

## The Crystal Structure of a Modification of Hexaphenylbenzene

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The structure of one of the polymorphic forms of hexaphenylbenzene,  $[C_6H_5]_6$ , has been determined by single-crystal X-ray diffraction work. The crystals are orthorhombic, space group  $Pna2_1$  with  $a=11.080$ ,  $b=21.777$ ,  $c=12.553$  Å. The orientation of the molecule in the asymmetric unit was obtained from the Patterson function, the position by trial and error. The parameters were refined by a block-diagonal least-squares method using 1404 observed intensities recorded with a linear diffractometer. No hydrogen atoms were included in the calculations. The final  $R$  value was 0.068. The non-centrosymmetric molecule adopts a propeller configuration with approximate sixfold symmetry. The peripheral rings are not perpendicular to the central ring but are twisted about  $25^\circ$  from this position. Bond distances and angles in the benzene rings are normal; the C-C bridge distances vary between 1.47 and 1.53 Å. Standard deviations are 0.013 Å and  $0.9^\circ$  for bond lengths and angles respectively. All benzene rings are essentially planar. The molecule is highly distorted as the result of out-of-plane bending of the exocyclic bonds. The molecules are packed in pseudo-hexagonal layers parallel to the  $bc$  plane.

### Introduction

In compounds such as hexaphenylbenzene the known tendency of the individual aromatic nuclei to adopt a coplanar configuration is counteracted by the steric requirements of the molecule. In fact one expects the atoms in the substituted phenyl groups to repel each other. Repulsion forces are present even in simple compounds such as biphenyl (Hargreaves & Rizvi, 1962; Trotter, 1961) and 1,4-diphenylbenzene (Clews, Maslen, Rietveld & Sabine, 1961) and bring about straining of the normal valency angles (C-C-H) in the plane of the latter molecule.

In 1,3,5-triphenylbenzene (Farg, 1954) the interaction of each peripheral ring with the central ring is comparable to the effect in biphenyl. Nevertheless the molecule adopts a configuration in which the phenyl groups are rotated by  $+34^\circ$ ,  $-27^\circ$  and  $+24^\circ$ , out of the plane of the benzene ring. The *meta* phenyl groups

do not interfere with each other to any appreciable extent (shortest H-H distance in a planar molecule is 3.3 Å), although the *ortho* hydrogen atoms in neighbouring rings do. The molecule has no symmetry element.

Previous results for  $C_6Ph_6$  and for other phenyl-substituted benzene derivatives, in which twisting effects occur, are given in Table 1. The hexasubstituted benzene derivative  $C_6(NO_2)_6$  (Akopyan, Struchkov & Dashevskii, 1966) adopts a propeller configuration with the  $NO_2$  groups twisted at about  $53^\circ$  around the C-N bonds, with non-bonded distances approaching the sum of the van der Waals radii. Partially owing to the hydrogen bonding the differences in the tilts of the carboxyl groups to the aromatic ring in benzenehexa-carboxylic acid (Darlow, 1961) are quite large.

The molecular geometry of  $C_6Ph_6$  has been the subject of some speculations in the past. According to Almenningen, Bastiansen & Skancke (1958), the limits

Table 1. *Interplanar angles in polyphenylbenzene derivatives*

	State†	θ denotes twist around the exocyclic bonds.		
		θ	Technique‡	Reference
Biphenyl	C	0°	X	Hargreaves & Rizvi (1962), Trotter (1961), Robertson (1961)
	V	42°	E	Almenningen & Bastiansen (1958)
	V	42°	AS	Suzuki (1949)
1,4-Diphenylbenzene	S	22°	AS	Suzuki (1949)
	C	1.5°	X, N	Clews, Maslen, Rietveld & Sabine (1961)
1,3,5-Triphenylbenzene	C	$+34^\circ, -27^\circ, +24^\circ$	X	Farg (1954)
	V	46° (statist.)	E	Bastiansen (1952)
1,2-Diphenylbenzene	C	$+ \sim 50^\circ, + \sim 50^\circ$	X+DA	Clews & Lonsdale (1937)
	V	$90^\circ \pm 15^\circ*$	E	Karle & Brockway (1944)
Hexaphenylbenzene	C	$+62^\circ$ to $+71^\circ$	X	Present study
	V	$90^\circ \pm 10^\circ*$	E	Almenningen, Bastiansen & Skancke (1958)

\* Denotes restricted oscillation.

† C, crystal; V, vapour; S, solution.

‡ X, X-ray diffraction; E, electron diffraction; N, neutron diffraction; AS, absorption spectrum; DA, diamagnetic anisotropy.

set by the non-bonded interactions in  $C_6Ph_6$  on the rotations around the pivot bonds are such that if a 'propeller' model is assumed serious steric conflicts arise at a twist of approximately  $40^\circ$ . Statistically the probability for such a symmetrical  $40^\circ$  propeller is rather low. On the other hand, if neighbouring peripheral rings are rotated towards each other (antipropeller model) H-H interactions impede deviations of more than  $10^\circ$  from the orthogonal conformation. The actual molecular configuration in the crystalline state will be determined by these non-bonded repulsions, to some extent by van der Waals forces and practically not at all by resonance requirements. The conjugation effect on the inter-ring bonds must be small. The single-crystal X-ray analysis was carried out in order to study the arrangement of the aromatic ring systems and type of bonding between the aromatic groups in this heavily substituted benzene derivative.

### Experimental

Although the compound is highly insoluble in most organic solvents crystals suitable for intensity measurements could be grown from  $CH_2Br_2$  and  $CH_2Cl_2$ . Crystalline  $C_6Ph_6$  is polymorphic; the two observed crystalline forms were found in the same batch. One is the same as that observed previously (Daly, 1967) from recrystallization in  $C_6H_5NO_2$ . The present pyramidal crystals are of much better quality and the cell dimensions have been redetermined from precession photographs, recorded with Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). These are  $a = 12.144$ ,  $b = 11.771$ ,  $c = 20.824 \text{ \AA}$ ,  $\sigma(a) = 0.009$ ,  $\sigma(b) = 0.007$ ,  $\sigma(c) = 0.010 \text{ \AA}$ ; space group orthorhombic:  $Pna2_1$  or  $Pnam$ . This modification was called hexaphenylbenzene *A*. The crystallographic constants of the second form, called hexaphenylbenzene *B*, which is also orthorhombic, are given in Table 2. The results of the analysis of the latter crystal modification are the subject of the present paper.

Table 2. Crystallographic and experimental data of hexaphenylbenzene, form *B*

$C_6(C_6H_5)_6$ ,  $M = 534.7$ , m.p.  $448-50^\circ$

$a = 11.080 \text{ \AA}$	$\sigma(a) = 0.008 \text{ \AA}$
$b = 21.777$	$\sigma(b) = 0.010$
$c = 12.553$	$\sigma(c) = 0.008$

Systematic absences:  $0kl$  for  $k+l=2n+1$ ,  $h0l$  for  $h=2n+1$ . Space group  $Pna2_1$  or  $Pnam$  (the former proved correct by the present analysis).

$V = 3028.83 \text{ \AA}^3$ ;  $d(\text{calc}) (n=4) = 1.172 \text{ g.cm}^{-3}$ .  
 $F(000) = 1128$   
 $\mu(\text{Mo } K\alpha) = 0.72 \text{ cm}^{-1}$   
 Crystal faces:  $\{110\}$ .

