The crystal structure of benzene at −3 °C

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A new X-ray analysis has confirmed that the space group is *Pbca*, with four molecules per unit cell, and $a = 7\cdot460$, $b = 9\cdot666$ and $c = 7\cdot034$ Å. 284 structure factors have been measured from oscillation photographs using Cu$K\alpha$ radiation. The structure suggested by Cox (1932) was refined by the Fourier transform method and by two-dimensional Fourier and difference syntheses. The co-ordinates derived from the projections were refined by three-dimensional differential syntheses in which isotropic thermal parameters were used and termination of series errors corrected by the backshift method. After five differential cycles, electron density and difference maps calculated in the mean molecular plane revealed appreciable angular oscillations of the molecules about their senary axes. The refinement was continued by means of three-dimensional differential syntheses with anisotropic thermal parameters for the carbon atoms, and difference syntheses computed in the plane of the molecule and adjacent parallel planes. The criterion finally used to determine the anisotropic parameters was the equality of the observed and calculated atomic peak curvatures, the scale factor being adjusted to give the corrected integrated number of electrons in the molecule.

The r.m.s. amplitude of angular oscillation about the senary axis is approximately 7·9°. An important consequence of the molecular angular oscillation is that the mean C—C bond length is increased by 0·015 Å to 1·392 Å, the likely limits of error being not less than 0·010 Å. The result agrees satisfactorily with other determinations of the C—C distance in benzene, notably Langseth & Stoicheff's value (1956) of $1\cdot397_4 \pm 0\cdot001$ Å from the Raman spectrum of the gas. The carbon ring is accurately planar, individual co-ordinates being only 0·0013 Å from the mean plane. The final value of the residual R was 9·9 %. During the refinement, an attempt was made to derive an accurate difference synthesis from which conclusions about bonding electrons could be drawn. The experimental data did not prove sufficiently reliable, and only very tentative conclusions have been obtained.

Detailed examination of the crystal structure has shown that the molecules pack together like sheets of six-toothed gear wheels. This allows an easy in-phase oscillation of the molecules about their senary axes, and explains the large r.m.s. amplitudes observed. Occasional rotations of molecules in groups are probably responsible for the narrowing of the nuclear magnetic resonance line above 120 °K.

1. Introduction

The general features of the crystal structure of benzene at temperatures not far below the melting-point have been known for some time (Cox 1932). The space group is *Pbca* and the unit cell contains four molecules, which lie on centres of symmetry at (000), $(0\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}0\frac{1}{2})$ and $(\frac{1}{2}\frac{1}{2}0)$, giving rise to a pseudo face-centring. Cox showed that the molecules were at least approximately planar and gave the approximate directions of the normals to the planes of the rings.

The present work was undertaken, first, as an ordinary crystal structure refinement to determine the atomic positions, and hence the bond lengths, with a precision of 0·01 Å or better, and secondly to discover how far it was possible, without resort to low temperatures, to expose features of the electron density distribution in the molecule which might be significant for valency theory. At −3 °C, the temperature of our experiments, the vibrational motion of the molecules is considerable ($B \sim 6$ Å²) and, as we discovered, so strongly anisotropic as to complicate the analysis considerably. In spite of this, we have been able to determine the mean C—C bond length with a precision of about 0·01 Å. We have not been able

to reach any satisfactory conclusions about the molecular electron density, partly because of the anisotropic thermal motion, but chiefly because our diffraction data did not meet the necessarily very stringent standards. Although it is possible with data obtained at a single temperature to separate analytically the effects of vibrational motion from those of the molecular electron density, it is now apparent, in view of the complexity of the anisotropic motions, that this may be done much more satisfactorily with data obtained at least at two widely separated temperatures.

We hope in due course to extend our experimental observations to much lower temperatures; the present paper gives the results of the structure analysis as far as it was reasonable to carry it with the -3 °C data. A large part of the paper is concerned with the detailed corrections for anisotropic thermal motion referred to above. As is usual in crystal structure refinement, the values of the additional thermal parameters are empirical in the sense that they are chosen to give a good fit between the observed and calculated structure amplitudes. There is no reason seriously to doubt the validity of this criterion and in the present case some of the conclusions of the analysis are supported by the results of nuclear magnetic resonance experiments (Andrew & Eades 1953) and by a study made by one of us (Cruickshank 1958) of the lattice vibrations of molecular crystals. The latter investigation, concerned with benzene, naphthalene and anthracene, shows that the amplitudes of the thermal motions deduced from the X-ray work are consistent with the specific heat data and with the low-frequency Raman spectra.

2. EXPERIMENTAL

The material used was B.D.H. Analar grade benzene; this was stated to contain less than 2×10^{-4} % thiophene and in fact gave no detectable reaction with isatin and sulphuric acid. It was further purified by partial freezing and drying over calcium chloride. Cylindrical crystals were obtained by sealing small quantities of liquid benzene into Lindemann glass capillary tubes and cooling slowly in a current of air, the method being very similar to that used by Keesom & Taconis (1935) and modified later by other workers (Kaufman & Fankuchen 1949; Abrahams, Collin, Lipscomb & Reed 1950). The orientation of the crystals so produced could be determined to within about 2° under the polarizing microscope by means of a crude form of the device described by Birks & Wing (1952); this could be done in a few minutes and was therefore much to be preferred to the very much slower X-ray methods, which, however, were used for the final adjustment of the crystals on the X-ray goniometer. Ideally, crystals should have been selected so that in each case a crystallographic axis was coincident with the axis of the containing glass tube, but as the orientation of the crystals obtained in a large number of repeated freezings appeared to be mainly random, the probability of obtaining ideally orientated crystals was very small and in fact the divergence between the two axes in the crystals used in our experiments ranged from 5 to 20°. The tube used for the b-axis photographs had a bore of 0·37 mm and a wall thickness of 0·04 mm and that used for the a- and c-axis photographs had a bore of 0·36 mm and a wall thickness of 0·07 mm. Under these conditions, the absorption errors were small and we have made no correction for them (nor for general absorption).

All the X-ray observations were made photographically in a small room refrigerated at $-3 \cdot 0 \pm 0 \cdot 5$ °C. Chromium $K\alpha$ radiation ($\lambda = 2 \cdot 291$ Å) was used to obtain accurate cell dimensions by the method of Straumanis. From observations on the 600, 064 and 606 reflexions, the unit cell dimensions at -3 °C were found to be

$$a = 7 \cdot 46(0), \quad b = 9 \cdot 66(6), \quad c = 7 \cdot 03(4) \text{ Å}.$$

The density calculated from these figures is $1 \cdot 022 \text{ g/cm}^3$; that interpolated for -3 °C from the curve given by Andrew & Eades (1953) is $1 \cdot 016$. The unit cell dimensions at $-195°$ C (Kozhin 1954) are

$$a = 7 \cdot 292, \quad b = 9 \cdot 471, \quad c = 6 \cdot 742 \text{ Å},$$

giving a calculated density of $1 \cdot 114 \text{ g/cm}^3$; the Andrew–Eades curve gives $1 \cdot 117$ at -195 °C. From the two sets of cell dimensions we calculate the mean coefficients of thermal expansion between 78 and 270 °K to be $\alpha(a) = 119, \alpha(b) = 106, \alpha(c) = 221$ (all $\times 10^{-6}$/°C) (compare Kozhin & Kitaigorodskii 1955). These figures are probably not accurate to better than about 10 %, but they show that the expansion along the c-axis is much greater than that in the other directions, as would be expected for the molecular arrangement (see §8).

