REVIEWS OF MODERN PHYSICS VOLUME 30, NUMBER 1 JANUARY, 1958

Crystal Structure of Benzene

E. G. Cox

School of Chemistry, The University, Leeds, England

THE problem of devising a formula which should reconcile the chemical properties of benzene and in particular the equivalence of its six carbon atoms with the generally accepted quadrivalence of carbon was recognized a hundred years ago, and the solution proposed by Kekulé in 1865 involving a plane hexagon of carbon atoms has never been disputed seriously in its essentials. Because of the unique position of benzene as the type substance of aromatic chemistry, however, a great deal of effort has been devoted to obtaining direct evidence for the correctness of Kekulé's hypothesis and to determining the actual dimensions of the molecule. In the past 30 years every physical method of investigating the molecular structure has been applied to benzene, ranging from x-ray diffraction, first used by Broomé in 1923, to neutron diffraction, which is at present being applied by Bacon at Harwell. Molecular dimensions of unassailable accuracy were not obtained until 1953, and it may be asked why it took 30 years from the first application of physical methods by Broomé to reach something approaching finality on such a simple molecule. The answer is, briefly, that for the first 10 years of that period, the development of techniques had not progressed sufficiently for benzene to be classed as simple; by that time it was reasonably certain from other evidence, for example, the work on hexa-methyl benzene[1] that the benzene molecule was, at any rate, not very different from a flat hexagon with a C—C distance of about 1.4 A, so that there was no point in further investigations so far at least as x-ray analysis was concerned, unless they were done with very high accuracy, and it is only during the last few years that the necessary techniques have been available for this.

The work on benzene up to about 1953, summarized here, had as its object the determination of the structure and dimensions of the isolated molecule of benzene, as far as possible independently of the state of aggregation of the material. In the early days of x-ray analysis it was not uncommon for chemists to treat x-ray results with reserve because of the possibility that the molecule in the solid state might be very different from that in solution or in the vapor phase. However, it has been clear for a long time that in the case of substances such as benzene the difference in molecular dimensions in different states of aggregation must be very small indeed. In the specific case of benzene, this is demonstrated by the very small differences between the ultraviolet spectra of the vapor and the solid.[2]

The paper of W. H. Bragg in 1922, quoted by Professor J. M. Robertson, was the first paper on the application of x-ray analysis to organic substances. In the following year about twelve authors published papers on organic compounds, and one of these was B. Broomé,[3] who took powder photographs of benzene out of doors in Stockholm; powder photographs were also taken by Eastman[4] whose best exposure was one of 330 hr, and Broomé took the first Laue photographs in 1925. The cell dimensions and space group were first determined in 1928[5] and this yielded the important information that in the solid state the benzene molecule has a center of symmetry.

In 1931 the first electron diffraction measurements were made,[6] but these were not then capable of any detailed interpretation. A direct attack on molecular dimensions by spectroscopic methods was not possible at that time, but attempts were made to find the molecular symmetry by determining the selection rules for the vibration spectrum. In the early thirties there were thought to be twelve coincident frequencies in the infrared and Raman spectra, so that according to the rule of mutual exclusion, the molecule could not be centro-symmetrical. Placzek,[7] discussing the possibility of C_{6v} symmetry, says, "All the hydrogen atoms may be above the carbon atoms or, what is more probable, each hydrogen atom may be half way between two carbon atoms, but out of the plane of the latter." One wonders whether this hypothesis might have had a longer lease of life if the existence of doubly linked hydrogen atoms in substances such as the boron hydrides had been known at that time. In 1936–1938, however, Ingold and his co-workers[8] showed that the apparent coincidences in the infrared and Raman spectra were due to the presence of condensed liquid films in the supposed vapor investigations. They showed, in agreement with the x-ray work on the solid, that the molecule of benzene in the vapor state has a center of symmetry. In addition, the comparison of the spectra of C_6H_6 and C_6D_6 made it possible to show that the number of normal modes of vibration and their distribution between the infrared and Raman spectra was in agreement with D_{6h} symmetry.