	Oscillation angle
$hk0-hk3$	$2.5^\circ$
$hk4-hk10$	3
$hk11-hk13$	4

A set of intensities (except  $00l$ ) were recorded with Mo  $K\alpha$  radiation on a Hilger and Watts Automatic Diffractometer (Arndt & Phillips, 1961), equipped with  $SrCO_3/ZrO_2$  balanced filters and a scintillation counter with pulse height discrimination. The data were collected with a needle-shaped crystal of approximate cross-section  $0.3 \times 0.45 \text{ mm}$  up to  $\theta = 23^\circ$ , as reciprocal lattice sections perpendicular to  $[001]$ . Only the asymmetric part of the reciprocal space was covered, although each reflexion was measured twice with each filter in position. A one-minute oscillation-motor was used. The average  $\Delta F_o$  was estimated as 2%. Scale factors between layers recorded with different oscillation angle (Table 2) were determined from carefully selected reflexions of medium intensity. A number of hand-measurements were carried out in the unstable ranges of the instrument. The intensities varied from 1 to 135,000. The background counts were rather high and were included in the normal manner. 1405 intensities were accepted as having a significant and accurate value and the analysis was carried out with them.

The reflexion data were corrected for Lorentz-polarization factor, but no absorption correction was needed. An approximate absolute scale factor and overall temperature factor were obtained by Wilson's (1942) method.

The results of the  $N(z)$  test (Howells, Phillips & Rogers, 1950) fitted reasonably well the error function expected from a non-centric distribution of atoms. The assumed class therefore is orthorhombic hemihedral ( $mm2$ ); the space group  $Pna2_1$  was accordingly accepted provisionally and refinement in it was successful.

### Structure determination and refinement

The orientation of the molecule rapidly followed from the intramolecular vectors  $P(uvw)$  in a three-dimensional Patterson function, in which the  $F_o^2$  coefficients were multiplied by the sharpening function  $1/|F_o| \{ \sum_i n_i f_i \exp(-B \sin^2\theta/\lambda^2) \}$ . The Harker section

$x, y, \frac{1}{2}$  did not permit rapid location of the position  $x_0, y_0, z_0$  of the centre of the molecule in the unit cell. Coordinate  $y_0$  was subsequently determined by scanning the molecule along  $[010]$  in the non-centric (100) projection, over those positions which give a plausible packing arrangement. The experimentally obtained curve  $R = \frac{\sum |kF_o - |F_o||}{\sum kF_o}$  as  $f(y)$  for  $0kl$  reflexions showed two definite minima near  $y = \frac{1}{8}$  and  $\frac{3}{8}$ , which are related solutions. Better agreement between observed and calculated  $0kl$  was obtained by slightly twisting the substituent phenyl groups around the bridge C-C bonds, in accordance with the observations on a spherical section ( $r = 2.4 \text{ \AA}$ ) around the origin of  $P(uvw)$ . Indications that  $x_0 \approx \frac{1}{4}$  were obtained from the Harker line  $x, \frac{1}{2}, \frac{1}{2}$ .

The  $x_0$  parameter was further improved by repeating the same procedure as above, scanning the molecule

parallel to [100] at one of the  $y_0$  coordinates specified. Further refinement in the centric [001] projection was not possible. From the  $P(u, v)$  map an acceptable set of sixfold C-C intermolecular vectors for all of the benzene rings was now found, which gave a sufficient interpretation of the Harker section  $x, y, \frac{1}{2}$ . The deviation from an entirely orthogonal molecular model could not be determined accurately by Patterson methods and the twists were arbitrarily assumed to be through the same angle ( $10^\circ$ ) for all phenyl groups ('propeller' model). For two such models, with opposite rotation sense of the propeller,  $F(hkl)$  were calculated for reflexions with  $\sin \theta/\lambda < 0.30 \text{ \AA}^{-1}$ . The correspondence between  $F_{\text{obs}}$  and  $F_{\text{calc}}$  gave a possibility for a choice as the  $R$  values were 0.33 and 0.43 respectively. At this stage a block-diagonal least-squares refinement was attempted with about 400 low-order planes, using an overall temperature factor and Cruickshank's weighting scheme. This procedure failed to work and improvement was only obtained after rejection of a number of weak planes and assignment of constant weights to all but the very strong reflexions, which were downweighted with respect to the others. Further refinement did not present additional problems, although the convergence was rather slow.

After a decrease in  $R$  to 0.12 thermal anisotropy was introduced and Cruickshank's (1961) weighting scheme  $w = 1/(6.0 + |F_o| + 0.05|F_o^2|)$  was again applied. The weighting parameters were so chosen as to down-weight the weak and strong reflexions. In view of the available computing facilities no hydrogen atoms were introduced. The reflexion 200 was removed from the calculation as it probably has a high hydrogen contribution. A comparison of  $kF_o$  and  $F_c$  during the final stages did not clearly indicate extinction effects, and accordingly no corrections were made.

Refinement was terminated when no appreciable improvement in  $R' [= \Sigma w|d|^2 / \Sigma wF_o^2]$  was made, even though the maximum drift was still about 0.75 of the corresponding standard deviation. The latter value could not be reduced; the shifts were random. At this stage  $R' = 0.007$  and  $R = 0.068$ . During the calculations no contributions to the least-squares totals were made by planes with  $3|F_c| \leq F_o$ ; in the last cycle 4 planes were thus rejected.

Analyses of  $\Sigma w d^2/n$  to  $|F_o|$  and  $\sin^2\theta/\lambda^2$  showed the weighting scheme to be satisfactory.

The atomic scattering factor was obtained from *International Tables for X-ray Crystallography* (1962).

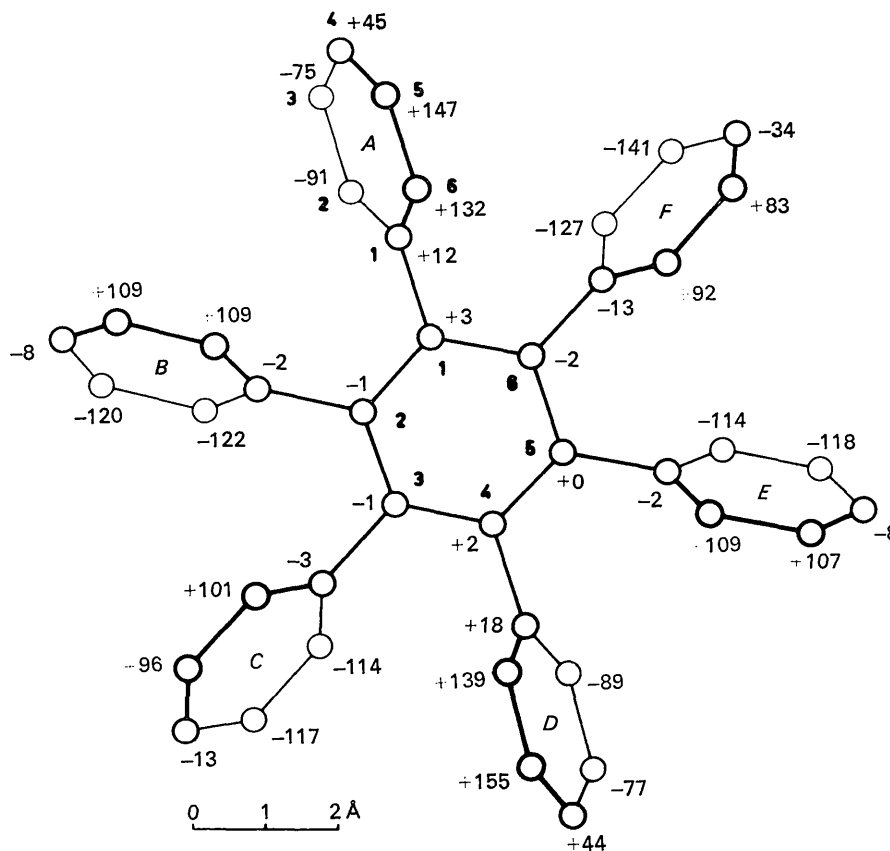


Fig. 1. The molecule projected onto the least-squares plane through the central benzene ring and the labelling of the atoms. The numbers adjacent to the atoms give the height in 0.01 Å above the plane.

