idealized molecule. The optical behavior would seem to support the conclusion that the molecular symmetry approximates closely to $\bar{4}m$.

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The Crystal Structure of *p*-Di-tertiary-butylbenzene*

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The structure of *p*-di-tertiary-butylbenzene was investigated by X-ray diffraction methods, using Weissenberg techniques. The principal refractive indices are $\alpha = 1{\cdot}570 \pm 0{\cdot}002$, $\beta = 1{\cdot}585 \pm 0{\cdot}002$ and $\gamma = 1{\cdot}588 \pm 0{\cdot}002$. The density is $(0{\cdot}985 \pm 0{\cdot}010)$ g.cm.$^{-3}$ and the calculated number of molecules per unit cell is $1{\cdot}98 \pm 0{\cdot}05$. Layer-line photographs were taken about [010], [001] and [$1\bar{1}0$]. The cell dimensions are $a = 9{\cdot}89 \pm 0{\cdot}06$, $b = 10{\cdot}13 \pm 0{\cdot}05$, $c = 6{\cdot}35 \pm 0{\cdot}03$ A., and $\alpha = \gamma = 90°$, $\beta = (94{\cdot}8 \pm 0{\cdot}2)°$. The cell is monoclinic and the most probable space group is $P2_1/n$. Patterson and Harker sections were plotted, but could not be used for direct structure determination. Harker–Kasper inequalities were applied to find the signs of 31 ($hk0$) planes. Trial-and-error methods were used to obtain the structure. On the two electron-density projections only two atoms are sufficiently resolved to locate their positions in space. A proposed orientation of the molecules in the cell was used as a solution, and the structure factors were calculated from it.

Introduction

The principal interest in the structure of *p*-di-tertiary-butylbenzene lies in the length of the bonds joining the benzene ring and the tertiary-butyl groups. The high chemical reactivities obtained from experiments on toluene and tertiary-butylbenzene indicate that hyperconjugation may exist between the benzene ring and the substituent groups (Berliner & Bondhus, 1948). If hyperconjugation between these groups and the ring does in fact exist, then the accepted single-bond lengths would be shortened to display a partial double-bond character.

In simpler cases of conjugation, the adjacent hydrogen electrons are delocalized and partake in the C–C bonding. The resultant shortening from single to partial double-bond length has been confirmed by electron diffraction work on butadiene-1,3 and cyclopentadiene, where the bond linking two CH units is 1·46 A. (Schomaker & Pauling, 1939). With X-ray diffraction, Robertson (1935), working on stilbene, found a distance of 1·44 A. between a benzene ring and a CH; and Jeffrey (1945) a value of 1·44 or 1·45 A. for the bond linking two isoprene units in geranylamine hydrochloride. The structure of *p*-di-tertiary-butylbenzene, although incomplete, is presented here because it does not indicate that a change of the order predicted above exists.

Morphology and optical properties

p-Di-tertiary-butylbenzene was obtained 98·5% pure from Standard Oil Corporation of Indiana. It was

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recrystallized five times from alcohol for further purification. The crystals had faces marked with growth lines.

Two-circle goniometer measurements of the crystals were made. The only complete form observed was $\{110\}$, although occasional faces of the forms $\{10\bar{1}\}$ and $\{01\bar{1}\}$ were also evident. Because the signals were indistinct, readings were taken at maximum brightness and resulted in the axial ratio $a:b:c=0{\cdot}98:1{\cdot}00:0{\cdot}74$. X-ray diffraction measurements yielded the ratio

$$a:b:c=0{\cdot}986:1{\cdot}000:0{\cdot}627,$$

with $\alpha=\gamma=90°$ and $\beta=94{\cdot}8°$.

The large discrepancy between the two sets of data is probably due to the poor optical signals.

The principal refractive indices of the crystal, determined by using monobrombenzene, bromoform and mixtures of these two as immersion oils, give values of

$$\alpha=1{\cdot}570\pm0{\cdot}002,\quad \beta=1{\cdot}585\pm0{\cdot}002$$

and $\gamma=1{\cdot}588\pm0{\cdot}002$.*

The angle $2V$, observed directly to be between 45 and 50°, is calculated from the refractive indices as 48°. In the plane of the optic axes, (010), the acute bisectrix lies in the obtuse angle β between a and c, and makes an angle of 86·3° with the a axis. The crystal is optically negative.