The determination[9] in 1932 of the approximate

---

[1] K. Lonsdale, Proc. Roy. Soc. (London) **A123**, 494 (1929).

[2] R. S. Halford and O. A. Shaffer, J. Chem. Phys. **14**, 141 (1946).

[3] B. Broomé, Physik. Z. 24, 124 (1923).

[4] E. D. Eastman, J. Am. Chem. Soc. **46**, 917 (1924).

[5] E. G. Cox, Nature **122**, 401 (1928).

[6] R. Wierl, Physik Z. **31**, 366, 1028 (1930).

[7] G. Placzek, *The Structure of Molecules*, edited by P. Debye (Blackie and Son, Ltd., London, 1932), English edition, p. 91.

[8] See, e.g., C. K. Ingold, Proc. Roy. Soc. (London) **A169**, 149 (1938).

[9] E. G. Cox, Proc. Roy. Soc. (London) **A135**, 491 (1932).

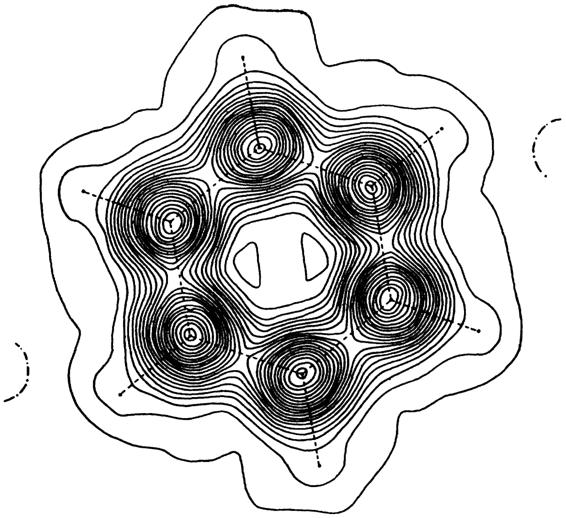

FIG. 1.

molecular arrangement in crystalline benzene was made from a limited number of x-ray intensity measurements, and on the assumption that the carbon skeleton of the molecule was a flat hexagon of side 1.4 A. The results were supported by optical measurements[10] and have been shown by later work to be very roughly correct.

Recently we determined all the *hkl* intensities obtainable by photographic methods from cylindrical crystals of benzene at −3°C. More systematic trial and error investigations by means of Fourier transforms improved our knowledge of the molecular orientation enough to provide a starting point for direct Fourier analysis, which was carried out on the Manchester University electronic computer. This analysis was carried out by a differential method, in which the atomic centers, assumed to be at the maxima in the electron density distribution, are sought by an iterative process which does not require the electron density to be plotted explicitly. Since, in the crystal, the molecule possesses only a center of symmetry, three carbon atoms are crystallographically independent of each other so that three independent measurements can be made of the C−C distance, and also of the bond angles. After five cycles of differential synthesis, the results obtained were as follows:

C−C bond	1.377 A	angle CCC	119°28′
	1.382		120°49′
	1.374		119°42′
Mean	1.378		

The standard deviation of these bond lengths calculated from the fit of the observed and calculated structure factors by Cruickshank's method[11] was 0.003 A, and the deviations of the carbon atoms from the best plane were found to be −0.0015, +0.0015, and −0.0015 A. The consistency of these results[12] was encouraging, but the mean C−C bond length of 1.378 A did not agree with the results on benzene vapor obtained about the same time by means of high resolution Raman spectroscopy[13] which gave a C−C bond length of 1.397 A ±0.001 A. The smallness of the standard deviations of these two results shows that either the C−C bond lengths in solid and vapor are significantly different (which is unlikely) or that one or both of the results was affected by some systematic error. We found[14] in fact there was a systematic error in the x-ray analysis caused by the special kind of thermal motion of the molecules of benzene in the solid state.