## Results

The labelling of the atoms is shown in Fig. 1. Table 3 lists the coordinates and the e.s.d. (in Å) of all atoms referred to the axes  $a, b, c$  of the orthogonal cell. Standard deviations of the positional parameters were estimated from the block-diagonal approximation in the usual way. In Table 4 the thermal parameters and their e.s.d. have been listed.

Table 3. Final atomic coordinates (Å)

Standard deviations are given as units in the last place.

	$x$	$y$	$z$
C(1)	2.533 (7)	8.451 (7)	1.323 (8)
C(2)	2.603 (7)	9.383 (8)	0.277 (8)
C(3)	2.495 (7)	8.942 (8)	-1.047 (8)
C(4)	2.306 (8)	7.604 (8)	-1.325 (8)
C(5)	2.176 (8)	6.655 (8)	-0.306 (8)
C(6)	2.268 (7)	7.097 (8)	1.052 (8)
C(1A)	2.742 (8)	8.889 (7)	2.751 (8)
C(2A)	1.838 (9)	9.687 (9)	3.412 (10)
C(3A)	2.102 (10)	10.063 (10)	4.750 (10)
C(4A)	3.269 (10)	9.617 (9)	5.382 (9)
C(5A)	4.161 (9)	8.836 (9)	4.704 (9)
C(6A)	3.904 (8)	8.452 (8)	3.388 (9)
C(1B)	2.823 (9)	10.819 (7)	0.588 (8)
C(2B)	1.742 (12)	11.717 (10)	0.319 (12)
C(3B)	1.984 (15)	13.120 (11)	0.677 (14)
C(4B)	3.193 (17)	13.492 (12)	1.262 (14)
C(5B)	4.248 (16)	12.573 (13)	1.478 (12)
C(6B)	4.027 (10)	11.235 (9)	1.152 (9)
C(1C)	2.584 (7)	9.935 (7)	-2.184 (8)
C(2C)	1.474 (8)	10.144 (8)	-3.015 (8)
C(3C)	1.542 (10)	11.054 (9)	-4.049 (9)
C(4C)	2.705 (10)	11.819 (9)	-4.250 (9)
C(5C)	3.808 (10)	11.627 (9)	-3.407 (10)
C(6C)	3.748 (9)	10.684 (8)	-2.375 (9)
C(1D)	2.350 (9)	7.138 (8)	-2.783 (8)
C(2D)	1.187 (10)	6.717 (9)	-3.412 (10)
C(3D)	1.208 (13)	6.361 (11)	-4.771 (10)
C(4D)	2.425 (13)	6.464 (10)	-5.456 (10)
C(5D)	3.635 (12)	6.853 (9)	-4.804 (10)
C(6D)	3.568 (10)	7.200 (9)	-3.465 (9)
C(1E)	1.930 (8)	5.231 (8)	-0.591 (8)
C(2E)	0.714 (8)	4.639 (9)	-0.225 (9)
C(3E)	0.487 (10)	3.295 (10)	-0.489 (11)
C(4E)	1.437 (11)	2.528 (10)	-1.125 (11)
C(5E)	2.671 (11)	3.088 (9)	-1.480 (10)
C(6E)	2.916 (9)	4.455 (9)	-1.215 (9)
C(1F)	2.046 (8)	6.128 (8)	2.152 (8)
C(2F)	0.940 (9)	6.275 (9)	2.990 (8)
C(3F)	0.692 (11)	5.368 (11)	4.018 (9)
C(4F)	1.616 (11)	4.307 (10)	4.243 (10)
C(5F)	2.754 (11)	4.191 (9)	3.427 (11)
C(6F)	2.951 (10)	5.081 (9)	2.373 (9)

Instead of a full list of  $F_{\text{obs}}$  and  $F_{\text{calc}}$  (which is held at this Institute and is available on request) Table 5 examines the structure factors as a function of the layer index  $l$ . A similar analysis in terms of the magnitudes of  $F_{\text{obs}}$  (Table 5) shows poorest agreement be-

tween experimental and calculated values for the weakest reflexions. The  $R$  value in terms of the parity of the indices (Table 6) reveals no irregularities.

The thermal parameters for the central ring atoms are nearly isotropic and significantly less in magnitude than those of the remaining carbon atoms. In the peripheral rings the motion of the atoms is markedly anisotropic; the smallest thermal movement is connected with the atoms directly bonded to the central ring, C(1), and reasonably enough gradually increasing values are found for the C(2,6), C(3,5) and C(4) atoms.

A very high thermal parameter  $U_{11}$  is found for C(3B,4B,5B). This may be real and might be explained by residual errors in the observed intensities or by assuming slight disorder. This may originate from distortions produced by steric interaction. The direction of maximum vibration is approximately perpendicular to the central ring. The atoms of the outer benzene rings in the molecule have a considerable freedom of movement. No corrections have been made for apparent atomic displacements caused by rotational oscillations of the phenyl rings (Cruickshank, 1956).

## Discussion

## Bond lengths and angles

The bond data and the standard deviations are listed in Table 7. Except for C(2B)-C(3B) (1.468 Å) and the angle C(1B)C(2B)C(3B) (115.4°) there are no significant deviations from the values for a regular hexagon. As noticed above, the thermal parameters for the atoms of ring B are very high.

The observation (see below) that there is no conjugation between the aromatic rings suggests that all bond lengths within the rings should be about 1.40 Å, as in benzene. There are no systematic differences between such bonds as C(2A)-C(3A) and C(3A)-C(4A).

The arithmetic mean value of the chemically equivalent bonds and angles in the aromatic rings is 1.401 Å and 120.0° respectively, or 1.399 Å and 120.1°, when the above mentioned bond length and angle are omitted. Standard deviations of the mean of the latter quantities are 0.002 Å and 0.14°. The mean values agree well with the standard values.

The C-C bonds linking benzene and phenyl rings in the molecule vary between rather large limits: 1.473-1.531 Å. The differences are beyond the limits of experimental error. There is no straightforward relation between the lengthening of the benzene-phenyl bonds and the angle of twist. A discussion of the distance between trigonally linked carbon atoms suggests that the ( $sp^2$ ) single bond length is about 1.477 Å. (Dewar & Schmeising, 1959; Cruickshank & Sparks, 1960.) The observed distances exceed this value by up to 0.054 Å ( $\sigma=0.011$  Å) or  $5\sigma$ , which is significant. This indicates that the separation between the atoms linking the aromatic rings is at least partly beyond the value for an undistorted molecule and suggests absence of  $\pi$ -bonding.

Additional support for this conclusion comes from the fact that any correction for rotational oscillations will generally still *increase* the bond lengths. Moreover, as the bonds exist between well-defined benzene nuclei, it is not possible to shorten the benzene-phenyl distances without unduly affecting bond lengths and/or angles in the rings. According to the calculations by Guy (1949) the resonance energy reaches zero at angles of twist between 45° and 68°. The observed interplanar angles (see below) therefore indicate almost complete absence of electronic interaction.

If we ignore contacts within a phenyl-group and those which subtend a bond angle then there are many non-bonded intramolecular contacts of less than 3.6 Å, as indicated in Table 8, where the shortest set is listed.