Experimental technique, cell dimensions and space group

All X-ray work was carried out with unfiltered Cu $K\alpha$ radiation, $\lambda=1{\cdot}54$ A. A Weissenberg moving-film camera was used to take oscillation, rotation and equi-inclinational layer-line diagrams. These photographs were made with the crystal rotating about the b axis, the c axis and $[1\bar{1}0]$. A thin coating of shellac had been sprayed over the surface of the crystal to prevent evaporation in air. The intensities of a long and a short exposure of each layer were calibrated against a series of spots of known exposure ratio.

Measurements of the films gave

$$a=9{\cdot}89\pm0{\cdot}06,\quad b=10{\cdot}13\pm0{\cdot}05,\quad c=6{\cdot}35\pm0{\cdot}03\text{ A.}$$

and $\alpha=\gamma=90°$ and $\beta=(94{\cdot}8\pm0{\cdot}2)°$,

and a unit cell volume of (633 ± 10) A.^{3} The density, determined by flotation, is $(0{\cdot}985\pm0{\cdot}010)$ g.cm.$^{-3}$. From the cell volume and the density, calculation gives $1{\cdot}98\pm0{\cdot}05$ molecules per unit cell.

There are no systematic absences in the planes (hkl); the cell, therefore, is primitive. The fact that

$$|\,F(hkl)\,|^2=|\,F(h\bar{k}l)\,|^2$$

verifies the cell as monoclinic, rather than triclinic. Of the 54 planes $(h0l)$ on the zero layer line, the only reflections present are those with $h+l=2n$. For planes $(0k0)$, there are reflections (020), (040) and (080), with $k=2n$; and none for (010), (030), (050) and (070), with $k=2n+1$. The space group is thus probably $P2_1/n$. There are only two molecules in the cell and they must occupy one of the four sets of twofold special positions, as listed in the *International Tables*. Set (a), $(0, 0, 0; \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$, was chosen arbitrarily. These positions being centers of symmetry, the parameters of only seven of the fourteen carbon atoms are to be found independently.

Structure determination

Patterson projections for the [010] and the [001] zones were computed. The intensities used in these maps were based on an arbitrary scale and were not corrected for polarization and Lorentz factors. These and all other Fourier summations were carried out by the method described by Patterson & Tunell (1942) for a 48 × 48 point net.

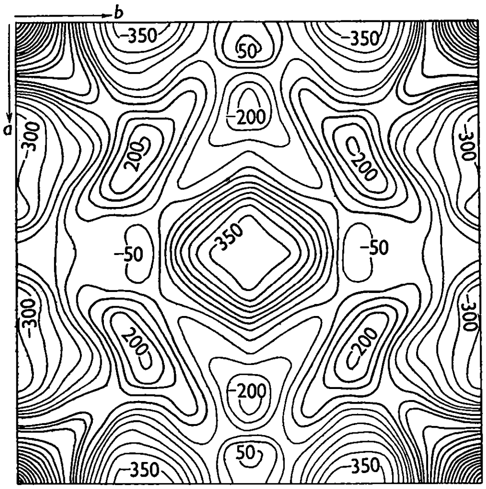

Fig. 1. Patterson projection on xy. Contours at every 50 (arbitrary) and at the origin at every 100.

The projection on (010) indicates that the long axis of the molecule is not in the (001) plane, but makes an angle with the plane. The peaks are unresolved and lie along the net diagonals. The positions and heights of the peaks on the (001) projection give the distance map an appearance of tetragonal symmetry (Fig. 1). Data corroborating this pseudo-tetragonality are: (1) the crystal is close to uniaxial in the sense that the principal refractive indices, $\beta=1{\cdot}585$ and $\gamma=1{\cdot}588$, are almost equal; (2) the axial lengths, $a=9{\cdot}89$ and $b=10{\cdot}13$ A., are nearly alike; and (3) the strong $(hk0)$ reflections exhibit approximate tetragonal symmetry. This tetragonality is displayed in the projection only, since the first and higher layer lines do not show any symmetry other than that of the space group $P2_1/n$. This map, again, gives no direct atomic positions, but it is clear that the long axes of the molecules are along the net diagonals.

The corrected intensities of 435 observed planes, as estimated visually from the Weissenberg layer-line films, were used to compute a Harker section in the

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* The author wishes to thank Prof. Dorothy Wyckoff, Geology Department, Bryn Mawr College, for assistance in determining the optical characteristics.

plane ($x, \frac{1}{2}, z$). There are ten peaks on this section, and the structure allows only seven true Harker peaks. The presence of the spurious peaks precluded the use of this map at an early stage of the analysis.