The intensities of the X-ray reflexions were estimated visually with the aid of suitable calibration spots on multiple films obtained with unfiltered copper $K\alpha$ radiation. Because of the large thermal motion of the molecules in crystalline benzene at -3 °C very long exposures were necessary to record the weaker reflexions, and oscillation photographs were therefore preferred to Weissenberg photographs. A suitably oriented crystal having been obtained and set up, a series of $15°$ oscillation photographs was taken, each with an exposure of 24 h. The crystal was then regrown with another suitable orientation and more photographs were taken. In this way all three principal axes were covered and the intensities of 284 independent reflexions recorded, this being 56 % of the total theoretically possible with copper K radiation. The final value of any structure factor was the mean of that derived from two to twenty-two intensities measured on three crystals, the number depending on the indices and the intensity of the particular reflexion. The experimental structure factors, on a scale referred to later as $1 \cdot 0 \times |F_{\text{obs.}}|$ are shown in table 1 together with the $F_{\text{calc.}}$ from the fifth and final cycle of calculations using anisotropic temperature factors.

3. The X-ray structure analysis

The approximate arrangement of the molecules proposed by Cox (1932) was adopted as the starting point of the structure analysis. In this model, a diameter of each molecule is parallel to [010] and the molecular plane makes an angle of $50°$ with [100]. Such an arrangement can only be approximate, because it is face-centred and therefore will not permit the occurrence of reflexions $hk0$, $h0l$ and $0kl$ with h, k and l odd; in fact, this is only approximately so for reflexions at low values of $\sin \theta$ and not at all at larger angles. A small reorientation of the ring was indicated and this was determined by a Fourier transform method (see, for example, Lipson & Cochran 1953).

I-2

TABLE 1. LIST OF OBSERVED AND CALCULATED STRUCTURE FACTORS

hkl	$|F_{\text{obs.}}|$	$F_{\text{calc.}}$	hkl	$|F_{\text{obs.}}|$	$F_{\text{calc.}}$	hkl	$|F_{\text{obs.}}|$	$F_{\text{calc.}}$
$k + l$ even								
200	38·2	41·1	820	1·5	2·0	551	2·5	2·7
400	17·4	−18·0	022	9·2	− 8·4	751	2·2	2·6
600	7·8	− 7·6	122	18·6	21·1	153	1·1	1·5
800	1·5	− 0·9	222	3·6	− 3·1	253	4·5	− 4·3
002	22·7	27·1	322	15·5	14·8	453	3·7	− 3·5
102	37·4	38·1	422	1·0	− 0·4	553	1·2	− 1·6
202	20·1	22·2	522	3·5	− 3·2	753	0·9	− 1·2
302	25·3	27·9	722	2·2	− 2·5	060	9·1	− 7·9
402	2·2	2·9	024	16·5	−17·4	260	1·8	− 0·8
502	1·8	− 2·0	224	4·1	− 3·2	460	3·9	4·3
602	1·1	− 1·3	424	7·3	6·7	660	2·7	3·1
702	3·4	− 3·9	126	3·7	− 3·7	062	2·7	2·9
004	12·1	−11·7	326	3·3	− 3·6	162	5·4	− 5·1
104	1·6	− 1·6	028	1·7	2·3	262	2·1	2·5
204	2·3	1·8	131	15·5	−16·0	362	6·6	− 6·9
304	1·8	− 1·3	231	6·6	6·2	462	1·6	1·7
404	11·2	10·8	331	13·6	−13·5	562	2·0	− 2·0
604	2·7	1·9	431	1·0	− 1·1	064	7·5	7·9
006	4·0	4·8	531	1·9	− 1·7	264	4·1	4·1
106	5·9	− 6·0	631	2·6	− 2·7	366	1·4	2·2
206	4·6	3·7	731	3·1	3·4	171	2·7	2·4
306	6·3	− 7·3	931	1·0	1·6	271	4·4	− 4·3
008	4·6	5·9	133	14·3	−14·4	371	4·9	4·7
208	1·4	2·1	233	6·3	5·8	471	1·7	− 1·9
111	50·6	60·8	333	1·7	− 0·6	571	2·3	2·3
211	38·1	38·1	433	1·1	− 1·0	173	7·0	7·5
311	3·3	− 2·7	533	1·9	1·8	273	3·8	− 3·9
411	6·9	6·0	633	1·8	− 1·7	373	1·8	1·5
511	9·2	− 8·1	135	6·1	− 5·8	473	1·2	− 1·4
611	3·7	− 3·8	235	2·7	− 2·6	573	1·3	− 1·8
711	1·1	− 1·2	337	1·2	− 1·8	175	4·0	4·5
811	1·6	− 1·0	040	24·1	− 27·3	275	1·4	1·6
911	0·8	− 0·5	240	17·4	−18·3	080	1·8	0·6
113	8·2	− 8·8	440	5·5	− 4·9	280	3·9	3·5
213	17·5	17·5	640	4·1	4·4	480	3·4	3·8
313	10·1	10·1	840	2·8	3·5	082	4·6	4·0
413	4·7	3·8	042	12·9	−12·5	182	2·5	− 2·7
513	6·5	6·0	242	10·7	−10·1	282	3·4	2·9
613	3·2	− 3·0	342	3·8	− 3·9	382	1·7	− 2·3
713	1·6	− 0·9	442	2·8	− 1·9	582	1·2	1·3
115	3·6	− 3·1	542	4·2	− 4·3	084	4·7	5·1
215	7·9	− 8·6	642	1·3	1·1	284	1·7	1·8
315	4·9	4·6	044	5·9	− 5·3	391	1·5	1·7
415	3·8	− 3·3	244	2·1	− 1·5	491	1·0	0·8
515	3·1	2·8	046	2·2	− 2·5	393	1·0	− 1·0
117	4·3	5·1	246	1·7	− 2·2	493	0·7	0·9
217	3·1	− 3·5	546	1·4	2·0	0.10.0	1·8	− 2·3
020	33·7	36·9	151	13·0	−12·5	0.10.2	1·5	− 1·9
220	2·6	− 2·0	251	6·2	− 5·5	1.10.2	1·1	− 0·6
420	13·0	−13·3	351	4·2	− 3·1	2.10.2	1·2	− 1·3
620	1·9	− 1·5	451	4·5	− 4·7	1.11.1	1·4	− 1·6

TABLE 1 (cont.)