The assumed hydrogen positions (C-H, 1.0 Å;  $\angle$ C-C-H, 120°) were included in the calculations. The values derived with those positions probably represent minimum values, as it is not impossible that several hydrogen atoms are distorted from their normal positions because of steric interactions in the molecule. The labelling of the hydrogen atoms is the same as for the carbon atoms they are attached to. There exist interesting correlations with the distortions found in the molecule. The strongest C-C and C-H repulsions are found for atoms 2 and 6 of the rings with the largest deviation from orthogonality with respect to the central ring (ring C). Where the largest difference in rotation angle exists between two neighbouring substituent phenyl groups (C and D) one finds the shortest H(2)-

Table 4. *Thermal parameters (Å<sup>2</sup>) in the form*

$$\exp [-2\pi^2 (h^2a^*2U_{11} + k^2b^*2U_{22} + l^2c^*2U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})]$$

Standard deviations are appended in brackets as units in the last place.

	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	0.041 (4)	0.041 (4)	0.041 (4)	0.011 (7)	0.002 (7)	-0.007 (7)
C(2)	0.042 (4)	0.049 (4)	0.044 (4)	0.009 (8)	-0.008 (7)	-0.007 (8)
C(3)	0.036 (4)	0.043 (4)	0.056 (5)	0.005 (7)	-0.003 (8)	-0.020 (8)
C(4)	0.045 (5)	0.053 (5)	0.044 (4)	-0.014 (8)	-0.014 (8)	0.006 (9)
C(5)	0.046 (5)	0.049 (5)	0.048 (5)	-0.003 (8)	0.015 (8)	0.006 (8)
C(6)	0.042 (5)	0.052 (4)	0.038 (4)	-0.003 (8)	-0.011 (7)	-0.013 (8)
C(1A)	0.047 (5)	0.038 (4)	0.041 (4)	-0.008 (8)	0.003 (7)	-0.008 (7)
C(2A)	0.068 (6)	0.060 (6)	0.057 (5)	0.010 (10)	-0.010 (10)	0.008 (10)
C(3A)	0.075 (6)	0.069 (6)	0.058 (6)	0.010 (11)	-0.018 (10)	0.036 (10)
C(4A)	0.081 (6)	0.061 (6)	0.046 (5)	0.009 (10)	0.001 (9)	0.007 (9)
C(5A)	0.070 (6)	0.062 (6)	0.051 (5)	-0.004 (10)	-0.014 (9)	-0.017 (10)
C(6A)	0.053 (5)	0.049 (5)	0.047 (5)	-0.001 (8)	-0.003 (8)	0.009 (9)
C(1B)	0.078 (6)	0.034 (4)	0.038 (4)	0.001 (9)	0.001 (7)	0.025 (8)
C(2B)	0.113 (8)	0.056 (6)	0.080 (7)	0.064 (12)	0.027 (11)	0.066 (13)
C(3B)	0.180 (13)	0.061 (7)	0.095 (9)	0.058 (16)	0.044 (13)	0.099 (18)
C(4B)	0.229 (16)	0.063 (7)	0.087 (8)	-0.049 (18)	0.007 (14)	0.096 (20)
C(5B)	0.175 (13)	0.096 (9)	0.060 (7)	-0.090 (18)	0.003 (13)	0.013 (16)
C(6B)	0.105 (8)	0.053 (5)	0.046 (5)	-0.088 (11)	0.000 (9)	-0.035 (10)
C(1C)	0.043 (4)	0.033 (4)	0.047 (4)	0.000 (7)	-0.016 (7)	0.005 (8)
C(2C)	0.049 (5)	0.058 (5)	0.050 (5)	0.027 (9)	0.008 (9)	0.017 (9)
C(3C)	0.073 (7)	0.069 (6)	0.048 (5)	0.026 (11)	0.038 (9)	0.014 (10)
C(4C)	0.088 (7)	0.060 (6)	0.044 (5)	0.040 (11)	0.010 (9)	0.020 (10)
C(5C)	0.068 (6)	0.053 (5)	0.069 (6)	-0.014 (10)	-0.019 (9)	0.051 (10)
C(6C)	0.063 (5)	0.038 (4)	0.061 (5)	-0.007 (8)	0.000 (8)	0.030 (9)
C(1D)	0.070 (6)	0.036 (4)	0.043 (4)	-0.020 (8)	-0.006 (8)	-0.033 (9)
C(2D)	0.080 (7)	0.058 (6)	0.069 (6)	-0.007 (10)	-0.024 (10)	-0.039 (11)
C(3D)	0.134 (10)	0.063 (6)	0.061 (6)	-0.019 (13)	-0.019 (11)	-0.068 (13)
C(4D)	0.142 (10)	0.054 (5)	0.060 (6)	-0.008 (13)	0.005 (10)	-0.052 (14)
C(5D)	0.103 (8)	0.052 (6)	0.054 (5)	0.002 (11)	-0.012 (9)	0.009 (11)
C(6D)	0.070 (6)	0.056 (5)	0.043 (4)	-0.013 (10)	-0.004 (8)	0.007 (9)
C(1E)	0.053 (5)	0.043 (4)	0.042 (4)	-0.015 (8)	0.015 (8)	-0.010 (8)
C(2E)	0.048 (5)	0.057 (6)	0.062 (5)	-0.044 (9)	0.007 (9)	-0.032 (9)
C(3E)	0.081 (7)	0.067 (6)	0.074 (7)	-0.040 (11)	0.018 (11)	-0.066 (12)
C(4E)	0.101 (8)	0.061 (6)	0.071 (7)	-0.003 (12)	0.003 (10)	-0.049 (12)
C(5E)	0.100 (7)	0.050 (5)	0.066 (6)	-0.001 (11)	-0.019 (10)	-0.017 (12)
C(6E)	0.077 (6)	0.056 (5)	0.042 (5)	-0.004 (10)	-0.004 (8)	-0.022 (9)
C(1F)	0.056 (5)	0.044 (5)	0.039 (4)	-0.027 (8)	0.019 (8)	-0.011 (8)
C(2F)	0.056 (5)	0.060 (6)	0.050 (5)	-0.042 (9)	0.016 (9)	0.002 (9)
C(3F)	0.085 (7)	0.089 (7)	0.051 (5)	-0.078 (12)	-0.009 (11)	-0.019 (10)
C(4F)	0.102 (8)	0.077 (7)	0.055 (6)	-0.078 (12)	0.022 (10)	-0.056 (12)
C(5F)	0.094 (7)	0.054 (6)	0.071 (6)	-0.031 (11)	0.008 (10)	-0.045 (12)
C(6F)	0.085 (6)	0.056 (6)	0.049 (5)	-0.022 (11)	0.021 (9)	-0.046 (11)

Table 5. Analysis of  $F_{\text{obs}}$  and  $F_{\text{calc}}$  as a function of (a) the index of the layer and (b) the magnitude of the observed structure factors

All figures are on absolute scale.