Harker & Kasper (1948) inequalities were then applied to the observed intensities, taking the maximum negative value of the Harker section as the relative value of $|F(000)|^2$. On this basis, $F(000)_{\text{arb.}}$ is equal to 65. The values of $\hat{F}(hkl)$ were calculated from the formula,

$$\hat{F}(hkl)=\frac{F(hkl)}{F(000)\,f_0(\sin\theta/\lambda)},$$

where $f_0=\frac{1}{6}f_C$. If $F(000)_{\text{arb.}}$ is underestimated, then $\hat{F}(hkl)$ will be too large. The larger, incorrect value of $\hat{F}(hkl)$ will in some cases lead to erroneous signs, and in others allow signs to be found which would ordinarily be indeterminate.

The signs of thirty-one ($hk0$) coefficients were fixed by the inequalities, using methods similar to those described by Gillis (1948). In addition, some signs were determined by non-integer indices, as described in a note which appears elsewhere. These coefficients were used in the computation of a trial electron-density map, which gave no further detailed information, but merely confirmed the orientation of the molecule as given in the distance maps. No attempt was made to sum a series for ($h0l$), since very few signs could be ascertained from inequalities.

Working with the information now available, three trial models, consistent with the vector maps, were considered. Two electron-density projections were computed, using those coefficients whose signs seemed to be well established by the models and the Harker–Kasper inequalities.

The superposition of Bragg & Lipson charts on the ($hk0$) map indicated that the change of signs of two high-intensity reflections would eliminate a spurious peak that appeared at ($0, \frac{1}{2}$). The model was revised and another set of maps plotted. These maps suggested further changes of the orientation of the molecules in the cell. With each new adjustment, density projections were computed in the $x\,y$ and $y\,z$ planes. Re-aligning the molecule at each step, a final solution was found by successive approximations.

From the penultimate to the final solution, only the signs of three high-order, low-intensity planes were changed. The structure factors calculated from the co-ordinates of the last pair of maps reproduced the signs used in the computations.

Orientation of the molecule

In the models calculated the benzene ring was assumed to be a regular planar hexagon with side of 1·39 A. and the tertiary-butyl group tetrahedral, with all C–C distances 1·54 A. Taking the pole as the normal to the xy plane, the long axis of the molecule was located by the polar angle $(90-\theta)$ and the azimuth Φ, which is zero at the x axis. The rotation of the ring about the molecular axis was expressed in terms of the angle Ψ_r which the plane of the ring makes with the plane containing the pole and the molecular axis. The rotation of the tertiary-butyl group was described in a similar way by Ψ_b, the angle between one of the planes of symmetry of the group and the reference plane, the zero being taken when one of the methyl groups points toward the pole.

In terms of these angles, the trial-and-error methods give the orientation of the molecule as

$$\theta=13{\cdot}5^\circ,\quad \Phi=42{\cdot}5^\circ,\quad \Psi_r=18{\cdot}7^\circ \text{ and } \Psi_b=7{\cdot}7^\circ.$$

Discussion of results

By comparing Table 1 with Table 2, it is apparent that the positions of the atoms as calculated from the model agree with those observed on the maps. Of the twenty-one co-ordinates needed to determine the structure, twelve are obtainable from the maps. The only atoms that are resolved on both electron-density maps, Figs. 2 and 3, are C_6 and C_7. Unfortunately, the co-ordinates of atoms C_3 and C_4, the most interesting from the point of view of hyperconjugation, cannot be obtained from either projection, and can only be estimated from structure-factor calculations.

Table 1. *Atomic co-ordinates obtained from final model*

(Values in fractions of the cell.)

	x	y	z
C_1	0·015	0·055	0·200
C_2	0·088	0·035	− 0·149
C_3	0·104	0·090	0·051
C_4	0·218	0·190	0·108
C_5	0·230	0·215	0·348
C_6	0·185	0·321	− 0·009
C_7	0·353	0·136	0·042

Table 2. *Atomic co-ordinates obtained from the electron-density maps*

(Values in fractions of the cell.)

	Projection on (010)			Projection on (001)		
	x	z	Peak height (in arbitrary units)	x	y	Peak height (in arbitrary units)
C_1	0·016	0·204	348	—	—	—
C_2	0·090	− 0·152	291	—	—	—
C_3	0·106	0·052	335	—	—	—
C_4	—	—	—	—	—	—
C_5	—	—	—	—	—	—
C_6	0·185	− 0·008	280	0·181	0·320	392
C_7	0·354	0·040	291	0·354	0·147	396

The density projections are all plotted on an arbitrary scale, and no calculation was made of the number of electrons in each atom. Figs. 2 and 3, and Table 2, reveal the areas of the peaks on each map to be almost the same size and the heights approximately equal, with the greatest difference in height 15 % on the xz plane.