hkl	$|F_{obs.}|$	$F_{calc.}$	hkl	$|F_{obs.}|$	$F_{calc.}$	hkl	$|F_{obs.}|$	$F_{calc.}$
k + l odd								
210	11·7	11·1	432	5·0	4·4	561	4·5	− 4·8
410	3·8	3·8	532	1·6	− 1·5	761	1·2	− 1·6
610	1·7	1·5	632	1·5	1·6	063	5·7	− 5·8
810	1·6	1·9	732	3·8	− 4·8	163	5·3	− 5·1
112	10·0	10·4	134	1·5	− 1·3	263	1·5	− 1·1
212	15·3	15·6	234	3·0	2·9	363	6·1	− 6·6
312	6·4	5·9	434	7·2	7·7	463	1·5	1·8
412	9·9	8·7	634	3·9	4·3	563	1·7	− 2·1
512	1·2	− 1·1	136	1·7	− 1·6	065	2·1	2·6
612	2·9	3·0	336	1·6	− 1·9	165	2·8	− 2·9
712	1·8	− 2·6	041	5·4	− 5·4	365	2·8	− 3·6
214	6·4	6·3	141	2·6	2·6	270	6·1	6·2
414	8·2	8·1	241	6·5	5·8	470	1·5	1·4
614	3·9	3·9	341	4·7	− 4·3	670	1·2	− 1·3
021	10·4	11·0	441	3·1	2·8	172	6·4	− 6·5
121	10·7	11·0	541	6·5	− 6·8	272	1·5	− 1·3
221	13·0	12·9	641	2·4	− 2·8	372	1·6	1·9
321	8·9	8·1	841	1·5	− 1·9	472	1·4	− 1·4
421	1·0	0·7	143	3·7	− 2·9	572	2·1	2·4
521	1·9	1·7	243	1·9	1·6	274	4·7	− 5·4
621	4·5	− 3·2	443	2·5	2·5	176	1·9	2·7
721	1·8	2·1	543	2·0	2·0	081	4·6	− 4·6
821	1·5	− 2·2	643	1·8	− 2·3	181	3·2	3·5
023	4·7	4·5	045	1·7	− 1·7	281	1·5	− 1·5
123	6·4	6·3	145	1·5	− 1·8	381	4·4	5·0
223	6·6	6·2	245	2·0	− 2·0	481	1·6	2·2
323	14·1	14·3	250	3·5	2·9	581	1·3	1·8
423	4·5	3·9	450	8·5	− 8·6	083	3·2	− 3·1
523	8·4	9·3	650	5·9	− 6·1	183	1·5	− 1·7
623	2·0	− 2·4	152	5·3	− 5·5	383	1·6	− 1·7
723	1·6	2·1	252	5·3	− 4·9	483	1·1	1·5
025	1·8	− 2·1	352	4·8	4·2	085	2·7	3·5
125	2·1	1·6	452	4·9	− 5·0	290	5·2	5·8
225	1·5	− 1·4	652	2·2	− 2·9	490	3·6	4·1
325	4·7	5·2	752	2·0	− 2·5	192	2·4	− 2·7
525	5·5	5·8	154	1·7	− 1·4	292	1·6	1·6
625	1·9	2·2	254	6·0	− 6·0	392	0·9	1·0
230	4·5	3·9	256	1·7	− 2·0	492	1·6	2·0
430	6·7	− 6·2	356	1·5	− 2·0	592	0·9	1·7
630	2·7	− 2·4	061	8·5	− 8·1	294	1·9	− 1·0
830	1·8	2·5	161	2·2	2·0	0.10.1	1·7	− 1·3
132	7·1	6·9	261	1·1	− 1·3	1.10.1	1·2	1·3
232	5·4	5·4	361	1·6	− 1·5	3.10.1	1·6	2·2
332	9·6	8·9	461	3·0	2·8			

The $|F_{obs.}|$ are on the scale found in the two-dimensional refinement. The $F_{calc.}$ are those from the fifth anisotropic refinement cycle.

In the unit cell of benzene, there are two differently oriented sets of molecules, whose transforms must be superimposed in order to derive the transform of the unit cell. For a given trial direction of the molecular plane normal, the procedure was to draw out a projection of the zone net on to the plane in which each reciprocal lattice point had a weighting factor equal to the structure factor divided by the

appropriate atomic scattering factor, a temperature factor B of $6 \cdot 0$ Å² being assumed. The transform contour map of the benzene molecule was then super-imposed and the two contributions combined at various orientations until the best fit with the weighted reciprocal lattice was obtained. This yielded the best mole-cular orientation for the given direction of the plane normal. Of the three principal zones, various projections of the $(0kl)$ net gave the most useful results. One in which the normal to the plane of the ring had direction angles $(44, 75, 50°)$ and the trans-form had been rotated by $7\frac{1}{2}°$ gave a residual $R(||F_{\text{obs.}}| - |F_{\text{calc.}}||/|F_{\text{obs.}}|)$ of 21%. These angles were quite close to the final values $44° \, 49'$, $77° \, 04'$ and $48° \, 04'$.

The co-ordinates derived from this model were then used to calculate a series of Fourier projections and difference maps on (100) and (001). The refinement of the co-ordinates was continued until R had dropped to about 10% for both projections. The C—C bond lengths were then $1 \cdot 39_2$, $1 \cdot 37_7$ and $1 \cdot 39_5$ Å, giving a mean value of $1 \cdot 38_8$ Å.

In the next stage of the refinement, all the three-dimensional data were used to calculate sets of differential syntheses based on the assumption of isotropic carbon atoms, with back shift corrections to allow for finite series errors (Booth 1946). These and many subsequent calculations were carried out on the Ferranti mark I electronic computer at Manchester University by means of programmes based on those described by Ahmed & Cruickshank (1953). Five cycles of refinement were computed. The value of the scale factor for the $|F_{\text{obs.}}|$ was estimated from the two-dimensional work. The $F_{\text{calc.}}$'s were based on McWeeny (1952) scattering factors for carbon and a temperature factor B of $6 \cdot 0$ Å². The hydrogen atoms were assumed to be situated at a distance of $1 \cdot 08$ Å radially from each carbon atom and to have a temperature factor of $9 \cdot 0$ Å². After each cycle on the computer, the corrections to the carbon maxima from the $F_{\text{obs.}}$ syntheses were combined with the back-shift corrections from the $F_{\text{calc.}}$ syntheses to give a new set of co-ordinates which were fed into the next cycle.

After the fifth cycle, the residual R had dropped to $14 \cdot 2 \%$. The equation of the best plane through the molecule was

$$0 \cdot 7109x + 0 \cdot 2229y + 0 \cdot 6671z = 0$$

and the perpendicular deviations of the carbon atoms were $C_1 - 0 \cdot 0015$, $C_2 + 0 \cdot 0015$ and $C_3 - 0 \cdot 0015$ Å. The C—C bond lengths were now $1 \cdot 377$, $1 \cdot 382$ and $1 \cdot 374$ Å, giving a mean of $1 \cdot 378$ Å. It may be remarked that the effect of the finite series corrections was to enlarge the ring from a mean C—C length of $1 \cdot 369$ to $1 \cdot 378$ Å, as they had in dibenzyl (Cruickshank 1949). An examination of the structure factors showed that of the sixteen reflexions with $\sin \theta < 0 \cdot 30$, only three, 200, 020 and 111, showed definite signs of extinction. After correction of these and three others (002, 211 and 102) for primary extinction, R dropped from $14 \cdot 2$ to $13 \cdot 1 \%$.

The standard deviation of the carbon co-ordinates was estimated by Cruick-shank's (1949) method to be $0 \cdot 0057$ Å. If the errors in the three carbon atoms were uncorrelated, the e.s.d. of the mean bond length would be $0 \cdot 0045/\sqrt{3}$ or $0 \cdot 0033$ Å. As some correlation is to be expected, the e.s.d. of the mean bond length should lie between $0 \cdot 0033$ and $0 \cdot 0057$ Å. On this basis, neither the small differences between

the three independent bond lengths nor the small deviations from planarity are significant. However, the results at this stage of the analysis (Cox & Smith 1954) revealed a significant difference between the X-ray mean value of 1·378 Å and the value of 1·397₃ Å obtained by Stoicheff (1954) from measurements of the Raman spectrum of the vapour at 61 °C. The reasons for this unexpected difference were not apparent until further computations of the electron density distribution in the molecule had been made.

4. THE ELECTRON DENSITY AND DIFFERENCE MAPS

Since the results from the differential syntheses refer only to the electron density near the atomic centres, the next step in the structure analysis was to examine the electron density of the molecule as a whole. The Manchester University computer
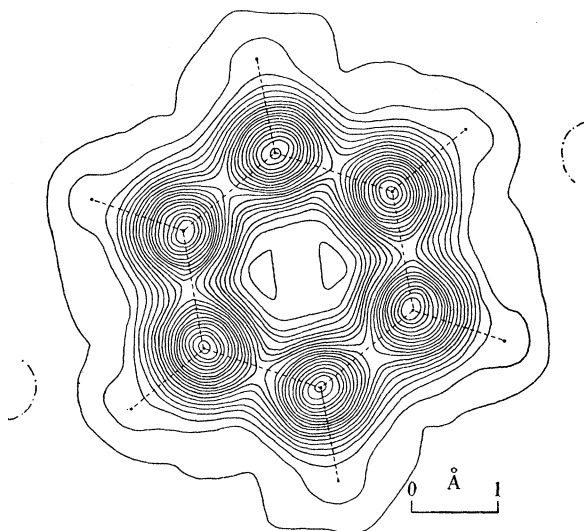
FIGURE 1. Electron density map of benzene in the plane of the molecule after the fifth isotropic cycle. Contour interval 0·25 e/Å³. —, positive contours; – · – · – ·, zero contour.