(a)					
$l$	$\Sigma  F_o $	$\Sigma  F_c $	$\Sigma  \Delta $	$N$	$R$
0	3014.19	3026.94	254.43	131	0.084
1	3553.41	3541.62	245.45	161	0.069
2	3112.72	3087.37	178.69	157	0.057
3	2977.39	2925.60	171.83	138	0.058
4	2346.57	2252.95	206.62	132	0.088
5	2073.22	2043.49	138.95	122	0.067
6	1932.86	1910.86	128.66	121	0.067
7	1571.33	1548.47	94.36	111	0.060
8	1245.42	1253.02	66.38	95	0.053
9	970.09	970.60	55.35	77	0.057
10	883.63	882.62	47.65	70	0.054
11	558.95	554.33	39.80	54	0.071
12	179.73	174.53	17.98	22	0.100
13	101.97	102.66	9.69	13	0.095
All	24521.48	24275.06	1655.84	1404	0.068

(b)					
Range of $ F_o $	$\Sigma  F_o $	$\Sigma  F_c $	$\Sigma  \Delta $	$N$	$R$
0.0–8.0	1277.72	1273.28	149.40	185	0.117
8.0–12.0	4520.83	4434.47	383.14	461	0.085
12.0–16.0	3128.84	3129.98	236.14	226	0.075
16.0–20.0	3238.28	3208.88	193.20	181	0.060
20.0–24.0	2437.76	2428.79	128.63	112	0.053
24.0–28.0	1709.53	1713.89	79.48	66	0.046
28.0–32.0	1462.54	1418.85	95.39	49	0.065
32.0–36.0	574.56	552.09	32.33	17	0.056
36.0–40.0	793.92	764.86	61.08	21	0.077
> 40.0	5377.50	5349.97	297.05	86	0.055

Table 6. Analysis of the  $R$  value as a function of the parity of the indices

	$R$
$h+k+l=2n$	0.067
$h+k+l=2n+1$	0.068
$h+k=2n$	0.067
$h+k=2n+1$	0.069
$k+l=2n$	0.064
$k+l=2n+1$	0.072
$h+l=2n$	0.067
$h+l=2n+1$	0.068
$h=2n$	0.068
$h=2n+1$	0.067
$k=2n$	0.068
$k=2n+1$	0.067
$l=2n$	0.071
$l=2n+1$	0.064
All planes	0.068

H(2) distance (2.97 Å) and consequently the longest H(6)–H(6) (3.29 Å). If we call C(2A)–C(2) and its corresponding H(2A)–C(2) distance a '1–4 contact' we feel that the limiting factors for the twists of the outer rings are the non-bonded '1–4 and 1–5, C–C and C–H contacts' listed, and not the '1–6' distances. The average 1–4 C–C and C–H, 1–5 C–C and C–H contacts are 3.19, 3.09, 3.17 and 3.05 Å respectively, which are to be compared with about 3.4, 3.4, 3.5 and 3.6 Å in an orthogonal model and with 2.8, 2.5, 2.5 and 1.8 Å in a planar configuration.

The distances as determined fall in a fairly narrow range and probably govern the twists around the exo-

cyclic bonds and the deformation of the molecule. For 1,2-diphenylbenzene (Clews & Lonsdale, 1937) a larger deviation from orthogonality has been reported than in  $C_6Ph_6$  (see Table 1), corresponding to shorter non-bonded distances, and increased 1–6 repulsions. In spite of short non-bonded interactions a planar configuration has been found in the solid phase for biphenyl as well as for *p*-diphenylbenzene, with distortion of the *ortho* hydrogen atoms from their normal positions in the last case (Clews *et al.* 1961).

#### Geometry of the molecule

The equations for the mean least-squares planes were calculated in terms of axes coinciding with the original orthorhombic axes (Table 9). The interplanar angles between the substituent rings *A* to *F* and the central ring are 68.8°, 68.5°, 62.0°, 70.7°, 67.3° and 65.9° (all  $\pm 1^\circ$ ) respectively. The individual rings are planar within the limits of error, although it might be significant that the largest deviations are observed for the central ring atoms which have the lowest e.s.d. and temperature factors.

The exocyclic bonds are significantly out of the plane of the central ring (Table 9, Fig. 2) and emphasize the large distortions that do occur in the carbon skeleton. There seems to be no direct relation between the out-of-plane bending of neighbouring bridge C–C bonds and the rotation around them. The distortions in the solid state in comparison with the vapour phase are

Table 7. Bond lengths (Å) and angles (°)

(i) Bond lengths							
Ring:	Central	A	B	C	D	E	F
C(1)–C(2)	1.402	1.376	1.430	1.402	1.387	1.401	1.396
C(2)–C(3)	1.400	1.415	1.468	1.379	1.405	1.388	1.394
C(3)–C(4)	1.380	1.400	1.394	1.406	1.400	1.377	1.425
C(4)–C(5)	1.398	1.366	1.416	1.401	1.428	1.400	1.405
C(5)–C(6)	1.432	1.394	1.394	1.399	1.385	1.414	1.394
C(6)–C(1)	1.407	1.396	1.393	1.398	1.398	1.402	1.401
Mean	<1.403>	<1.391>	<1.416>	<1.398>	<1.400>	<1.397>	<1.402>
Average e.s.d.	0.011	0.013	0.017	0.012	0.014	0.013	0.013
Exocyclic		1.508	1.486	1.512	1.531	1.473	1.482

(ii) Inner bond angles							
Ring:	Central	A	B	C	D	E	F
C(1)–C(2)–C(3)	119.6	119.1	115.4	120.2	120.2	120.1	121.0
C(2)–C(3)–C(4)	120.4	119.8	120.0	120.5	117.9	120.9	119.1
C(3)–C(4)–C(5)	121.6	120.2	122.5	119.4	122.2	120.2	119.7
C(4)–C(5)–C(6)	118.5	120.4	118.0	120.1	118.0	119.4	120.0
C(5)–C(6)–C(1)	119.5	119.9	121.2	119.9	120.2	119.8	120.4
C(6)–C(1)–C(2)	120.3	120.6	122.8	119.9	121.5	119.5	119.7
Mean	<120.0>	<120.0>	<120.0>	<120.0>	<120.0>	<120.0>	<120.0>
Average e.s.d.	0.7	0.8	1.1	0.8	0.9	0.9	0.9

(iii) Outer bond angles			
C(1A)–C(1)–C(6)	119.2	C(1)–C(1A)–C(2A)	122.2
C(1A)–C(1)–C(2)	120.5	C(1)–C(1A)–C(6A)	117.2
C(1B)–C(2)–C(1)	119.5	C(2)–C(1B)–C(2B)	117.1
C(1B)–C(2)–C(3)	120.9	C(2)–C(1B)–C(6B)	120.1
C(1C)–C(3)–C(2)	120.0	C(3)–C(1C)–C(2C)	119.8
C(1C)–C(3)–C(4)	119.6	C(3)–C(1C)–C(6C)	120.3
C(1D)–C(4)–C(3)	118.9	C(4)–C(1D)–C(2D)	120.0
C(1D)–C(4)–C(5)	119.4	C(4)–C(1D)–C(6D)	118.4
C(1E)–C(5)–C(4)	122.1	C(5)–C(1E)–C(2E)	120.2
C(1E)–C(5)–C(6)	119.5	C(5)–C(1E)–C(6E)	120.2
C(1F)–C(6)–C(5)	119.5	C(6)–C(1F)–C(2F)	119.7
C(1F)–C(6)–C(1)	121.0	C(6)–C(1F)–C(6F)	120.6
E.s.d.	0.7		

Table 8. Non-bonded interactions (Å)

