule and the C(4)–C(5) bond do not differ greatly in length from the carbon–carbon bond length of 1.395 Å in benzene. The C(1)–C(2) and C(6)–C(7) bonds are shorter, which causes appreciable distortion in the rings. The bond C(2)–C(4) has a length of 1.496 ± 4 Å, which is in close agreement with the central bond of biphenyl (1.497 ± 3).

The explanation of these variations of bond lengths simply in terms of the degree of hybridization of the end carbon atoms seems rather difficult, for while the atoms C(2), C(4) and C(1), C(5) have the same immediate environment the bond lengths C(1)–C(2) and C(4)–C(5) differ considerably. This is in direct contrast with the theory that the lengths should be simply dependent on the bond environment (Stoicheff, 1962). This would seem to indicate that the effects of conjugation and hyperconjugation, in this case at any rate, are far from negligible. A feature of the analysis which is rather puzzling is the marked shortening of the C(6)–C(7) bond. One can explain the bond length chan-

ges in the remainder of the molecule, at least in general terms, by the π -electron redistribution associated with the bonding of the three rings, but it is difficult to see why this bond should be affected so strongly.

A further puzzling feature of the structure is the shortening of the average C–C bond length within the rings (1.388 Å) compared with the value of 1.395 Å generally accepted for benzene. A similar situation exists in the biphenyl structure (Robertson, 1961). It is difficult to explain such a large change on purely chemical grounds, which suggests that there may be a systematic error in the bond length determination procedure. O'Connell, Rae & Maslen (1965) have deduced that the asymmetry in the bonding electron distribution about an aromatic carbon atom with a hydrogen substituent results in shifts of the carbon atom position in an X-ray analysis away from its true position. The line of displacement is in the opposite direction to the C–H vector. This is accompanied by an increase in the calculated thermal vibration perpendicular to the C–H bond but in the plane of the ring, coupled with a reduction in the density due to the bonding electrons in the adjacent C–C bonds. The final difference synthesis [Fig. 2(b)] supports this hypothesis. The largest peak is on the bond between the C(2) and C(4) atoms, which have no hydrogen substituents, while those on the other C–C bonds are all considerably lower. The latter are rather dumb-bell shaped, being extended above and below the planes of the rings, as predicted by O'Connell, Rae & Maslen. The situation in orthanilic acid (Hall & Maslen, 1967) is very similar, and in the final difference synthesis for biphenyl (Robertson, 1966) the largest peak is also on the bond between the carbon atoms with no hydrogen substituents. The magnitude of the carbon shift has been estimated by O'Connell, Rae & Maslen to be 0.008 Å, but this must be regarded as only approximate, in view of the limitations of the wave functions involved. Nevertheless it is interesting to note that a correction of this magnitude would alter

Table 10. Bond lengths in Å corrected for molecular librations*

Bond	Set I	Set II	Weighted	
			mean	σ
C(1)–C(2)	1.375	1.377	1.376	0.006
C(2)–C(3)	1.383	1.371	1.377	0.006
C(3)–C'(1)	1.411	1.402	1.407	0.006
C(2)–C(4)	1.495	1.497	1.496	0.004
C(4)–C(5)	1.392	1.395	1.394	0.005
C(5)–C(6)	1.393	1.400	1.397	0.005
C(6)–C(7)	1.371	1.375	1.373	0.006
C(7)–C(8)	1.390	1.375	1.383	0.006
C(8)–C(9)	1.400	1.384	1.392	0.005
C(9)–C(4)	1.391	1.388	1.390	0.005
C(1)–H(1)			1.09	0.08
C(3)–H(3)			1.11	0.07
C(5)–H(5)			1.08	0.05
C(6)–H(6)			1.09	0.08
C(7)–H(7)			1.12	0.02
C(8)–H(8)			1.05	0.08
C(9)–H(9)			1.02	0.09

* Atoms at position $\bar{x}, \bar{y}, \bar{z}$ are denoted prime.

the mean length to 1.393 Å, which is close to the standard value. The shortening of C(6)–C(7), which is difficult to explain chemically, would also be somewhat reduced.

The hydrogen positions from the analysis (Fig. 8) show displacements relative to the undistorted positions, calculated assuming a C–H bond length of 1.08 Å, with the bonds directed radially from the ring centre. The displacements are listed in Table 12.

The only values greater than 2σ are the displacements of the *ortho* hydrogen atoms H(1), H(3) and H(9), and for H(7) in the direction of the *L* axis. The significance of the last of these would be reduced a little by correcting for the bonding asymmetry of C(7), and it is unlikely that it represents a real deviation. The direc-

tions of the displacements of the *ortho* hydrogen atoms, on the other hand, are such as to relieve steric strain. The difference in magnitude for the chemically equivalent pairs is in accordance with what is expected from the packing. The atoms H(1) and H(5) are approached more closely by carbon atoms belonging to neighbouring molecules than are H(3) and H(9). The resulting interaction seems to act in opposition to the steric forces and to check the displacements. The distances between H(1), H(5) and H(3), H(9) are 1.97 ± 0.05 and 2.11 ± 0.06 Å respectively. The weighted average value of 2.02 ± 0.04 Å is significantly less than 2.34 Å, which is twice the van der Waals radius for hydrogen in the 'hard sphere' approximation (Kitajgorodskii, 1958). Thus, although there is some steric displacement, the