was therefore programmed by Drs F. R. Ahmed and D. W. J. Cruickshank and Miss D. E. Pilling to compute the electron density directly in the (non-crystallographic) plane of the molecule. The computation was done at intervals of about 0·18 Å with all the three-dimensional data (with extinction corrections). The resulting contour map is shown in figure 1; the contour interval is 0·25 e/Å³, the zero contour being the dot-dash line. (In examining this, the reader should remember that each molecule lies at a crystallographic centre of symmetry, so that one half of the diagram is necessarily an inversion of the other.) The map shows clearly the electron density maxima of about 5·25 e/Å³ corresponding to the six carbon atoms. Because of the large thermal motion, the hydrogen atoms do not appear as distinct peaks but as spurs running out from the carbon atoms, producing noticeable extensions in the 0·50 e/Å³ contour. In the diagram, the C—H bonds are represented by lines of lengths corresponding to 1·08 Å drawn radially from each carbon atom. Other features of this map will be discussed later, but it must

be stressed that care is needed in its interpretation, since it represents the time-averaged electron density, subject to finite-series and experimental errors, of the benzene crystal at -3 °C and not the density of a benzene molecule at rest.

Difference maps were also computed in planes coincident with and at distances of $\frac{1}{6}$, $\frac{1}{3}$ and $\frac{1}{2}$ Å above and below the molecular plane. For these, the Fourier coefficients were ($F_{obs.} - F_{calc.}$), the $F_{calc.}$'s having been calculated for the carbon atoms only at positions obtained after the fifth differential synthesis, with the McWeeny (1952) scattering factor curve for the sp^3 valence state reduced by an
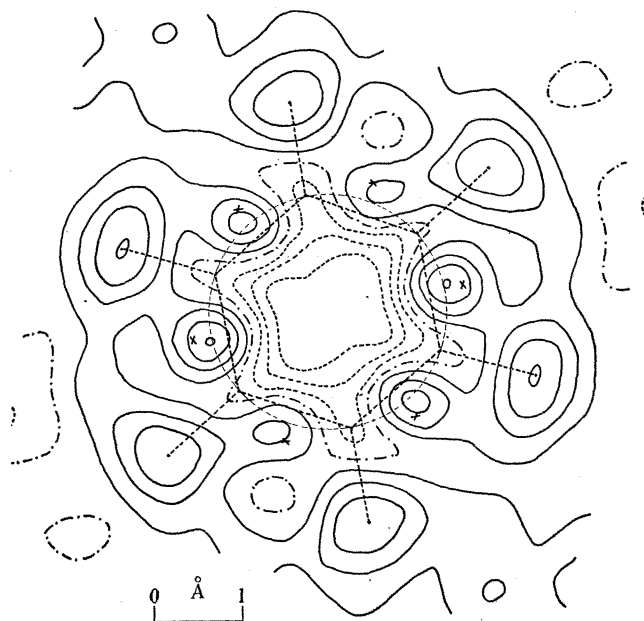
FIGURE 2. Difference map of benzene in the plane of the molecule after the fifth iso-tropic cycle. Contour interval 0·1 e/Å³. ——, positive contours; $- \cdot - \cdot -$, zero contour; $----$, negative contours.

isotropic temperature factor of $B = 6\cdot0$ Å² as in the earlier calculations. This map should give the difference between the actual benzene crystal electron density and that of isotropically vibrating 'molecules' of six carbon atoms with the Duncanson & Coulson (1944) wave functions, subject possibly to the effects of incorrect scaling of the experimental data. The difference map in the plane of the molecule is shown in figure 2. The contour interval is $0\cdot1$ e/Å³ and the standard deviation of the electron density as calculated by Cruickshank's (1949) formula is $0\cdot11$ e/Å³. The hydrogens are now revealed as distinct peaks of approximately $0\cdot35$ e/Å³ maximum density. The other significant features are six peaks of approximately $0\cdot3$ e/Å³ lying on a circle, one peak just outside the mid-point of each C—C line. (For comparison, the circumscribing circle of the carbon hexagon is shown, and the intersections of its tangents at the carbon atoms are marked by crosses.)

These peaks show that the time-averaged electron density of the carbon atoms is not spherically symmetrical, but is greater in directions roughly tangential to the circumscribing circle. This can be accounted for by supposing that the thermal

motion of each carbon atom is anisotropic with maximum amplitude in the directions of the tangent, and that the separate peaks so produced by each pair of adjacent atoms are unresolved (and therefore nearer the centre than the intersection of the tangents). Superimposed on this there may be an effect due to the concentration of bonding electrons between the atoms, but any such effect must be slight since the peaks (which are sharper than the hydrogens) are too sharp to be accounted for in this way and are not on the lines of centres of the atoms.

Thus the difference map shows that in the plane of the molecule each carbon atom has its maximum vibration at right angles to the radius. As the difference maps in the planes adjacent to the central molecular plane showed no features as large as these, the maximum vibrations are all in the plane of the molecule. Since, at the temperature in question, the total r.m.s. amplitude of a carbon atom in the internal vibrations of a molecule is only of the order of 0·04 Å (see, for example, Higgs 1955), these directions of maximum atomic vibration can only be explained by the supposition that in the crystal each molecule performs appreciable rigid-body oscillations about its senary axis. This is supported by the elliptical contours of the hydrogen atoms in the difference map, figure 2. Examination of figure 1 shows that the carbon contours near the maxima are also slightly elliptical and that the contours in the C—C bridges are displaced a little outside the centres of the C—C lines. This conclusion regarding angular oscillations accords well with proton magnetic resonance experiments on crystalline benzene by Andrew & Eades (1953), who showed that rotational transitions of the molecules about their senary axes began to narrow the absorption line above 120 °K.

The remaining important feature of the difference map is the large negative area within the hexagon. This will be mentioned again later.

The existence of molecular angular oscillations explains why the C—C length of 1·378 Å derived from the fifth differential synthesis is shorter than Stoicheff's value (1954) of $1·397_3$ Å derived from the rotational Raman spectrum. This is because the time-averaged density-maximum of an atom vibrating along the arc of a circle will lie inside the arc (Cox, Cruickshank & Smith 1955). A detailed formula for the effect will be introduced later, but order of magnitude considerations show that the displacement is approximately $\frac{1}{2}r\theta^2$, where r is the radius of the arc and θ the r.m.s. angular amplitude. In benzene, if θ were 10°, then with $r = 1·39$ Å, the error would be 0·021 Å. The effect is thus of the right order of magnitude to explain the bond-length difference.

5. DETERMINATION OF THE ANISTROPIC THERMAL MOTION

There are two possible methods of estimating the r.m.s. amplitudes of the molecular angular oscillations (assumed harmonic) and of determining the correct atomic positions. The direct method involves the calculation of structure factors for an angularly oscillating molecule, the magnitude of the oscillations being adjusted to remove the peaks from the difference map. The co-ordinate corrections can then be found by comparing the positions of the maxima in the calculated

electron density before and after the introduction of the angular oscillations. The chief difficulties of this method are the rather elaborate calculations required.

The alternative approximate method, which was that actually used, is to determine the anisotropic thermal motion of each atom separately, on the assumption that, as a first approximation, it vibrates linearly rather than along arcs of circles. The individual linear vibrations can then be interpreted in terms of the translational and angular oscillations of the molecule as a whole. The maxima of the calculated electron density computed with the linear vibrations are not shifted by any angular oscillation effects, so that the positional corrections have to be found by a separate analysis based on the inferred oscillation amplitudes. The errors of this approximate procedure should not be serious for the fairly small angular oscillations involved.