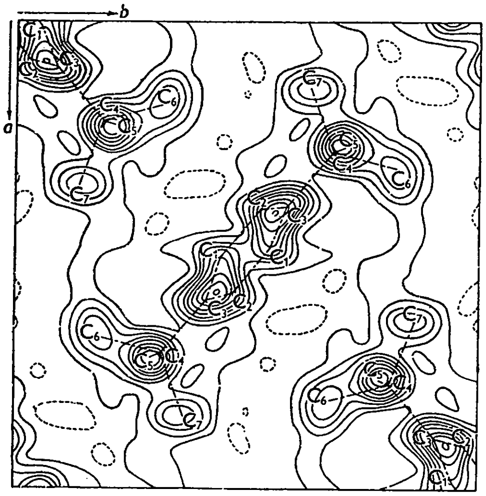

Fig. 2. Electron density on (001). Contours at every 100 (arbitrary). Negative values indicated by dashed lines.

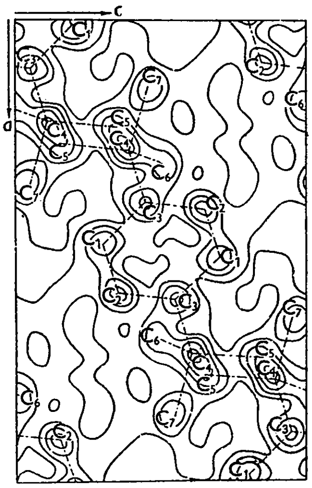

Fig. 3. Electron density on (010). Contours at every 100 (arbitrary). Lowest negative value − 93, not shown.

This discrepancy will be reduced if $F(000)_{\text{arb.}}$ is increased. The large negative regions on the maps indicate that the assumed value $F(000)_{\text{arb.}} = 65$ is too small.

The final model of the structure gives the best correspondence between the observed and the calculated values of the structure factors, as listed in Table 3 (p. 180). Using a temperature factor, with $B = 3 \times 10^{-16}$ cm.^{2}, the discrepancies, given by

$$\Sigma \,||\, F(hkl)\,|_{\text{obs.}} - |\, F(hkl)\,|_{\text{calc.}}\,| / \Sigma \,|\, F(hkl)\,|_{\text{obs.}},$$

are 0·26 for both the [001] and the [010] zones. All peaks in the Harker section and in the Patterson projections can be accounted for by the structure. The values of the angles, given above and used in the structure-factor calculations, are derived from the final density maps. Although the uncertainty in the angles cannot be easily calculated, a change in the orientation of the molecule, to $\theta = 13{\cdot}7°$, $\Phi = 40{\cdot}8°$, $\Psi_r = 17{\cdot}5°$ and $\Psi_b = 6{\cdot}7°$, will increase the discrepancy by 10%. This gives an indication of the order of accuracy of the structure.

In order to verify the possibility of a shortened C_3–C_4 bond length due to hyperconjugation, the angles were readjusted to permit a change in bond distance while maintaining agreement with the co-ordinates as measured from the electron-density map. Structure factors calculated under these conditions, with lengths of 1·49 and 1·59 A., yielded a large increase of discrepancy in each instance. If hyperconjugation acts to change only the distance between the two atoms, C_3 and C_4, then these calculations argue its probable absence.

Evidence from 1:4-dimethoxybenzene (Goodwin, Przybylska & Robertson, 1950) indicates a shortening of the bond length between the oxygen and the carbon of the benzene ring accompanied by a distortion of the ring. Such a condition may also exist in this molecule, but cannot be recognized from the two electron-density projections. Since no clue is found of the kind of distortion that may exist here, no change of the bond angles of either the ring or the tertiary butyl group could be made. If such a distortion does in fact exist and had been introduced, in addition to the shortened distance between the two atoms, the calculated and observed structure factors would have shown closer correspondence. Because of the possibility of distortion, no unequivocal statement can be made about hyperconjugation in this molecule even though the discrepancies are increased with the change of the bond length from the normal.