C(2A)–C(2)	3.24	C(2B)–C(3)	3.18	C(2C)–C(4)	3.16
C(2A)–C(1B)	3.20	C(2B)–C(1C)	3.19	C(2C)–C(1D)	3.14
C(6A)–C(6)	3.16	C(6B)–C(1)	3.16	C(6C)–C(2)	3.19
C(6A)–C(1F)	3.22	C(6B)–C(1A)	3.12	C(6C)–C(1B)	3.11
C(2D)–C(5)	3.26	C(2E)–C(6)	3.18	C(2F)–C(1)	3.17
C(2D)–C(1E)	3.27	C(2E)–C(1F)	3.11	C(2F)–C(1A)	3.18
C(6D)–C(3)	3.17	C(6E)–C(4)	3.21	C(6F)–C(5)	3.20
C(6D)–C(1C)	3.18	C(6E)–C(1D)	3.16	C(6F)–C(1E)	3.14
H(2A)–C(2)	3.17	H(6B)–C(1)	3.07	H(6C)–C(2)	3.05
H(2A)–C(1B)	3.09	H(6B)–C(1A)	2.98	H(6C)–C(1B)	2.93
H(2A)–C(2B)	3.23	H(6B)–C(6A)	3.07	H(6C)–C(6B)	3.05
H(6A)–C(6)	3.04	H(2B)–C(3)	3.12	H(2C)–C(4)	3.04
H(6A)–C(1F)	3.14	H(2B)–C(1C)	3.09	H(2C)–C(1D)	3.01
H(6A)–C(6F)	3.26	H(2B)–C(2C)	3.24	H(2C)–C(2D)	3.00
H(2D)–C(5)	3.20	H(2E)–C(6)	3.06	H(2F)–C(1)	3.06
H(2D)–C(1E)	3.17	H(2E)–C(1F)	2.95	H(2F)–C(1A)	3.08
H(2D)–C(2E)	3.39	H(2E)–C(2F)	3.11	H(2F)–C(2A)	3.14
H(6D)–C(3)	3.09	H(6E)–C(4)	3.11	H(6F)–C(5)	3.11
H(6D)–C(1C)	3.15	H(6E)–C(1D)	2.99	H(6F)–C(1E)	3.01
H(6D)–C(6C)	3.31	H(6E)–C(6D)	3.07	H(6F)–C(6E)	3.16
H(2A)–H(2B)	3.36	H(6A)–H(6B)	3.12		
H(2B)–H(2C)	3.32	H(6B)–H(6C)	3.11		
H(2C)–H(2D)	2.97	H(6C)–H(6D)	3.29		
H(2D)–H(2E)	3.48	H(6D)–H(6E)	3.10		
H(2E)–H(2F)	3.20	H(6E)–N(6F)	3.26		
H(2F)–H(2A)	3.06	H(6F)–H(6A)	3.20		

probably necessary in order to reduce the non-bonded repulsions in a model with fairly large, but unequal deviations from full orthogonality. If in such a model a ring is out of order, the rest is expected to assume near-orthogonal conformation, according to Almenningen, Bastiansen & Skancke (1958). This can be interpreted differently by requiring deformation of the molecule while maintaining large angles of twist. The less substituted 1,3,5-triphenylbenzene is undistorted. The molecule projected along the normal to the least-squares plane through the central ring is shown in Fig. 1. It clearly indicates the departures from pure six-fold symmetry. Instead of the maximum symmetry  $6/m\ 2/m\ 2/m$  for an orthogonal model, the molecule has adopted approximately a 622 symmetry and is therefore non-centrosymmetric. As a rule (Kitaigorodskii, 1961), molecules of hexagonal symmetry retain only their inversion centers (if they have such) in the crystal. A molecule of high symmetry will only retain its symmetry partially or completely if it is simple or of ex-

ceptionally convenient shape, as in most cases retention of this symmetry involves material loss in packing density. As a typical example of loss of symmetry, one considers *sym*-triphenylbenzene.

Hexaphenylbenzene is supposed to be one of the few representatives of molecules with symmetry falling in point group 622. Hexanitrobenzene behaves similarly; this molecule is quite undistorted.

One is tempted to compare the molecular structure of  $C_6Ph_6$  with a molecule like hexaphenylcyclohexane. Unfortunately, no structure determination has been reported on this substance. However, two modifications of a related compound  $P_6Ph_6$  are known (Daly, 1965, 1966). The geometry of the molecules in both polymorphic forms is much the same. The six-membered ring of phosphorus atoms is in the chair form with phenyl groups occupying the equatorial positions. The same is true for the corresponding arsenic compound (Hedberg, Hughes & Waser, 1961). In all these cases the phenyl rings make only small angles (up to

Table 9. *Least-squares equations in their normal form of the mean planes through groups of atoms and deviations of the atoms from these planes (Å), according to Schomaker, Waser, Marsh & Bergman (1959)*

(i) Equation:  $lX + mY + nZ = p$ , where  $X, Y, Z$  are orthogonal coordinates in Å.

Plane	$l$	$m$	$n$	$p$
Central ring	0.9879	-0.1517	-0.0319	1.1514
Ring A	0.4808	0.8147	-0.3241	7.6689
Ring B	0.3676	0.1746	-0.9134	2.3932
Ring C	-0.3474	0.7049	0.6184	4.7621
Ring D	-0.1968	0.9487	-0.2473	6.9874
Ring E	-0.3813	0.2437	-0.8917	1.0602
Ring F	0.5241	0.5861	0.6180	6.0015

(ii) Deviations from the planes

C(1)	0.027	C(1A)	-0.000	C(1B)	-0.004
C(2)	-0.012	C(2A)	0.001	C(2B)	0.001
C(3)	-0.009	C(3A)	0.001	C(3B)	0.009
C(4)	0.016	C(4A)	-0.005	C(4B)	-0.016
C(5)	-0.001	C(5A)	0.006	C(5B)	0.014
C(6)	-0.020	C(6A)	-0.004	C(6B)	-0.004
		C(1)	0.006*	C(2)	-0.051*
C(1C)	-0.007	C(1D)	0.011	C(1E)	0.006
C(2C)	0.012	C(2D)	-0.004	C(2E)	-0.002
C(3C)	-0.009	C(3D)	-0.010	C(3E)	-0.007
C(4C)	0.001	C(4D)	0.017	C(4E)	0.011
C(5C)	0.005	C(5D)	-0.012	C(5E)	-0.006
C(6C)	-0.002	C(6D)	-0.002	C(6E)	-0.002
C(3)	0.027*	C(4)	0.101*	C(5)	0.005*
C(1F)	-0.008			C(1)	0.032
C(2F)	0.017			C(2)	-0.022
C(3F)	-0.009			C(3)	-0.033
C(4F)	-0.007			C(4)	-0.005
C(5F)	0.017			C(5)	-0.006
C(6F)	-0.010			C(6)	-0.012
C(6)	-0.003*			C(1A)	0.141
				C(1B)	-0.035
				C(1C)	-0.076
				C(1D)	0.141
				C(1E)	-0.022
				C(1F)	-0.104

The atoms denoted by asterisks do not contribute to the least-squares plane.



about  $10^\circ$ ) with the  $\bar{3}$  axis of the puckered central ring. Neighbouring outer rings are displaced with respect to one another in the direction of the  $\bar{3}$  axis. Therefore, the non-bonded distances between the phenyl groups are larger than in  $C_6Ph_6$ . It looks as if  $C_6Ph_6$  tends to reduce the intramolecular repulsions by displacing neighbouring peripheral rings in a direction perpendicular to the central ring, thereby distorting the molecule.

#### Packing arrangement

Fig. 2 illustrates the packing of the molecules. The structure forms approximately a layer arrangement, with molecules lying in or near the (200) planes. Hexaphenylbenzene, although orthorhombic, is pseudo-hexagonal or pseudo-trigonal, with the present  $a$  axis as the unique direction ( $b:c \approx \sqrt{3}:1$ ). Close packing with sixfold coordination occurs in the basal plane  $bc$  (Fig. 2). The (200) layers are very nearly trigonal whereas the molecules themselves are approximately hexagonal (622). The deviations from trigonal symmetry include a slight tilt of the molecules out of the (200) plane. A layer has  $t_1t_2[\bar{1}]$  symmetry in Kitaigorodskii's notation. The coordinates of the centres of the molecules in a layer are approximately

$$\frac{1}{4}, \frac{3}{8}, 0; \frac{1}{4}, \frac{7}{8}, \frac{1}{2}; \frac{1}{4}, \frac{3}{8}, 1.$$

The stacking of the layers, which is determined by closest-packing requirements and by the tendency for the symmetry of the molecular arrangement to be as high as possible, resembles the effect of applying a translation of  $\frac{1}{2}, -\frac{2}{8}, 0$ , destroying the trigonal symmetry of the whole structure.

