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Electron Diffraction Studies of Hexaphenylbenzene Vapour

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Electron diffraction studies of hexaphenylbenzene in vapour have been carried out. The peripherical rings are found to be nearly orthogonal to the central ring. The model is, however, not found to be rigid and it is concluded that the outer rings of the molecule oscillate with no appreciable restriction in a rather limited angle interval of approcimately $\pm 10°$ from the orthogonal form.

The arrangement of aromatic ring systems connected with single bonds have been studied in a series of papers [1-5]. In this connection we found it of interest to include hexaphenylbenzene.

A sample of the compound was kindly placed at our disposal by Professor E. R. H. Jones, Oxford. The diagrams were taken at a temperature of approximately 340°C using a modified s^3-sector. The intensity data were read off from the photometer curves and the various corrections were carried out [6]. In Fig. 1 is presented the final intensity curve after subtraction of the background. The theoretical background gave as a whole a fairly good agreement with the experimental curve, but corrections had to be carried out particularly for the innermost and the outermost part of the intensity curve.

Radial distribution curves were calculated using the damping factor $\exp(-ks^2)$.

The results for $k = 0.0009$ and 0.0036 are reproduced in Fig. 2. An analysis of the position of the maxima of these curves gives the following bond distances: C—C in the rings 1.40 Å, C—C bridge distance 1.52 Å and C—H 1.08 Å. The error of the first C—C distance and of the C—H distance is less than 0.005 Å. The situation is less favourable for the bridge C—C distance as this is determined indirectly by larger internuclear distances between two different rings. Error estimates suggest that the error is probably less than 0.01 Å.

By applying the observed bond distances and the assumption of 120° valence angles all through the molecule, the internuclear distances of the whole molecule have been calculated. There is a large group of distances which depend upon the angle of twist around the C—C bridges, but there are also altogether 23 CC distances which are independent of the angle of twist. In

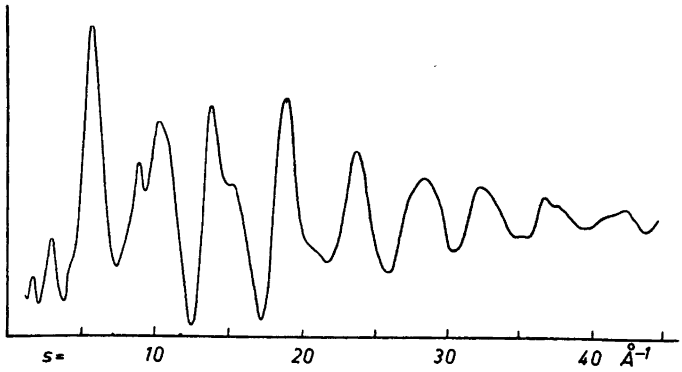

Fig. 1. Intensity curve of hexaphenylbenzene.

addition there is a whole series of CH distances. In Fig. 2 all the invariable CC distances for the calculated radial distribution curve are represented by vertical lines. The length of each line is proportional to the weight of the corresponding distance. The CH distances are omitted with the exception of the two shorter ones. The line diagram of the invariable distances explains essential features of the radial distribution curve. For r values less than 7 Å there are, however, three easily detectable irregularities. The first one is a well resolved peak at 3.39 Å, the second one is a maximum at 4.63 Å, and the third is an extra contribution to the peak at approximately 6 Å. The position of this latter peak is at higher r-values than expected from the invari-

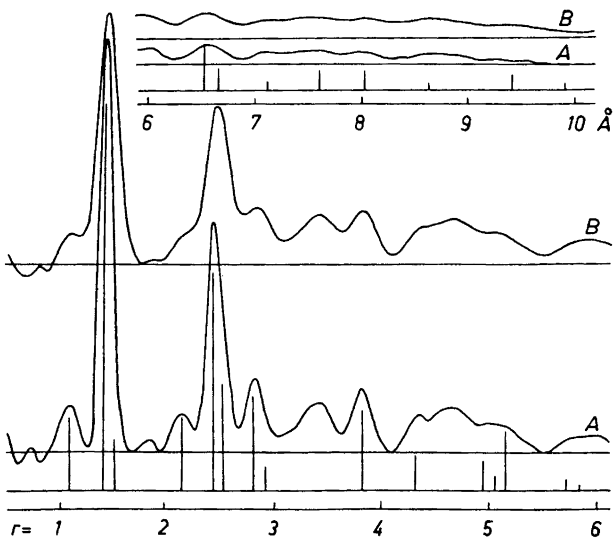

Fig. 2. Radial distribution curves of hexaphenylbenzene. A, $k = 0.0009$; B, $k = 0.0036$.