Table 11. Bond angles in degrees*

	Set I	Set II	Weighted mean	σ
C(3')–C(1)–C(2)	121.4	121.5	121.5	0.3
C(1)–C(2)–C(3)	117.3	116.6	116.9	0.3
C(1)–C(2)–C(4)	121.1	122.1	121.6	0.3
C(3)–C(2)–C(4)	121.6	121.3	121.5	0.2
C(2)–C(3)–C'(1)	122.3	121.9	122.1	0.3
C(2)–C(4)–C(5)	121.4	120.6	121.0	0.2
C(2)–C(4)–C(9)	120.6	121.6	121.1	0.3
C(9)–C(4)–C(5)	118.1	117.8	117.9	0.3
C(4)–C(5)–C(6)	121.0	120.7	120.9	0.3
C(5)–C(6)–C(7)	120.3	119.9	120.1	0.3
C(6)–C(7)–C(8)	120.1	119.9	120.0	0.3
C(7)–C(8)–C(9)	119.3	120.3	119.8	0.3
C(8)–C(9)–C(4)	121.2	121.3	121.3	0.3
C(3')–C(1)–H(1)			114.8	2.0
C(2)–C(1)–H(1)			123.7	2.0
C(1')–C(3)–H(3)			110.1	1.5
C(2)–C(3)–H(3)			128.0	1.5
C(4)–C(5)–H(5)			120.6	1.6
C(6)–C(5)–H(5)			118.6	1.6
C(5)–C(6)–H(6)			122.3	2.7
C(7)–C(6)–H(6)			117.8	2.7
C(6)–C(7)–H(7)			122.2	5.7
C(8)–C(7)–H(7)			117.9	5.7
C(7)–C(8)–H(8)			119.5	2.4
C(9)–C(8)–H(8)			120.1	2.4
C(8)–C(9)–H(9)			115.6	2.3
C(4)–C(9)–H(9)			123.0	2.3

* Atoms at position $\bar{x}, \bar{y}, \bar{z}$ are denoted prime.

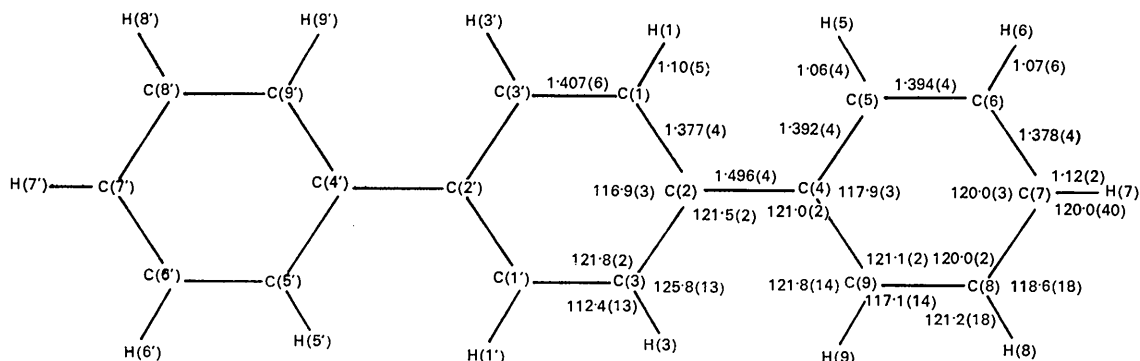


Fig. 7. Mean bond-lengths in Å and angles in degrees. E.s.d.'s in the last decimal place are given in parentheses.

Table 12. Displacement in Å of hydrogen atoms from the undistorted positions referred to molecular axes

The undistorted positions are calculated assuming C-H bond lengths of 1.08 Å with the bonds directed radially from the ring centres.

	<i>X</i>	$\sigma(X)$	<i>Y</i>	$\sigma(Y)$	<i>Z</i>	$\sigma(Z)$
H(1)	-0.097	0.036	0.080	0.090	0.027	0.069
H(3)	-0.158	0.030	0.125	0.076	0.008	0.058
H(5)	0.026	0.030	0.016	0.056	0.024	0.047
H(6)	0.037	0.036	-0.010	0.094	0.046	0.071
H(7)	0.040	0.016	-0.053	0.121	0.066	0.081
H(8)	-0.020	0.036	0.026	0.086	0.044	0.065
H(9)	0.114	0.052	0.014	0.093	0.004	0.069

atoms are 'softer' than has often been supposed, in accordance with the findings of Haigh (1963). There are no significant deviations of the hydrogen atoms from the mean molecular plane.

The results of the analysis appear to establish that there is appreciable steric strain between the *ortho* hydrogen atoms, and it seems reasonable to assume that a similar situation holds in biphenyl. A two-dimensional neutron analysis which has been carried out is consistent with this conclusion (Rietveld, 1963) but its accuracy is not adequate to decide the matter conclusively. Similar conclusions based on other evidence have been drawn by Krebs, Sandroni & Zerbi (1964).

While the preparation of this manuscript was in progress reports of another refinement of this structure (Dejace, 1964, 1966) were received. This refinement was carried out using one set of partial three-dimensional X-ray data. The results appear to be consistent with those from the present analysis.

The authors wish to acknowledge the extensive assistance given by Mr T. M. Sabine in the collection of the neutron diffraction data. Thanks are also due to Drs J. S. Rollett, H. C. Freeman, G. Mair and F. R. Ahmed for the use of their computer programs and to Drs F. M. Lovell and K. J. Watson who supervised a number of the calculations.

Financial assistance was provided by the Australian Institute of Nuclear Science and Engineering and the University of Western Australia.

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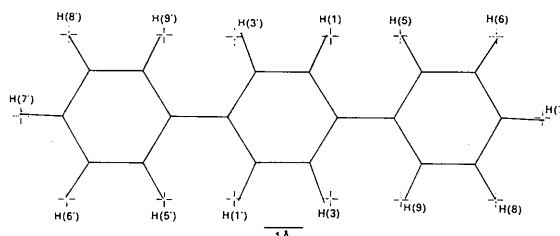


Fig. 8. Hydrogen positions for *p*-terphenyl. The crosses indicate the undistorted positions.

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