

Further Investigation of X-Ray Diffraction in Liquids

Part II

Benzene, Cyclohexane and their Homologues

By

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Abstract

In the present experiment, the authors used two narrow long slits to limit the X-rays instead of circular ones, and obtained finer photographs of the diffraction patterns. Fourteen substances, nine of which had been already studied in the former experiment, were investigated and the new results are discussed. A second maximum was found in the diffraction band of benzene, and the diameter and the thickness of the benzene molecule, which was assumed to have a flat discal form, was determined. The substitution group CH_3 changes the molecular form as a group or a branch in the benzene homologues. The diffraction bands of cyclohexane and its homologues all gave a single sharp maximum which suggested that the form of the molecules was spherical. The substitution group CH_3 seems to increase their diameter uniformly.

Experimental Part

In the previous investigations of X-ray diffraction in liquids, two circular slits of about 2 mm. in diameter standing about 3.5 cms. apart were used to limit the X-rays coming from the tube. Now two narrow slits of 0.4 mm. in breadth and 1.9 cms. in length were placed in the same relative positions, so that bands were obtained in the diffraction patterns, instead of the circular haloes of the previous experiment, and the former exhibited a finer structure than the latter. The distance between the sample and the photographic film was increased to 3.8 cms. in order to have a good separation of the diffraction bands. By these two improvements the structure of the intensity distribution in the diffraction pattern was observed more precisely,

and consequently the molecular constitution of the several liquids could be somewhat more clearly considered.

The Shearer metal tube with a copper anticathode excited at about 50 K.V.s by a transformer was employed as the source of the X-rays. Notwithstanding that the current through the tube was 4-5 milliamperes, an exposure of 4 hours was required to obtain a good photograph, on account of the great distance between the sample and the photographic film, and the narrow slits. The sample was contained and sealed in a long thin glass tube of elliptical cross-section and examined always at the room temperature, 20°-25°C. The same glass tube, carefully cleaned every time, was employed for all the samples, so that the slight confusion in the diffraction patterns due to the scattering by the container was constant.

The samples now examined were benzene^K, toluene^K, ortho-, meta-, para-xylene^K, mesitylene^K, para-cymene^K, cyclohexane^T, cyclohexene^T, ethyl-benzene^T, pseudo-cumene^K, isopropyl-benzene^E, monomethyl-cyclohexane^T, meta-dimethyl-cyclohexane^K, some of which have already been studied by the present authors and others¹. The results, however, were somewhat unclear, and did not agree with each other in some points. The marks K, E and T, attached to the names of the samples indicate Kahlbaum, Eastmann and Takeda (Japan), the manufacturers.

Results

Nine of the above mentioned samples have already been investigated by the present authors and reported on in the previous papers. The finer results now obtained did not, in general, differ from the ones already reported and consequently our previous descriptions have been made more reliable. The spacings d calculated by the present data with Bragg's formulae are given in Table I, which shows the small differences due to the improvement of the apparatus. These values correspond to the maximum intensity of each band and if there are two maxima, we have two values of d . It must be noted, however,

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- 1 The present authors, These Memoirs, **8**, 1 (1930)
 Stewart, Phys. Rev. **33**, 889 (1929)
 Sogani, Ind. Jour. Phys. **2**, 97 (1927)
 Krishnamurti, Ind. Jour. Phys. **2**, 491 (1928)
 Katz, Zeit. Phys. **45**, 97 (1927)
 Katz and Selman, Zeit. Phys. **46**, 392 (1928)

that the following new interesting facts have been observed: 1) There is a small maximum of intensity near the outer limit of the scattering outside the principal band of benzene. 2) We found a clear second maximum outside the principal maximum of the diffraction band of ortho-xylene. 3) Two maxima are clearly observed in the diffraction band of meta-xylene which gave a single broad diffuse halo in the previous experiment, and the difficulty in ascertaining the position of the intensity maximum caused us to give too small a value to d in that case.