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Table 3. *Observed and calculated values of the structure factors*

hkl	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$
020	12·8	− 5·6	550	6·1	5·9	301	11·6	13·9
040	4·1	− 1·7	560	20·4	− 14·3	$30\bar{1}$	20·3	− 25·5
060	0	2·6	600	7·0	− 3·0	303	6·3	− 5·3
080	10·9	11·9	610	10·5	− 16·1	$30\bar{3}$	8·8	− 9·5
0,10,0	0	− 0·6	620	0	− 1·8	305	9·3	− 10·8
110	32·4	39·6	630	7·5	6·2	$30\bar{5}$	20·6	19·2
120	31·4	− 34·5	640	7·1	− 7·8	307	6·0	− 6·5
130	23·1	22·8	650	0	3·6	$30\bar{7}$	0	− 0·1
140	4·9	1·1	660	5·6	4·4	402	15·4	− 16·6
150	7·8	− 3·9	670	4·0	− 4·7	$40\bar{2}$	22·6	− 21·6
160	8·3	− 6·3	710	9·1	− 7·2	404	12·1	− 9·2
170	10·0	− 10·3	720	10·8	9·7	$40\bar{4}$	4·4	− 3·4
180	6·6	4·9	730	8·4	8·0	406	6·3	− 5·8
190	0	2·0	740	2·3	− 3·7	$40\bar{6}$	10·2	9·9
1,10,0	0	− 5·0	750	3·7	− 4·6	501	9·6	− 5·5
200	16·5	− 18·3	800	8·6	3·9	$50\bar{1}$	10·2	7·9
210	21·3	− 21·2	810	12·7	12·3	503	0	2·2
220	43·3	50·2	820	0	2·0	$50\bar{3}$	6·7	1·7
230	7·5	− 7·1	830	0	1·1	505	7·1	7·9
240	5·2	− 2·3	840	3·2	− 1·8	$50\bar{5}$	0	− 2·2
250	11·5	− 13·8	910	11·5	10·4	507	0	− 0·3
260	9·2	− 9·4	920	4·7	− 4·6	$50\bar{7}$	5·4	3·5
270	6·4	− 9·0	930	5·9	− 6·1	602	0	− 0·2
280	0	0·2	940	3·3	6·0	$60\bar{2}$	7·1	8·9
290	0	7·7	10,0,0	6·3	8·3	604	12·0	11·4
2,10,0	6·0	− 5·4	10,1,0	2·3	− 3·3	$60\bar{4}$	9·2	12·6
310	18·3	− 15·5	10,2,0	5·2	4·9	701	11·8	− 9·7
320	12·5	− 12·3	11,1,0	6·4	4·1	$70\bar{1}$	11·4	− 11·2
330	9·8	− 5·0	002	17·6	19·3	703	7·4	0·6
340	22·9	− 24·5	004	7·8	− 3·7	$70\bar{3}$	9·1	− 9·4
350	1·9	− 2·9	006	7·5	6·7	705	9·2	6·3
360	0	3·6	008	0	− 0·2	$70\bar{5}$	0	1·1
370	0	5·1	101	4·3	1·0	707	0	0
380	0	− 5·1	$10\bar{1}$	48·3	54·5	$70\bar{7}$	3·9	− 2·2
390	8·0	− 6·5	103	24·0	− 25·2	802	0	− 4·6
400	4·0	1·2	$10\bar{3}$	9·1	6·7	$80\bar{2}$	0	− 3·3
410	8·2	10·9	105	0	2·8	804	9·8	10·1
420	15·7	− 13·6	$10\bar{5}$	8·2	6·8	$80\bar{4}$	10·6	− 14·1
430	22·4	− 21·2	107	0	− 0·7	901	3·3	− 1·3
440	16·6	14·3	$10\bar{7}$	0	0·4	$90\bar{1}$	15·9	14·2
450	7·1	− 8·1	202	12·4	− 12·2	903	0	− 0·2
460	0	− 0·2	$20\bar{2}$	21·0	− 23·7	$90\bar{3}$	0	− 0·2
470	0	4·9	204	0	1·4	905	3·3	0·3
480	4·0	− 8·2	$20\bar{4}$	10·1	7·5	$90\bar{5}$	11·5	− 3·8
510	8·8	− 6·1	206	0	− 2·2	10,0,2	7·0	− 7·8
520	5·2	− 3·7	$20\bar{6}$	7·4	− 0·6	$10,0,\bar{2}$	7·4	4·1
530	2·5	− 4·0	208	0	0·6	$11,0,\bar{1}$	10·1	10·0
540	5·6	4·7	$20\bar{8}$	4·3	− 9·0			

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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X-Ray absorption in crystals set at the Bragg angle.

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In considering the intensity of reflection of X-rays from a crystal it is usually assumed that the incident beam in reaching the interior of the crystal is weakened by two effects: ordinary absorption, and the reflection of part of the beam by the upper layers of the crystal. Thus, in effect, a crystal set at the Bragg angle should show a