Only a few cases are known where molecules of trigonal or hexagonal symmetry pack in hexagonal cells while occupying general positions in the crystals.

The upper layer is translated so that the molecular centres lie over intermediate positions in the lower layer. The molecular coordination number is 14. In hexaphenylbenzene packing of molecules stacked directly above and below each other would be unfavourable and would result in a loose assembly with large voids. The structure is built up from repetition of one planar independent layer consisting of asymmetrical molecules. In the unit cell such a layer contains two molecules related by  $n$  symmetry, which transforms a left-handed molecule into a right-handed one and conversely. The layers are related by the  $2_1$  axis. The phenyl groups of each layer are twisted about the C-C bridge bonds to make fairly large angles with the planes of phenyl groups in the next molecular layer twisted in the opposite sense. This arrangement is best suited to obtain a minimum of empty space between the mol-

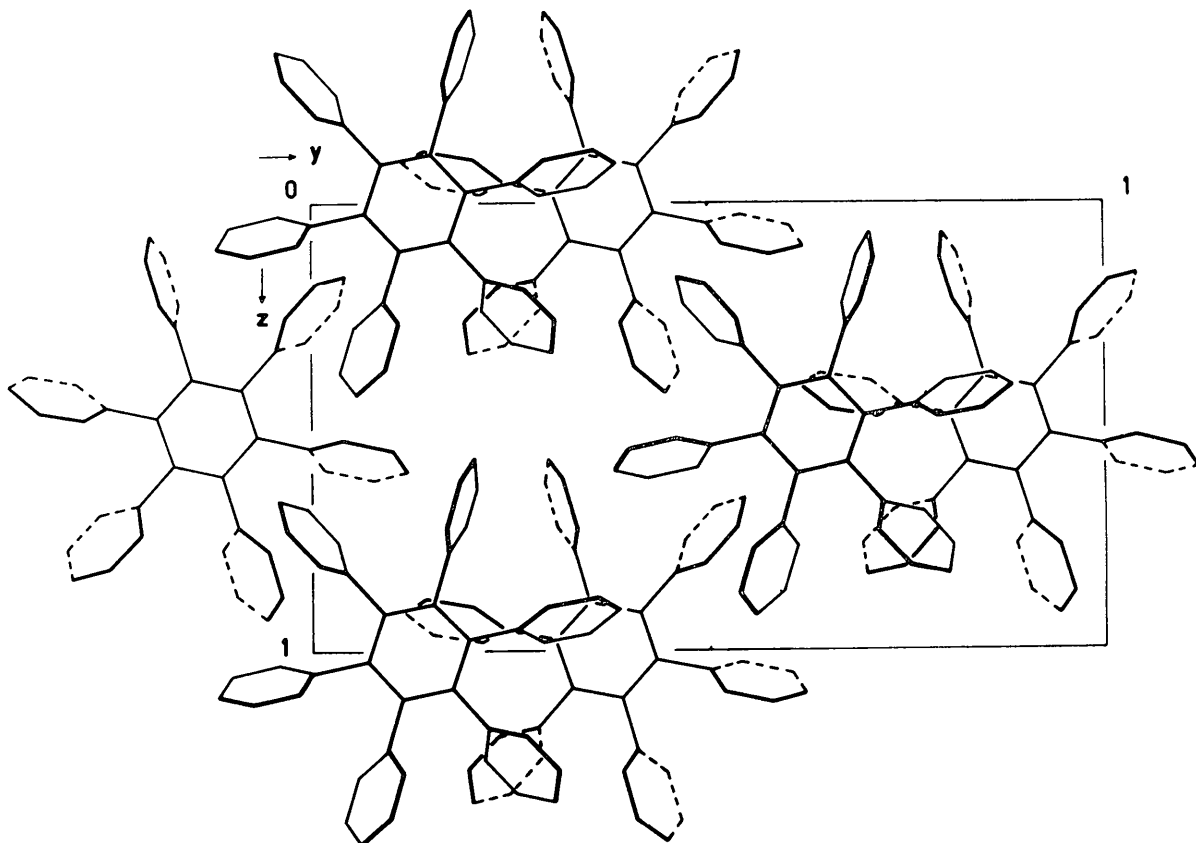


Fig. 2. The structure of  $C_6Ph_6$  projected down [100].

ecules. The packing, the large and dissimilar deviations from orthogonality can thus be understood.

If the gain in energy resulting from a fairly close packing of the rather symmetrical molecules is greater than the energy loss due to steric interactions and distortions within the molecule, this would be a possible explanation for the observed configuration in the solid state as opposed to the one in the vapour phase.

Using Kitaigorodskii's table for the volumes of atomic groupings, the coefficient of molecular packing

$$k' = \frac{NV_0}{V} = \frac{4 \times 517}{3028.8} = 0.68.$$

This value is the same as for benzene, but lower than for biphenyl and 1,2-diphenylbenzene (0.74 and 0.73 respectively). In general the closer the shape is to ellipsoidal, the closer  $k'$  is to 0.74, as for the closest packed spherical and ellipsoidal arrays. The other crystalline modification of  $C_6Ph_6$ , *A*, has a similar value for  $k'$  (0.69), as expected. As the primary determinant of  $k'$  is the entire shape of the molecule, molecules of similar shape give similar  $k'$ :  $C_6Ph_6$  is somewhat closer packed than  $C_6(NO_2)_6$  ( $k' = 0.64$ ). The higher  $k'$  value (0.72) for 1,3,5-triphenylbenzene (Kitaigorodskii, 1961) can be understood because this molecule has more internal degrees of freedom to search for the closest packing. Nevertheless this packing is surprisingly similar to that of hexaphenylbenzene. The difference lies probably mainly in a more effective layer stacking in the first compound.

C-H contacts mainly seem to determine the packing, the number of such independent contacts  $< 3.4$  Å being 61; the shortest one is 2.75 Å whereas there are three other distances smaller than 2.9 Å. The minimum C-C intermolecular distance is 3.55 Å, giving a normal  $R_c$ . There are 47 independent C-C contacts  $< 4.0$  Å and 16 H-H contacts  $< 2.8$  Å (shortest H-H distance is 2.29 Å). It must be kept in mind that the H atom positions are assumed. The packing of the molecules in the crystal involves practically only phenyl-phenyl contacts. The central ring is hardly involved in van der Waals contacts: only 10 such intermolecular benzene-phenyl distances were found.

*A priori* it cannot be excluded that the molecules of modification *A* contain some symmetry element involving reflexion (inversion centre, planes of symmetry, inversion axes). On the other hand the possibility of an inversion centre in the molecule is rather small as it would imply an antipropeller arrangement for some of the rings and this sets a limit to the maximum deviation from orthogonality. Symmetry planes require models ranging from partially antipropeller ( $2/m$  or  $mm2$ ) with equal twists of opposite sign around the pivot bonds to a full orthogonal model ( $6/m2/m2/m$ ). All these possibilities are not very likely. Although the unit-cell dimensions and space group of hexaphenylbenzene modification *A* bear some relation to the corresponding values for the other polymorphic form, its packing arrangement need not necessarily be the same

as the one described here. The *A* structure will be slightly closer packed (compare the packing coefficients).