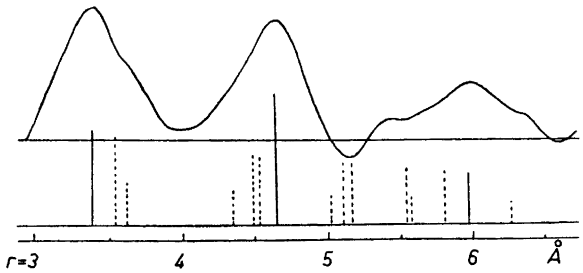

Fig. 3. Difference radial distribution curve when the contribution of invariable distances have been subtracted.

able distances only. The subtraction of the contribution of the invariable distances gives at these three points peaks with maxima 3.39 Å, 4.63 Å and 5.97 Å, respectively. The result of such a subtraction of the invariable distances is demonstrated in Fig. 3 ($k = 0.0036$). The variable distances which would first of all be expected to contribute to this radial distrubution curve are the following: C_2C_8, C_2C_{12}, C_2C_9, C_2C_{11}, C_3C_9, and C_3C_{11}. (For the numbering of the atoms see Fig. 4). In the case of an angle of 90° the six indicated distances will be reduced to three, as pairs like C_2C_8 and C_2C_{12} will be equal. The three main peaks of the curve in Fig. 3 correspond to an angle of 90° between the central ring and the outer rings, as the theoretical distances in an orthogonal

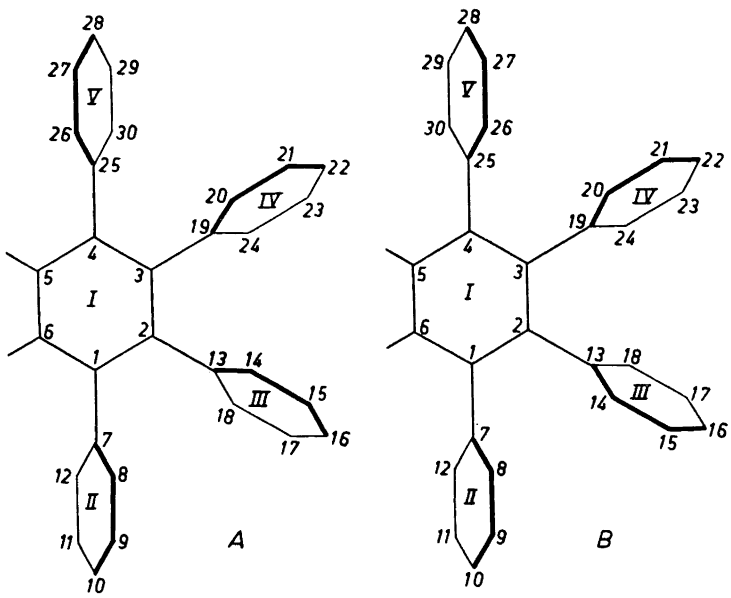

Fig. 4. Structure models of hexaphenylbenzene. A "propeller" and B "antipropeller" model.

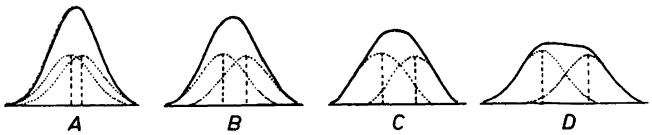

Fig. 5. Radial distribution peak for the C_2C_8 and C_2C_{12} distances corresponding to various angle deviations from orthogonality. A, 5°; B, 10°; C, 15°; and D, 20°.

case are 3.39 Å, 4.65 Å, and 5.97 Å, respectively. The positions and the weights of the three distances in question are given as solid vertical lines under the peaks of Fig. 3. The conclusion one would be tempted to draw from this is that all the peripherical rings are orthogonal to the central ring. On the other hand, it can easily be shown that a limited deviation from orthogonality will not appreciably change the maximum position of the three peaks under consideration. In case of a rotation from the orthogonal position each of the three distances will split up in two distances, one of which is smaller and one larger, leaving the average very nearly the same. As a demonstration of this the theoretical form of the 3.39 Å peak is given in Fig. 5 for four various angles of twist from the orthogonal position. The half width of the Gaussian-normal curve used for this construction is obtained from the corresponding resolved peak in the radial distribution curve of biphenyl [5]. A comparison of the peaks in Fig. 5 with the corresponding experimental one in Fig. 3 shows that the split, if any, cannot be larger than 15°. On the other hand, the comparison also indicates that a rigid model is less probable. An angle of 10° seems to be the right order of magnitude. It is of course impossible from the study of the three peaks in Fig. 3 to decide between a rigid model with a deviation of say 10° from orthogonality and a model with some oscillation around an orthogonal conformation. In fact the latter assumption would from usual structural experience be the more probable one.