Table I

Name of liquid	Rational formula	Spacing (A.U.)	
		d_1	d_2
Benzene	C_6H_6	4.76	3.12
Toluene	$C_6H_5(CH_3)$	5.26	
Ethyl-benzene	$C_6H_5(C_2H_5)$	5.58	
Ortho-xylene	$C_6H_4 \begin{smallmatrix} \diagup CH_3(1) \\ \diagdown CH_3(2) \end{smallmatrix}$	5.67	3.54
Meta-xylene	$C_6H_4 \begin{smallmatrix} \diagup CH_3(1) \\ \diagdown CH_3(3) \end{smallmatrix}$	5.78	3.82
Para-xylene	$C_6H_4 \begin{smallmatrix} \diagup CH_3(1) \\ \diagdown CH_3(4) \end{smallmatrix}$	5.26	
Mesitylene	$C_6H_3 \begin{smallmatrix} \diagup CH_3(1) \\ \diagdown CH_3(3) \\ \diagdown CH_3(5) \end{smallmatrix}$	6.43	3.77
Pseudo-cumene	$C_6H_3 \begin{smallmatrix} \diagup CH_3(1) \\ \diagdown CH_3(3) \\ \diagdown CH_3(4) \end{smallmatrix}$	5.72	
Isopropyl-benzene	$C_6H_5CH \begin{smallmatrix} \diagup CH_3 \\ \diagdown CH_3 \end{smallmatrix}$	5.58	
Para-cymene	$C_6H_4 \begin{smallmatrix} \diagup CH_3(1) \\ \diagdown CH(3) \end{smallmatrix} \begin{smallmatrix} \diagup CH_3 \\ \diagdown CH_3 \end{smallmatrix}$	5.39	
Cyclohexane	C_6H_{12}	4.94	
Cyclohexene	C_6H_{10}	4.87	
Monomethyl-cyclohexane	$C_6H_{11}CH_3$	5.26	
Meta-dimethyl-cyclohexane	$C_6H_{10} \begin{smallmatrix} \diagup CH_3(1) \\ \diagdown CH_3(3) \end{smallmatrix}$	5.53	

Five new liquids—ethyl-benzene, pseudo-cumene, isopropyl-benzene, monomethyl-cyclohexane and meta-dimethyl-cyclohexane—were examined. The diffraction patterns of monomethyl-cyclohexane and meta-dimethyl-cyclohexane give a very sharp band like cyclohexane, and the inner scattering in both is slightly greater than the outer one.

The spacing d , is gradually increased with the addition of CH_3 groups as in the case of benzene and its homologues. The diffraction pattern of ethyl-benzene has a broad band accompanied by a considerable scattering outside of it. The pseudo-cumene and isopropyl-benzene bands are very diffuse, especially the former, which seems to have a faint second maximum in the outer region. The photographs taken in our present experiment are reproduced in Plate I.

Discussion

Consideration of the benzene and the cyclohexane molecule:—

The X-ray diffraction haloes of benzene and its homologues have generally an intense maximum accompanied by a considerable scattering on both sides of it, and sometimes it develops into a second one on the outside of the principal maximum. From this fact and from experiment on the monomolecular liquid layer, many authors have taken the form of the benzene molecule to be a flat disc, and determined its diameter and thickness. Sogani determined those values as 6.2 A.U. and 3.2 A.U. respectively, and Stewart took 4.70 A.U. as the thickness of the disc, from their X-ray diffraction data. They observed only a single maximum of intensity accompanied by a considerable scattering on both sides of it. The former calculated the above values from the positions of the inner and the outer limit of the scattering, and the latter, from the maximum intensity.

In our present experiment, the second maximum could be observed near the outer limit, so that we could calculate two spacings corresponding to these two maxima which could be naturally taken as the thickness and the diameter. These values are 3.12 A.U. and 4.76 A.U. This value for the thickness coincides with that determined for benzene in the solid state by W. H. Bragg,¹ Morse,² Caspari³ and others. Moreover the second maximum in the diffraction pattern of ortho-, meta-xylene and mesitylene gives a somewhat greater thickness for each molecule owing to the modification by the substituted groups. If we calculate the density of the benzene molecule from our above data and the molecular weight we naturally obtain a greater value for benzene.

1 W. H. Bragg, Proc. Phys. Soc. Lond. **34**, 33 (1921)

2 Morse, Proc. Nat. Acad. **13**, 789 (1927)

3 Caspari, Phil. Mag. **26**, 1276 (1927)

Cyclohexane and its homologues have a single sharp maximum of intensity in their diffraction patterns. There is only a very slight scattering on both sides of it and no second maximum. This seems to suggest that the molecular shape of these substances is spherical, and the spacings corresponding to this maximum give the diameters of the molecules.

The effect of the substitution group:—The increases in the spacing d_1 for benzene, toluene, meta-xylene and mesitylene are 0.50 A.U., 0.52 A.U. and 0.65 A.U. respectively and those for cyclohexane, monomethyl-cyclohexane and meta-dimethyl-cyclohexane are 0.32 A.U. and 0.27 A.U. which are very small. In the case of the chain compounds, there is a regular increase in the spacings with the attachment of CH_3 as the side branch, the value of which as determined by Stewart and Skinner¹ and the present authors² is nearly equal to the former values. The increase in the spacing d_2 for the above benzene homologues also nearly equal in value. Consequently, CH_3 is added to the benzene molecule as a group making a branch, and increases the diameter or the thickness of it. In the case of cyclohexane, however, the substitution group CH_3 increases uniformly the diameter of the spherical molecules and the increased values are smaller than those of the benzene homologues.