The linear anisotropic harmonic oscillations of an atom require six parameters for their specification, so that in the atomic scattering factor the usual isotropic temperature term $\exp\{-B(\sin\theta/\lambda)^2\}$ is replaced by

$$\exp-(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2), \tag{1}$$

in which the b_{ij}'s are related to the components of the mean-square vibration tensor (Cruickshank 1956a). The six b_{ij}'s may be determined by making the six second derivatives ($\partial^2\rho/\partial x^2$, $\partial^2\rho/\partial x\partial y$, etc.) equal for the observed and calculated electron densities at the atomic position (Cochran 1951). The actual calculation of the b_{ij}'s for the carbon atoms in benzene was carried out by a process of successive Fourier refinement (Cruickshank 1956a) similar to that used for the determination of the anisotropic thermal motion in anthracene (Cruickshank 1956d, 1957a) and naphthalene (Cruickshank 1957b). For benzene, however, the scale factor of the $|F_{\text{obs.}}|$ was unknown and so had to be treated as an additional parameter. A convenient technique for determining the scale and anisotropic thermal parameters simultaneously is to add to the curvature criteria the requirement that the mean observed and calculated peak densities shall be equal.

In the earlier stages of the refinement of the thermal and scale parameters an attempt was made, as with anthracene and naphthalene, to reduce the possible influence of bonding electrons by determining these parameters from reflexions of high $\sin\theta$. The high-order reflexions used were those with $\sin\theta > 0\cdot50$. With these high-order planes, fairly good refinement of the parameters were achieved by the third anisotropic cycle (overall $R = 10\cdot1\%$), the scale factor of the $|F_{\text{obs.}}|$, relative to that derived from the two-dimensional refinement, then being $0\cdot92$. Unfortunately, the difference map sections computed at this stage were most implausible, as the difference density was negative over almost the whole volume of the molecule, the net deficiency being about five electrons. The most likely reason for this is a slight systematic variation of the $|F_{\text{obs.}}|$ with $\sin\theta$, due possibly to a lack of correction for absorption and to systematic errors in the estimation of the photographic intensities.

A fourth anisotropic cycle, based on all the observed reflexions rather than only the high-order ones, gave better but still unsatisfactory difference map sections, the scale factor being $1\cdot02$. The requirement of equal mean observed and calculated

peak densities was therefore abandoned, and the scale and thermal parameters were then determined from the criteria that the difference map density should integrate to zero in a reasonable molecular volume and that the observed and calculated peak curvatures (all reflexions) should be equal. A fifth and final anisotropic cycle, with overall $R = 10.5 \%$, in which the structure factors were calculated from parameters appropriate to a scale factor of 1.07, indicated that these new criteria would be met by a scale factor of 1.14. Before we analyze the corresponding thermal parameters, it will be convenient to describe some features of the molecular electron density shown by the difference maps.
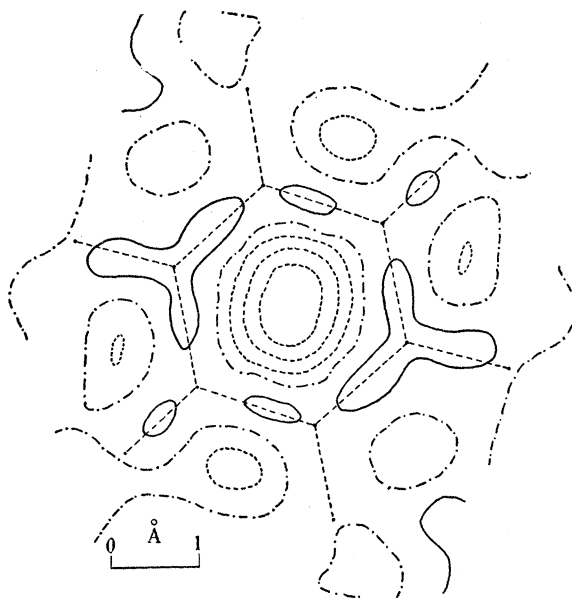
FIGURE 3. Difference map of benzene in the plane of the molecule after the fifth anisotropic cycle. Contour interval 0.1 e/Å³. ——, positive contours; –·–·–·, zero contour; – – – –, negative contours.

As we have said, the last set of structure factors was calculated from parameters appropriate to a scale of 1.07. The difference-map section, $(1.07\rho_{obs.} - \rho_{calc.})$, which was then computed for the central plane of the molecule is shown in figure 3. (Hydrogen atoms, at the same assumed positions, with isotropic B's of 7.6 Å², were included in the $F_{calc.}$'s.) By extrapolation from the difference maps of earlier cycles, it may be conjectured that a difference map calculated with parameters appropriate to a final scale of 1.14 would show a depression at the centre of the ring of about -0.35 e/Å³, slight depressions in the areas between the C—H spokes of perhaps -0.15 e/Å³, and positive regions around the lines of the bonds with maxima of perhaps 0.25 e/Å³. These features, although probably rather unreliable in view of the difficulties encountered, are very similar to those obtained in the final difference maps of anthracene and naphthalene. Reference may be made to the paper on anthracene (Cruickshank 1956d) for some discussion of them in terms of the bonding electron distribution.

6. Description of the anisotropic thermal motion

The final set of anisotropic thermal parameters b_{ij} were determined after the fifth anisotropic cycle from the peak curvatures calculated with all the observed reflexions and the scale factor of $1 \cdot 14$ for the $|F_{\text{obs.}}|$. The b_{ij}'s for each atom were then transferred to symmetric tensors $\mathbf{U}$ defined so that

$$\overline{u^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} l_i l_j \tag{2}$$

is the value of the mean-square oscillation in Å^2 in a direction $\mathbf{l} = (l_1, \ l_2, \ l_3)$ (Cruickshank 1956 a). (For isotropic motion the ordinary temperature parameter $B = 8\pi^2 \overline{u^2}$). These tensors were referred to the (natural) molecular axes shown in figure 4: axis 1 passes through the centre and C_1, axis 2 through the mid-point of
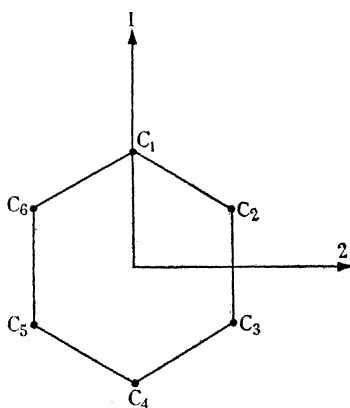

FIGURE 4. Molecular axes used in defining the U_{ij} tensor.

TABLE 2. U_{ij} (Å^2) FOR THE CARBON ATOMS

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
C_1	0·0633	0·0901	0·0601	$-0 \cdot 0057$	0·0013	$-0 \cdot 0004$
C_2	0·0830	0·0630	0·0672	$-0 \cdot 0196$	0·0006	$-0 \cdot 0029$
C_3	0·0918	0·0610	0·0542	0·0132	0·0025	$-0 \cdot 0057$

C_2—C_3, and axis 3 is the senary axis perpendicular to the plane. The values of the six independent U_{ij}'s for each atom are shown in table 2. The angular oscillation about the senary axis is very clearly illustrated by figure 5 which shows the values of $\overline{u^2}$ for each atom in the radial and tangential directions in the molecular plane, and also the values perpendicular to the plane. For each atom the tangential component is considerably larger than the radial component. The mean values of $\overline{u^2}$ and the corresponding B's are

tangential	0·0934 (Å^2)	7·38 (Å^2)
radial	0·0572	4·52
out of plane	0·0605	4·78

There is thus a difference of $0\cdot0362$ Å² in the tangential and radial $\overline{u^2}$ which is due to the angular oscillation about the senary axis. This corresponds to an oscillation of $7\cdot9°$ r.m.s. amplitude.