For further information on this point a study of the internuclear distances between the peripherical rings would obviously be necessary. The line diagram of broken lines under the difference radial distrubution curve of Fig. 3 gives the positions and weights of all variable internuclear CC distances in the presented interval between peripherical rings, in a rigid and orthogonal model. A study of this diagram leads to the rejection of the entirely rigid orthogonal model. To obtain information about the possibility of other rigid models than the orthogonal one a whole series of various models was considered. None of them lead to a decisive conclusion. As an example both the experimental and two theoretical radial distrubution curves are presented in Fig. 6 for the interval 3 to 6.5 Å. The two calculated models are a "propeller" and an "antipropeller" model described in Fig. 4 with an angle of twist from orthogonality of 10°. The correspondence between experimental and calculated curves in Fig. 6 is not satisfactory and do not give possibilities for a choice, though the "antipropeller" model seems to be somewhat more favourable. Further considerations along this line lead to abandoning rigid models. A natural conclusion should then be that the outer rings of the molecule oscillate with

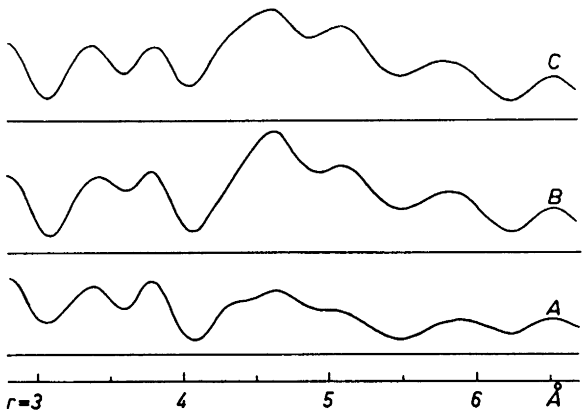

Fig. 6. Radial distribution curves. A, experimental curve; B, "propeller" model; C, "antipropeller" model. (10° deviation from orthogonality.)

no appreciable restriction in a rather limited angle interval of approximately $\pm 10°$ from the orthogonal form.

So far the discussion is based upon the radial distribution curve interval up to approximately 7 Å. The outer part of the curve is also of considerable interest in this connection. Studying the theoretical contribution to this part of the curve it is easily seen that the total weight of the variable distances should be considerably larger than the total weight of the invariable distances. On the other hand, a comparison of the line diagram of the invariable distances with the radial distribution curve shows that the curve can to a great extent be explained by the invariable distances alone (Fig. 2). The contribution of all the variable distances seems to have been evened out. The fact that practically all peaks in the interval 7—10 Å are interpretable is a strong argument for the correctness of the curve. The variable distances in this interval are of the type going between ring II and IV and between II and V. The fact that these distances are smoothed is in agreement with the general idea presented above and serves as a demonstration of the nonrigidity of the hexaphenylbenzene molecule. The variable distances, of course, contribute to the diffraction patterns, but they do not lead to detectable peaks and are therefore to a great extent lost when drawing the envelope [6].

It is no doubt of interest to study if our general sturucture picture can be brought into accordance with steric considerations. The effect of p orbital is no doubt insignificant for the bridge C—C bond so far away from the planar form. If two neighbouring peripherical rings are rotated towards each other the hydrogen atoms of the type H_8 and H_{14} will be the first pair of atoms to be brought into contact. If a packing distance of 2.4 Å is applied corresponding to the Pauling van der Waals radius for hydrogen [7] of 1.2 Å, contact will be reached at an angle of 10.5° from orthogonality. If a "propeller" model is assumed, steric conflicts will not lead to serious difficulties until a rotation

of approximately 40° is performed. In order to realize such a form it is necessary to rotate all the peripherical rings in the same direction. If only one ring is out of order the rest would have to assume an arrangement near the orthogonal conformation. The probability of the symmetrical 40° "propeller" should, therefore, be rather small for pure statistical reasons. On the other hand, this symmetrical form might well be present in the crystalline state. X-Ray crystallographic studies are in progress in the Institute of Theoretical Chemistry, Trondheim.

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REFERENCES

1. Bastiansen, O. *Acta Chem. Scand.* **3** (1949) 408.
2. Bastiansen, O. *Acta Chem. Scand.* **4** (1950) 926.
3. Bastiansen, O. *Acta Chem. Scand.* **6** (1952) 205.
4. Bastiansen, O. and Smedvik, L. *Acta Chem. Scand.* **8** (1954) 1593.
5. Almenningen, A. and Bastiansen, O. *Kgl. Norske Videnskabs Selskabs Skrifter* (1958). *In press.*
6. Almenningen, A. and Bastiansen, O. *Acta Chem. Scand.* **9** (1955) 815.
7. Pauling, L. *The Nature of the Chemical Bond*, Ithaca 1945.

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