Notwithstanding that the change in the spacings and the diffuseness of the diffraction band due to the addition of CH_3 in the benzene homologues is very complex, it seems to suggest that CH_3 exercises its effect on the molecular form as a single group or a branch. Of the three xylenes, the orth- and the meta-xylene show two intensity maxima and the para-xylene only one maximum, which gives the smallest spacing d_1 .

The diameter of the cyclohexene molecule is slightly smaller than that of the cyclohexane molecule due to the lack of the two hydrogen atoms.

Physical Laboratory,
The Osaka University of Engineering,
Jan. 20, 1930.

¹ Stewart and Skinner, Phys. Rev. **31**, 1 (1928)

² *loc. cit.*

Plate I

Fig. 1. Benzene

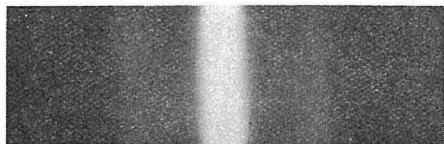


Fig. 8. Pseudo-cumene

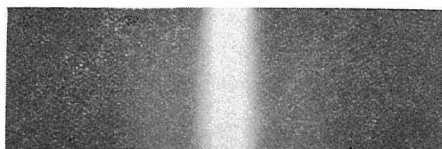


Fig. 2. Toluene

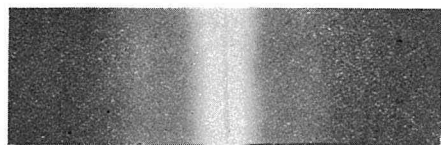


Fig. 9. Isopropyl-benzene

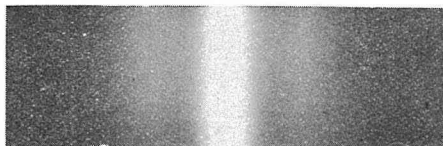


Fig. 3. Ethyl-benzene

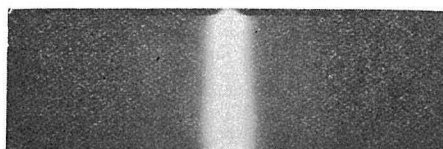


Fig. 10. Para-cymene

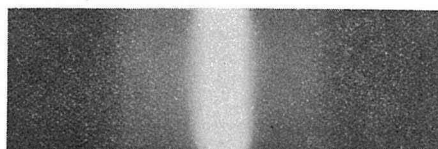


Fig. 4. Ortho-xylene

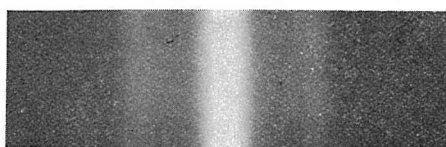


Fig. 11. Cyclohexane

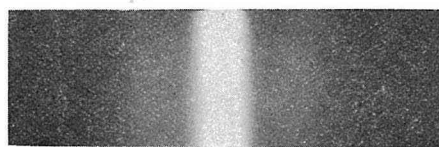


Fig. 5. Meta-xylene

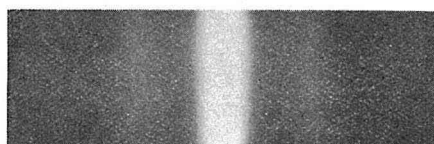


Fig. 12. Cyclohexene

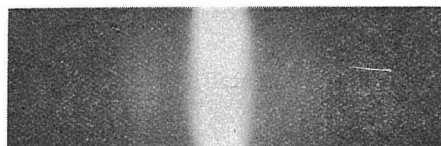


Fig. 6. Para-xylene

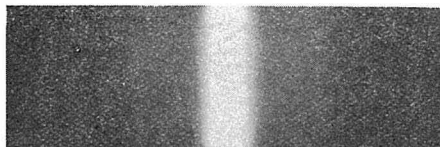


Fig. 13. Monomethyl-cyclohexane

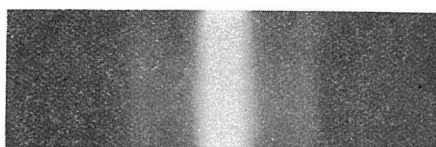


Fig. 7. Mesitylene

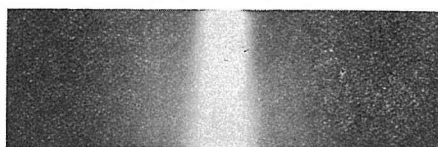


Fig. 14. Meta-dimethyl-cyclohexane