It is possible to give a fuller description of the anisotropic thermal motion in the manner suggested by Cruickshank (1956*b*). At $-3\ ^{\circ}\mathrm{C}$ the internal vibrations are sufficiently small for the whole molecular motion to be analyzed in terms of rigid body vibrations. The harmonic vibrations of a rigid body can be expressed in terms of two symmetric tensors, each with six independent components, namely, **T**,
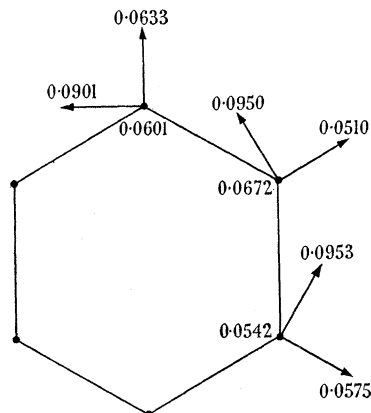
FIGURE 5. Components of $\overline{u^2}$ (Å²); values perpendicular to the plane given inside the ring.

TABLE 3. COMPONENTS OF THE **T** AND **ω** TENSORS

$$T_{ij} = \begin{pmatrix} 0\cdot0615 & -0\cdot0041 & -0\cdot0022 \\ & 0\cdot0536 & 0\cdot0024 \\ & & 0\cdot0610 - 0\cdot0241\omega_{11} \\ & & (0\cdot0456) \end{pmatrix}$$
(Å²)

$$\omega_{ij} = \begin{pmatrix} \omega_{11} & -0\cdot0035 & 0\cdot0008 \\ (0\cdot0082) & & \\ & \omega_{11} - 0\cdot0005 & 0\cdot0010 \\ & (0\cdot0077) & \\ & & 0\cdot0189 \end{pmatrix}$$
(radians²)

giving the translational vibrations of the mass centre, and **ω**, giving the angular oscillations about axes through the centre. The value of $\overline{u^2}$ in a direction **l** at a point **r** in the body is then

$$\overline{u^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} l_i l_j = \sum_{i=1}^{3} \sum_{j=1}^{3} \{T_{ij} l_i l_j + \omega_{ij} (\mathbf{l} \times \mathbf{r})_i (\mathbf{l} \times \mathbf{r})_j\}. \tag{3}$$

Conversely, given the **U** tensors for a sufficient number of atoms, the 12 components of the **T** and **ω** tensors can be determined by the method of least squares. The **T** and **ω** tensors so obtained for benzene are given in table 3, though only 8 out of the 12 molecular parameters can be determined unambiguously from the 18 atomic U_{ij}'s. The difficulty arises with the magnitudes of the vibrations perpendicular to the plane of the molecule, for which the four parameters T_{33}, ω_{11}, ω_{22} and ω_{12} are functions of the three U_{33}. In table 3, T_{33}, ω_{12} and ω_{22} have been expressed in terms of ω_{11} as the residual unknown.

An attempt to estimate ω_{11} may be made by comparison with the results for anthracene (Cruickshank 1956d, 1957a) where the motion can be determined uniquely. The projection of the anthracene molecule viewed down its long axis is rather similar to that for benzene viewed along axis 2, as the distances of the carbons and hydrogens from these axes are common to the two molecules. In anthracene $T_{33} = 0.0266$ Å^2 and the contribution to U_{33} of the angular oscillation about the long axis, for an atom at the same distance as C_1 in benzene is from axis 2, is 0.0087 Å^2. If the same proportion between the angular and translational oscillations holds in benzene, $T_{33} = 0.0456$ Å^2, $\omega_{11} = 0.0082$ and $\omega_{22} = 0.0077$. These estimates are necessarily rather approximate.

The accuracy of the data hardly justifies a precise determination of the principal axes of the $\mathbf{T}$ and $\boldsymbol{\omega}$ tensors, but within this accuracy axis 3 is the direction of maximum angular oscillation. ω_{33} represents an r.m.s. angular oscillation of 7·9° about the senary axis, while the rather rough values for the maximum and minimum r.m.s. vibrations about axes in the plane are 6·2 and 3·8°. The component of $\overline{u^2}$ tangential to the ring for a carbon atom is $\omega_{33}r^2 = 0.0357$ Å^2, which agrees closely with the value of 0.0362 Å^2 derived earlier. The r.m.s. translational amplitudes in the directions 1, 2 and 3 are 0·25, 0·23 and 0·21 Å, respectively.

The chief errors in these estimates of the magnitudes of the vibrations undoubtedly arise from the causes of the uncertainty of the scale factor, rather than from random errors in the experimental data. In the third anisotropic cycle, in which only the high-order planes were used, the mean $\overline{u^2}$ values for the tangential, radial and out of plane vibrations were 0·105, 0·073 and 0·073 Å^2, compared with the final values of 0·0934, 0·0572 and 0·0605 Å^2. If the high-order results are in fact correct the final $\overline{u^2}$ values are some 15 % too low, though the value of ω_{33}, needed for the bond length correction, was only 0·017 in the third cycle as compared with the final 0·0189.

7. The final C—C bond length

The co-ordinates of the carbon atoms derived after the fifth anisotropic cycle are given in table 4. They have been corrected for the usual finite series errors by Booth's back-shift method (1946), but not for the effects of the angular oscillations, which will be discussed shortly. The bond lengths and bond angles derived from these co-ordinates are given in table 5. The differences between the three crystallographically independent bond lengths are not significant and the mean value is 1·377 Å.

The best plane through the carbon co-ordinates is

$$0.70939x + 0.22394y + 0.66830z = 0,$$

the origin being at the centre of symmetry and the co-ordinates (x, y, z) in Å. The perpendicular distances of the atoms from this plane are $C_1 + 0.0013$, $C_2 - 0.0013$ and $C_3 + 0.0013$ Å, which are not significant, showing that the molecule is accurately planar. The plane normal is inclined at 44° 49′ to the a-axis, 77° 4′ to the b-axis and 48° 4′ to the c-axis.

The corrections to the co-ordinates due to the angular oscillations must now be considered. A carbon position is in error not only because of the oscillation of the molecule about the axis perpendicular to the molecular plane, but also because of the oscillation about an axis in the molecular plane perpendicular to the radius to that atom. In this second oscillation, the atom is moving on the arc of a circle in a plane perpendicular to the molecular plane. As mentioned in §4, these oscillations cause an atom to appear closer to the centre than it should. Cruickshank (1956c) has shown that for small oscillations the corrections for the two are additive, and that for any one oscillation the error in position is

$$\Delta r = \frac{1}{2r} \frac{s^2}{1 + s^2/q^2},\qquad (4)$$

where r is the radius, s^2 the mean-square amplitude of vibration along the circular arc and q^2 is the variance of a Gaussian function selected to fit the atomic shape

TABLE 4. CARBON CO-ORDINATES WITHOUT CORRECTIONS FOR ANGULAR
OSCILLATIONS AS FRACTIONS OF THE CELL SIDES

	x	y	z
C_1	−0·05080	0·13702	−0·00563
C_2	−0·12871	0·04756	0·12272
C_3	−0·07836	−0·08909	0·12952

TABLE 5. CARBON BOND LENGTHS AND ANGLES

C_1—C_2	1·379 Å	$C_6\widehat{C}_1C_2$	119° 50′
C_2—C_3	1·374 Å	$C_1\widehat{C}_2C_3$	120° 42′
C_3—C_4	1·379 Å	$C_2\widehat{C}_3C_4$	119° 28′

TABLE 6. FINAL CARBON CO-ORDINATES (Å) AFTER ALLOWING FOR
THE EFFECT OF THE ANGULAR OSCILLATIONS

	x	y	z
C_1	−0·3834	1·3398	−0·0401
C_2	−0·9713	0·4650	0·8732
C_3	−0·5914	−0·8711	0·9216

after allowing for finite series and translational vibrations. For the ω_{33} oscillation in benzene, $s^2 = 0.0362$ Å^2; q^2 is considerably larger than s^2 and so need not be determined accurately; its approximate value is 0·13 Å^2. With $r = 1.39$ Å, the correction to the oscillation about the senary axis is $\Delta r = 0.010$ Å.