The nature of the error became clear from the map of the electron density in the plane of the molecule and still more from the "difference map" in the same plane. Both these maps show unmistakeably that the thermal motion of the carbon atoms is much greater tangentially to the ring than radially, and this means that whole molecules execute substantial oscillations about their sixfold axes.

The electron density map (Fig. 1) shows that, consistent with the idea that the atoms are moving on arcs of the circumscribing circle of the apparent C_6 hexagon, the "cols" between the atoms are in every case outside the hexagon. The difference map (Fig. 2) is obtained by subtracting from the electron density derived from the experiments a density calculated for the carbon atoms only, assumed to have isotropic thermal motion. In addition to the hydrogen atoms, which such a map is expected to show, the sites of the carbon atoms are seen to be negative, and strong positive regions occur halfway between them on the

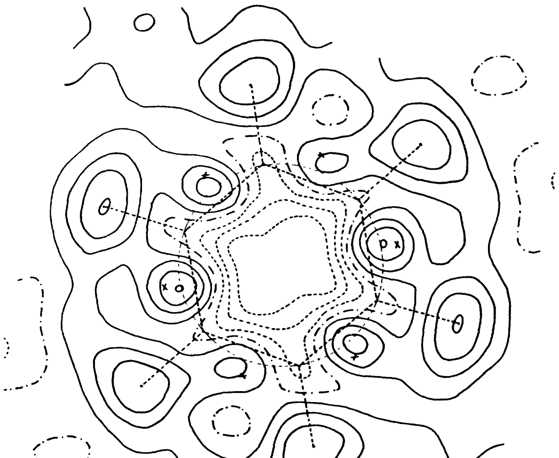

FIG. 2.

---

[10] E. G. Cox, quoted by N. H. Hartshorne and A. Stuart, *Crystals and the Polarising Microscope* (Edward Arnold and Company, London, 1950), second edition, p. 151.

[11] D. W. J. Cruickshank, Acta Cryst. 2, 65 (1949).

[12] E. G. Cox and J. A. S. Smith, Nature **173**, 75 (1954).

[13] B. Stoicheff, J. Chem. Phys. **21**, 1410 (1953).

[14] Cox, Cruickshank and Smith, Nature **175**, 766 (1955).

circumscribing circle. This shows clearly that the carbon atoms do not have the isotropic motion assumed but instead oscillate along arcs of the circumscribing circle. This conclusion is in agreement with the results of nuclear magnetic resonance measurements[15] which show that in benzene just below the melting point, one in 10^3 or 10^4 molecules may be rotating in its own plane; this figure is of the order of magnitude to be expected from the amplitudes given below.

The sections in the plane of the nuclei are not sufficient to give a full picture of the thermal motion but detailed study confirms that, although oscillations about other axes are not negligible, the main part of the anisotropy is the oscillation about the sixfold axis. The mean square amplitudes which appear best to fit the experimental facts are

normal to the plane of the ring	0.060 A^2
radially	0.057
tangentially	0.093

The difference between the last two figures corresponds to a rms amplitude of oscillation in the plane of the ring of 7.9°.

The introduction, into the iterative refinement process, of the anisotropic thermal parameters makes very little difference to the position of the maxima in the electron density distribution function (the apparent mean bond length becomes 1.377 A). Nevertheless it is clear that the maxima do not give the true positions of the atoms; the oscillations of the molecules cause each atom to move on a curved surface, so that the maximum of its time-averaged electron distribution lies nearer to the center of the molecule than the equilibrium position of the atom. The correction to be made is not calculable with quite as high accuracy as we should like at present, but it is approximately 0.015 A, so that the best C—C distance determined so far for crystalline benzene is 1.392 A, which is not significantly different from the Raman spectra result, and is in excellent agreement with the electron diffraction results.[16] The position of the hydrogen atoms has not yet been determined with any great accuracy by x-ray analysis, but this deficiency should be remedied by the neutron diffraction experiments which are now in hand. It is unlikely that any major discrepancies between the different methods of investigation will come to light in future, and it can be assumed that in all states of aggregation the benzene molecule is hexagonal and flat with a C—C distance of 1.397 A and a C—H distance of 1.085 A, both figures being accurate to a few thousandths of 1 A.