#### Comparison with electron-diffraction data

Another direct measurement of the shape of  $C_6Ph_6$  has been carried out by Almenningen, Bastiansen & Skancke (1958), who have studied the vapour of hexaphenylbenzene by electron diffraction. They find an average C-C bond length in the ring of 1.40 Å (*cf.* 1.40 in the solid); bridge C-C distance is 1.52 Å (*cf.* average 1.50 Å but individual values with rather large spread), whereas the molecule is non-rigid with the outer rings nearly orthogonal to the central ring, oscillating with no appreciable restriction in a rather limited angle interval of approximately  $\pm 10^\circ$  from the orthogonal form. By indicating this configuration, the electron diffraction experiment seems to support our observation that there is no conjugation in the molecule. This would lead one to expect that the phenyl rings would also adopt the nearly orthogonal configuration in the solid phase so as to avoid strain due to steric interaction. The fact that they do not must presumably be attributed to intermolecular forces. This is still supported by the fact that in  $P_6Ph_6$  and  $As_6Ph_6$ , where the non-bonding repulsions between the phenyl groups are already greatly reduced with respect to an orthogonal  $C_6Ph_6$ , the outer rings nevertheless occupy positions closer to orthogonality.

The results collected in Table 1 indicate that  $\theta$  can vary widely depending on the state the molecule is in. It shows that measurements for one state cannot necessarily be used for another. The apparent strength of the intermolecular forces in the crystal suggests that the angles of twist may be different in solution.

Duculot (1959) applied an L.C.A.O. molecular orbital calculation to hexaphenylbenzene assuming planarity ( $D_{6h}$  symmetry). Although slight deviations from this symmetry can be treated as a perturbation of the starting configuration, we feel that the calculated values for bond order, free valencies, electronic and resonance energy, the ultraviolet  $N-V_1$  transition energy and interatomic distances need revision. Thus the calculated distance of the pivot bonds (1.441 Å) is not in accordance with our experiment. The resonance energy  $E_R$  (327 kcal.mole<sup>-1</sup>) must be considerably less as the electron delocalization is probably comparable to the one in benzene. We estimate  $E_R$  to have a value of about  $7E_R(C_6H_6)$ . In the same way the frequency of the  $N-V_1$  transition (33650 cm<sup>-1</sup>) does not seem to be compatible with the observed non-planarity of the molecule. We have measured the electronic absorption spectra of  $C_6Ph_6$  in solution, as well as in the solid state (KCl pressed disk technique), down to 230 m $\mu$ . Apart from a normal slight red shift there is no significant difference between the solution (hexane) and the solid state spectra ( $\lambda_{max}$  at 247 and 251 m $\mu$ , shoulders at 275 and 280 m $\mu$  respectively). Despite the spectral

similarity probably no conclusions can be made with regard to the angles of twist existing in solution.

The spectral change going from the planar biphenyl (253  $m\mu$ ) and non-planar *o*-diphenylbenzene (237  $m\mu$ ) (Dale, 1957) to  $C_6Ph_6$  is rather surprising.

All the calculations were performed on an Elliott 803B computer using the programming system devised by Daly, Stephens & Wheatley (1967).

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### References

- AKOPYAN, Z. A., STRUCHKOV, YU. T. & DASHEVSKII, V. G. (1966). *Zh. Strukt. Khim.* **7** (3), 408.
- ALMENNINGEN, A. & BASTIANSEN, O. (1958). *K. Norske Vidensk. Selskabs Skrifter*, No. 4, 1.
- ALMENNINGEN, A., BASTIANSEN, O. & SKANCKE, P. N. (1958). *Acta Chem. Scand.* **12**, 1215.
- ARNDT, U. W. & PHILLIPS, D. C. (1961). *Acta Cryst.* **14**, 807.
- BASTIANSEN, O. (1952). *Acta Chem. Scand.* **6**, 205.
- CLEWS, C. J. B. & LONSDALE, K. (1937). *Proc. Roy. Soc. A* **161**, 493.
- CLEWS, C. J. B., MASLEN, E. N., RIETVELD, H. M. & SABINE, T. M. (1961). *Nature, Lond.* **192**, 154.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757.
- CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*, p. 32. Oxford: Pergamon Press.
- CRUICKSHANK, D. W. J. & SPARKS, R. A. (1960). *Proc. Roy. Soc. A* **258**, 270.
- DALE, J. (1957). *Acta Chem. Scand.* **11**, 650.
- DALY, J. J. (1965). *J. Chem. Soc.* p. 4789.
- DALY, J. J. (1966). *J. Chem. Soc. A*, p. 428.
- DALY, J. J. (1967). Private communication.
- DALY, J. J., STEPHENS, F. S. & WHEATLEY, P. J. (1967). Unpublished results.
- DARLOW, S. F. (1961). *Acta Cryst.* **14**, 159.
- DEWAR, M. J. S. & SCHMEISING, H. N. (1959). *Tetrahedron*, **5**, 166.
- DUCULOT, C. (1959). *Bull. ints. agron. stas. recherches Gembloux*, **27**, No. 1, 5. (*Chem. Abs.* **54**, 2002i).
- FARAG, M. S. (1954). *Acta Cryst.* **7**, 117.
- GUY, J. (1949). *J. Chim. Phys.* **46**, 469.
- HARGREAVES, A. & RIZVI, S. H. (1962). *Acta Cryst.* **15**, 365.
- HEDBERG, K., HUGHES, E. W. & WASER, J. (1961). *Acta Cryst.* **14**, 369.
- HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
- KARLE, I. L. & BROCKWAY, L. O. (1944). *J. Amer. Chem. Soc.* **66**, 1974.
- KITAIGORODSKII, A. I. (1961). *Organic Chemical Crystallography*. New York: Consultants Bureau.
- ROBERTSON, G. B. (1961). *Nature, Lond.* **191**, 593.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
- SUZUKI, H. (1949). *Bull. Chem. Soc. Japan*, **32**, 1340.
- TROTTER, J. (1961). *Acta Cryst.* **14**, 1135.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.

*Acta Cryst.* (1968). B24, 1287

## The Crystal Structures of Sodium Chromium Alum and Caesium Chromium Alum

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Sodium chromium alum with  $a = 12.40 \text{ \AA}$  and caesium chromium alum with  $a = 12.50 \text{ \AA}$  both have space group  $Pa3$ . Refinement of the structure of the sodium alum has resulted in a residual of 0.165 but no attempt has been made to refine the structure of the caesium alum. Sodium chromium alum, which has the  $\alpha$  structure, does not fit into the classification scheme of Lipson, whereas caesium chromium alum, with the  $\beta$  structure does. In view of earlier work by Ledsham & Steeple it is concluded that the class of an alum structure is governed by the particular combination of monovalent and trivalent ions that is involved, and that there is no infallible rule for the pre-determination of a given structure.

### Introduction

It has been shown by Lipson (1935) that the alums are polymorphous and can be classified as  $\alpha$ ,  $\beta$  and  $\gamma$  according to which of three different types of structure they belong to. Lipson suggested that the class was determined by the size of the monovalent ion, the  $\gamma$  class for small ions, the  $\beta$  class for large ions and the  $\alpha$  class for those intermediate in size; with the exception of potassium chromium alum the investigations were confined to samples in which the trivalent ion was aluminum. The results are summarized in the fol-

lowing table, from which it can be seen that potassium chromium alum fitted into the classification scheme.

Alum	Class
NaAl(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> O	$\gamma$
NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> O	$\alpha$
KAl(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> O	$\alpha$
KCr(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> O	$\alpha$
RbAl(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> O	$\alpha$
CH <sub>3</sub> NH <sub>3</sub> Al(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> O	$\beta$
CsAl(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> O	$\beta$