No such precise estimate can be given for the correction due to the oscillation about the axis in the plane of the molecule because of the uncertainty in the value of ω_{11}. With the conjectured value of T_{33}, and using a mean of ω_{11} and ω_{22}, $\Delta r = 0.005$ Å. The total correction to the C—C bond length is thus $0.010 + 0.005 = 0.015$ Å, giving a final length of $1.377 + 0.015 = 1.392$ Å. The revised co-ordinates obtained by shifting each carbon atom by 0·015 Å radially outwards are given in table 6. The equation of the molecular plane is not affected by the angular oscillation corrections, as these shift the atoms radially only.

The accuracy of the value for the mean bond length is not easy to estimate.

Cruickshank's (1949) formula for the estimated standard deviation of a carbon co-ordinate gives $\sigma(x) = 0\cdot0041$ Å. However, this formula, which uses $|F_{obs.} - F_{calc.}|$ as an estimate for each $\sigma(F)$, is only valid if there is no correlation between the $|F_{obs.} - F_{calc.}|$ for different hkl. Such correlations are caused by any imper-fections of the calculated model and by systematic experimental errors such as absorption errors. Cruickshank showed that the formula would, nevertheless, generally give a reasonable estimate of the combined effects of imperfect finite series correction and of all experimental errors on the co-ordinates of any one atom, though the effects on the atoms of a benzene ring might be interrelated. The only definitely uncorrelated effects for the three independent atoms in benzene are those due to the random errors in the intensity estimates. The e.s.d. of a co-ordinate due to these random errors is estimated from the multiple observations of each $|F_{obs.}|$ to be $0\cdot0023$ Å. Assuming the worst case, namely, that the remaining sources of error in the individual e.s.d. of $0\cdot0041$ Å affect each atom radially by the same amount, Cruickshank's method gives the e.s.d. of the mean C—C distance as

$$\{0\cdot0041^2 - \tfrac{2}{3}(0\cdot0023)^2\}^{\frac{1}{2}} = 0\cdot0036 \text{ Å},$$

since the mean C—C distance is effectively the mean distance of the three carbons from the symmetry centre.

To this e.s.d. must be added allowances for any errors in the correction for the angular oscillations. The chief uncertainty in the correction arises from the use of a conjectural value for ω_{11}. Any revision of this would seem unlikely to alter the correction for oscillations about axes in the molecular plane, now $0\cdot005$ Å, by more than $0\cdot003$ Å. The value for ω_{33} is also subject to some error, while equation (4) is valid only for small harmonic oscillations of peaks of Gaussian shape.

It is therefore perhaps prudent to claim no more than that the most probable X-ray value of the C—C bond length in benzene is $1\cdot392$ Å and that differences of less than $0\cdot010$ Å from this cannot be considered significant. The small difference of $0\cdot005$ Å between this and Stoicheff's value of $1\cdot397_3$ Å is thus not significant.

Some other important determinations of the dimensions of the benzene molecule are as follows. Langseth & Stoicheff (1956), extending Stoicheff's earlier work on the rotational Raman spectrum of the gas, obtained C—C $1\cdot397_4 \pm 0\cdot001$ Å and C—H $1\cdot084 \pm 0\cdot005$ Å. Bastiansen (1957) from electron diffraction of the gas obtained C—C $1\cdot397_4$ Å and C—H $1\cdot081$ Å. Andrew & Eades (1953) from proton magnetic resonance experiments on the solid obtained $2\cdot495 \pm 0\cdot018$ Å for the shortest intra-molecular H—H distances. If C—H is taken as $1\cdot084$ Å, this gives C—C $1\cdot411 \pm 0\cdot018$ Å.

The errors quoted for the Raman determination are for random errors only. The method yields very accurate moments of inertia I_0 for the ground vibrational states of C_6H_6, $C_6H_3D_3$ and C_6D_6, but in the determination of the molecular dimensions the I_0's are treated as if they were the equilibrium I_e's. This introduces some sys-tematic error, almost certainly less than $0\cdot005$ Å, into the results. Though they may in fact measure slightly different things, the four methods yield C—C distances which are not significantly different. Certainly there is no significant evidence for different bond lengths in the solid and vapour phases.

8. THE CRYSTAL STRUCTURE

As already mentioned in §4, the appreciable angular oscillations of the molecules about their senary axes accord well with the proton magnetic resonance experiments of Andrew & Eades (1953), who showed that occasional rotations of the molecules narrow the absorption line at temperatures above 120 °K. The description of the packing of the molecules in the crystal which follows will enable the probable nature of these occasional rotations to be understood.
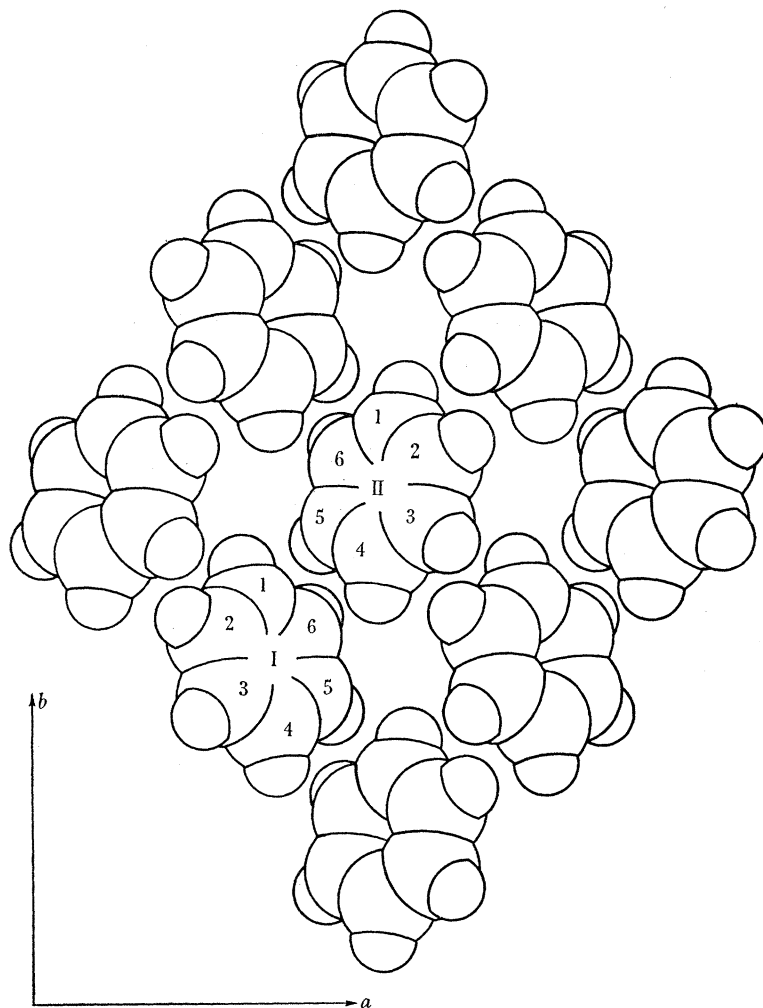

FIGURE 6. Diagram of the crystal structure of benzene viewed down the *c*-axis.

There are four molecules in a unit cell. The molecule whose co-ordinates are given in table 6 will be denoted as molecule I. Molecule II is related to I by reflexion in the plane at $x = \frac{1}{4}a$ followed by a translation of $\frac{1}{2}b$; III by reflexion in $y = \frac{1}{4}b$ and a translation of $\frac{1}{2}c$; and IV by reflexion in $z = \frac{1}{4}c$ and a translation of $\frac{1}{2}a$.