Although some improvement in the accuracy of the interatomic distances may well be possible, the main interest in the study of crystalline benzene is no longer in the determination of the atomic arrangement. Two quite separate lines of inquiry, both of great importance, now suggest themselves. In the first place, benzene can be regarded not only as the type substance of aromatic chemistry, but also as almost the ideal type substance of molecular crystals. Simpler molecules exist, but benzene is probably the simplest molecular substance which can be studied in the solid state over a range of more than 250° with no complications because of polymorphic transitions, molecular disorder, or hydrogen bonding. Extensive specific heat data are available and some Raman spectroscopy on single crystals has been done, so that an x-ray investigation extended over a range of temperatures should provide information which will enable us, in conjunction with the other information available, to build a fairly complete picture of the thermal motions of the molecules in this important substance. The other line of investigation, which cannot be pursued very far until the problems of thermal motion have been thoroughly investigated, is the study of the detailed electron distribution in the molecule. The importance of this for theoretical chemistry needs no emphasis.

For completeness, and in order to provide the information necessary for understanding of the following paper by Dr. D. W. J. Cruickshank, I conclude with a description of the crystal structure of benzene.

SYMMETRY

Orthorhombic, space group *Pbca*.

UNIT CELL DIMENSIONS

a	b	c	
$a=7.460$	$b=9.666$	$c=7.034$ A	at −3°C.[12]
7.292	9.471	6.742	at −195°C.[17]

The accuracy in both cases is a few parts in a thousand; the calculated densities (1.022 and 1.114) agree very well with experimental values e.g. those quoted by Andrew and Eades.[15]

POSITION OF MOLECULAR CENTERS

The centers of the (centrosymmetrical) molecules lie at the corners and face centers of the unit cell. Their positions are therefore known with the same accuracy as the cell dimensions.

ORIENTATION AND DIMENSIONS OF THE MOLECULES

There are four differently oriented molecules in the unit cell, *viz.*, at the cell corners and at the centers of the three cell faces. The coordinates at −3°C of the three carbon atoms in the molecule centered on the origin (cell corner) are as follows:

	x	y	z
C_1	−0.383	1.339	−0.040 A
C_2	−0.971	0.465	0.873
C_3	−0.591	−0.870	0.921

---

[15] E. R. Andrew and R. G. Eades, Proc. Roy. Soc. (London) **A218**, 537 (1953).

[16] I. L. Karle, J. Chem. Phys. **20**, 65 (1952).

[17] B. M. Kojen, Zhur. Fiz. Khim. **28**, 566 (1954).

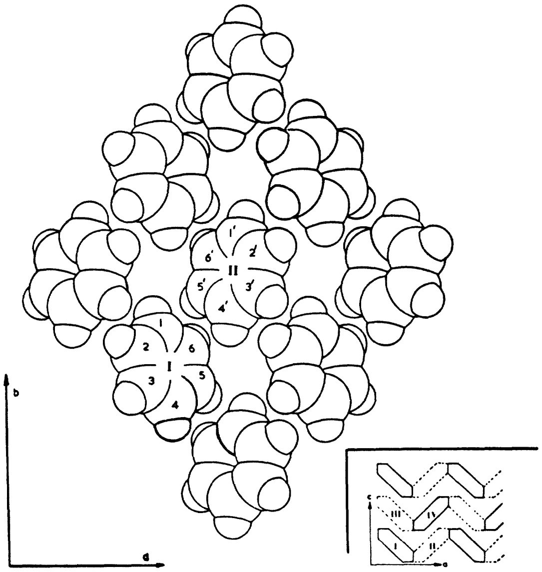

FIG. 3.

(The coordinates of C_4, C_5, and C_6 are obtained from the above by inversion in the origin.)

The foregoing coordinates are accurate to better than 0.01 A. They give a mean C—C distance of 1.392 A.

The molecule is accurately planar and the normal to its plane makes angles of 44° 49′, 77° 04′ and 48° 04′ with the *a*, *b*, and *c* axes, respectively. The radius through C_1 makes angles of 74°, 16°, and $88\frac{1}{2}$° with the *a*, *b*, and *c* axes respectively. The other three differently oriented molecules in the unit cell are derived from the one at the origin (molecule I) as follows:

II. At the center of the *c* face: by reflection in a mirror plane at $x=\frac{1}{4}$ followed by a translation $\frac{1}{2}b$, *or* by rotation about a twofold axis at $(x,\frac{1}{4},0)$ followed by a translation of $\frac{1}{2}a$.

III. At the center of the *a* face: by reflection in a mirror plane at $y=\frac{1}{4}$ followed by a translation of $\frac{1}{2}c$, *or* by rotation about a twofold axis at $(0,y,\frac{1}{4})$ followed by a translation of $\frac{1}{2}b$.

IV. At the center of the *b* face: by reflection in a mirror plane at $z=\frac{1}{4}$ followed by a translation $\frac{1}{2}a$, *or* by rotation about a twofold axis at $(\frac{1}{4},0,z)$ followed by a translation of $\frac{1}{2}c$.

MOLECULAR PACKING

Each molecule has twelve neighbors with H···H contacts of $2\frac{1}{2}$–3 A. These contacts are of three different kinds according to the types of molecules concerned, the most intimate being between molecules of types I and II (or III and IV) which form puckered layers parallel to (001). The arrangement in one of these layers (Fig. 3) resembles strongly that of a set of six-toothed bevel gear-wheels in which each wheel meshes with four others at right angles to it. The stacking of successive layers is shown schematically in the inset, Fig. 3, in which the "gear-wheels" are viewed, nearly edge-on, parallel to the *b* axis. The full lines indicate molecules centered on $y=0$ and the broken lines those centered on $y=\frac{1}{2}$.

The gear-wheel arrangement is of great interest in connection with the discussion of the oscillation of the molecules about their sixfold axes. The H···H distances between molecules I and III and between I and IV are of the same order as those between I and II, but it will be clear from Fig. 3 that the last may be greatly affected by oscillation of the molecules about their sixfold axes whereas the other two will not. It is also evident that the I···II contacts will be affected very differently according as the molecular motion is in-phase or out-of-phase. In the long wavelength normal mode vibrations of the crystal the relative motion of I and II must be either exactly in phase or exactly out of phase with respect to the space-group; for the positive direction of in-phase motion as viewed in Fig. 3 I turns anti-clockwise and II turns clockwise, whereas for the (positive) out-of-phase motion I and II both move in an anticlockwise direction. Thus the in-phase motion is analogous to that of a gear-train, in which alternate wheels turn in opposite directions, so that small oscillations of this type can occur very easily. With larger oscillations the meshing of the molecular gears is not so good, but the barriers to complete rotation are considerably lower in phase than out of phase. At equilibrium for example H atom 6 (molecule I) is 2.64 and 2.78 A from atoms H5′ and H4′ (molecule II), respectively, and these distances can be reduced to minima of 2.56 and 2.23 A by in-phase displacements of −10° and +24° respectively; on the other hand the minimum distances for out-of-phase displacements are 2.03 and 2.49 A, while for (non-normal-mode) motion in which I rotates between stationary type II molecules minimum distances of less than 2.1 A also occur. Thus a molecule can most easily rotate when its neighbors in the (001) plane are rotating in phase with it, so that the 0.01–0.1% of molecules inferred from the NMR work to be rotating may be clustered in small sheets rather than distributed singly throughout the crystal. There is very little coupling of oscillation between molecules in successive sheets, and the large coefficient of thermal expansion in the direction of the *c* axis is in accord with the idea of rather looser binding in this direction.