The arrangement of these molecules in space is illustrated in figures 6 and 7. Each has close contacts ($\sim 2 \cdot 75$ Å) with the others, and by the operations of the

space group every molecule has twelve near neighbours, the distances being the same in sets of four. Four molecules of type IV at the level $y = 0$ make contacts with I, while in each of the levels $y = \pm \frac{1}{2}b$ two molecules of type II and two of type III make contacts with I. There are no close contacts between similarly orientated molecules in adjacent unit cells.

The most interesting of the close contacts are those of the type between I and II (or III and IV). These pairs of molecules fit together like six-toothed bevel gear wheels whose axes are almost at right angles (actually $90°\ 22'$). The hydrogen H6 of molecule I ($H6_I$) meshes in between $H4_{II}$ and $H5_{II}$, the distances $H6_I$ to $H4_{II}$ and $H6_I$ to $H5_{II}$ being $2\cdot78$ and $2\cdot64\,\text{Å}$, respectively. In the long wave normal mode vibrations of the crystal the relative oscillations of I and II about their hexad axes
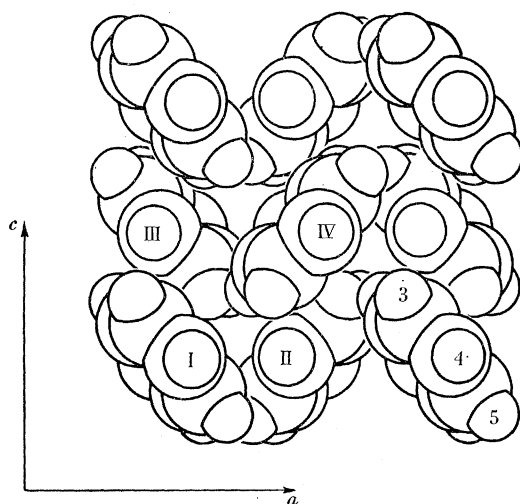

FIGURE 7. Diagram of the crystal structure of benzene viewed down the b-axis.

will either be exactly in phase or exactly out of phase with respect to the space group. The variation of the $H6_I$ to $H4_{II}$ and $H6_I$ to $H5_{II}$ distances with the angle of displacement in the two possible normal mode motions is shown in figure 8 (the positive sense is from $H1_I$ towards $H2_I$ and, in the in-phase motion, from $H4_{II}$ towards $H5_{II}$). In agreement with the idea of the two molecules as a pair of bevel gears the molecules keep farther apart in the in-phase motion than in the out-of-phase motion. In the in-phase motion the closest approach of $H6_I$ and $H4_{II}$ is $2\cdot23\,\text{Å}$ at $+24°$ displacement, and of $H6_I$ and $H5_{II}$ is $2\cdot56\,\text{Å}$ at $-10°$, whereas the closest approaches in the out-of-phase motion are $2\cdot49\,\text{Å}$ at $-14°$ and $2\cdot03\,\text{Å}$ at $19°$, respectively. Thus in the in-phase motion the molecules can rotate completely without the inter-hydrogen distances dropping below $2\cdot23\,\text{Å}$, while in the out-of-phase motion the distances would fall to $2\cdot03\,\text{Å}$.

An examination was also made of the non-normal-mode motion in which molecule I rotates while the adjacent molecules of type II remain stationary. In this motion the distances between I and the two molecules of type II at the level $y = \frac{1}{2}b$ are no longer the same. Though the distances between I and II are rather

favourable, the distances between I and II′ drop to 2·07 Å. Accordingly, unless co-operation with the translational vibrations momentarily increases all the distances from a molecule to its neighbours, rotation of a single molecule of type I most easily occurs when the adjacent molecules of type II are also rotating in phase. The molecules so related form corrugated sheets perpendicular to the *c*-axis, so that it is possible that all the molecules in a single sheet could rotate together. In this sense, the molecules of a sheet form a two-dimensional interlocking train of gears, in which the molecules of type II, though in phase with type I according to the space group, actually turn in the opposite direction, as is necessary in a gear train. The parallel sheets of molecules of types I and II are interleaved by similar sheets of molecules of types III and IV.
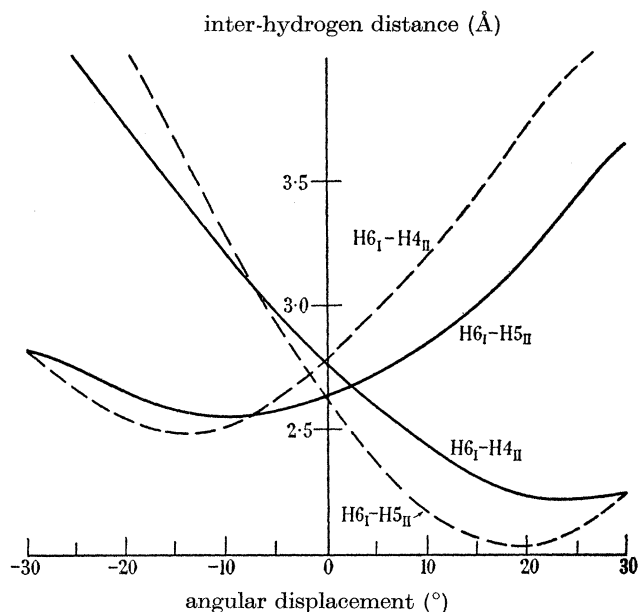

FIGURE 8. Variation of the inter-hydrogen distances during two normal mode motions. ——, in-phase motions; – – – –, out-of-phase motions.

The concept of a sheet of intermeshing rotating molecules is undoubtedly extravagant, since very high energies would be needed to set a whole sheet in rotation. It does, however, suggest that the observed occasional molecular rotations may be rotations of all the molecules within a small cluster rather than of single molecules. In general, a molecule moves more easily in phase than out of phase with its neighbours in the sheet. Some molecules will be temporarily almost at rest, while others will be near positions of maximum oscillation. One may suppose that the maximum amplitude of oscillation in a region occasionally exceeds 30°. When this occurs, it may sometimes be easier for the cluster of molecules whose oscillation has exceeded 30° to move on to a new mean position at 60° rather than to return to their original mean.

The axes of molecules I and III are inclined at 27° and they are not intermeshed, though this might have been possible. Whereas $H6_I$ meshes between $H4_{II}$ and $H5_{II}$,

2-2

here $H1_I$ and $H2_I$ lie over $H6_{III}$ and $H1_{IV}$, the distances being 2·76 and 2·71 Å, respectively. Accordingly, there can be very little 'drive' between I and III. In the in-phase motion of these molecules, the closest approach to $H1_I$ is 2·43 Å for $H6_{III}$ at $+30°$ (or equivalently for $H2_I$ to $H1_{IV}$ at $-30°$). For small oscillations the closest approaches in the out-of-phase motion are at the equilibrium position (2·76 and 2·71 Å), but in large oscillations $H1_I$ and $H2_I$ approach to within 2·43 Å of $H1_{IV}$ and $H6_{III}$, respectively. The distances between I and III during oscillations are thus greater than those between I and II, so that it is probable that any rotation of molecules of types I and II within a cluster does not extend to the neighbouring parallel sheets of molecules of types III and IV.

The planes of molecules I and IV are inclined at 84° and the extension of the plane of IV passes close to the centre of I. The closest approaches are $H4_I$ to $H3_{IV}$ 2·82 Å, $C4_I$ to $H3_{IV}$ 2·95 Å and $C1_I$ to $H2_{IV}$ 3·18 Å. No very close approaches can occur during angular oscillations about the senary axes. The closest a hydrogen of IV can come to the plane of I is 2·52 Å. The contacts between I and IV thus have a relatively small influence on possible molecular rotations.

The large coefficient of thermal expansion in the c-direction may then be explained, since the sheets of molecules of types I and II bind the structure more tightly in the a- and b-directions than do the sheets of molecules of types I and III extending in the b- and c-directions.

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