An Electron Diffraction Investigation of the Molecular Structure of Azulene

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Electron diffraction studies have been carried out on the structure of azulene. Assuming a planar, symmetrical molecular model, the peripheral bond lengths were found to be nearly equal with an average bond length of 1.403 Å. The transannular bond was found to be 1.501 Å. The results are presented in Tables 1 and 2 and are compared with theoretical values and with results from X-ray crystallography studies.

Several attempts have been made to determine the molecular structure of the aromatic hydrocarbon azulene, $C_{10}H_8$. In the crystal the structure is disordered, and the structure parameters as determined by Robertson and collaborators [1] show very large standard deviations. A recent X-ray study of the crystalline molecular complex of azulene and s-trinitrobenzene by Hanson [2] has been published after the completion of the present work. For comparison both these X-ray results have been listed in Table 2 together with the values obtained by the present authors.

Quantum mechanics studies both based upon the M. O. [3] calculations and on the valency bond method [4] have been carried through by den Boer *et al.* at the State University of Utrecht. These results are also included in Table 1.

EXPERIMENTAL WORK AND CALCULATION PROCEDURE

A sample of azulene puriss. from Fluka A. G. was used. The electron diffraction intensity data were obtained with the Oslo electron diffraction camera.[5] Diffraction photographs were taken using nozzle-to-plate distances of about 48 and 19 cm, and a nozzle temperature of about 80°C. The usual procedure [6] was followed and an experimental background was subtracted in order to obtain the molecular intensity curve. An experimental blackening correction was used. This sometimes introduces difficulties, but in general does not influence the geometry of the molecule, which is the main interest of this molecule. The plates were very light and only small corrections had to be made. In the overlap region between plates covering different s intervals the agreement was

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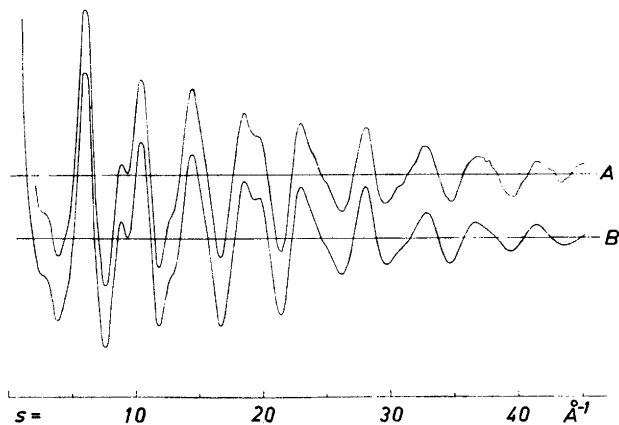
Fig. 1. Intensity curves, A experimental and B theoretical.

very good. In Fig. 1 the final experimental intensity curve is shown. The experimental radial distribution curve, with an artificial damping factor of $\exp(-0.0009s^2)$, is shown in Fig. 2. This curve was obtained including a theoretical inner intensity peak from $s = 0$ to $s = 1.5$. The influence of changes in the molecular model on this peak was considered and appeared to be very little.

INTERPRETATION OF THE EXPERIMENTAL RESULTS

The electron diffraction method for gas molecules produces only one-dimensional radial distribution curves, and in the azulene molecule the number of parameters is rather large. Even for a planar model with all the C—H bond
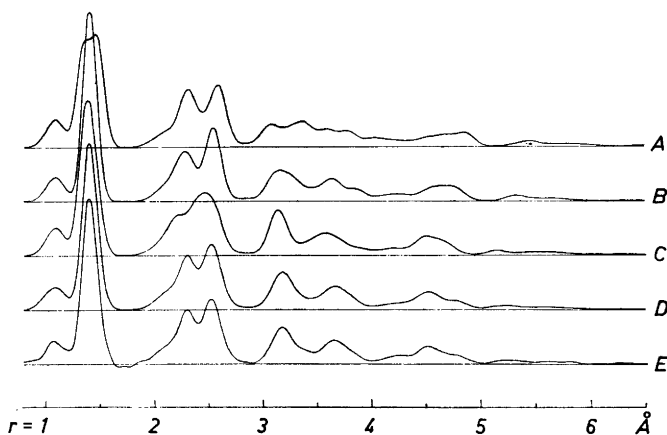

Fig. 2. Radial distribution curves, A through D theoretical curves and E experimental curve. A, valence bond model,[4] B, M. O. model,[3] C, X-ray model,[1] and D final electron diffraction model.

distances equal altogether 18 geometrical and approximately 100 vibrational parameters should be considered. It is therefore obvious that structure chemical arguments have to be included. The following assumptions were made: 1) The molecule is planar; 2) All C—H distances are equal; 3) There is a plane of symmetry perpendicular to the plane of the molecule and through atoms C_2 and C_6 (See Fig. 3); 4) Certain groups of u values (the vibrational parameters) are equal; 5) The C—H bond bisect the corresponding C—C—C angles. The assumption 1) is supported by microwave spectroscopy in a recent work by Tobler and Bauder.[7] Hanson's X-ray studies[2] indicate a minor deviation from planarity. As to assumption 4) it should be noted that the geometry parameters are not very sensitive to uncertainties in the u-value determinations. By these assumptions the number of parameters can be drastically restricted. The number of geometrical parameters is reduced to nine. Even if the above assumption holds, one should not be too optimistic as to the possibility of presenting a very accurate set of parameters, one may even be prepared for ambiguity. From an examination of the experimental radial distribution curve we tried to draft a rough model. The position of the C—C bond peak was 1.403 Å and the position of the C—H bond peak was 1.085 Å. The width of the C—C bond peak indicated that there should not be too large difference between the various C—C bond lengths. This conclusion is based on u-value estimates from molecules like benzene.

The experimental radial distribution curve (Fig. 2) was first compared with calculated ones based on: 1) the valency bond model (A), 2) the M. O. model (B), and 3) Robertson's X-ray model) (C). From general experience we feel safe to exclude all these three models, the values are outside our error range. As to the X-ray model the standard errors are so high that our statement is only concerned with the best estimate presented by Robertson's X-ray study.

After a few trial and error attempts, a systematic least squares approach appeared inevitable, and was carried out with the restriction as to the model as mentioned above. A systematic study of all combinations of "long" and "short" C—C bonds led to 20 types of models, having either 4 short and 6 long, or 6 short and 4 long peripheral bonds. All these models were refined, assuming the short bonds to be approximately 1.365 Å and the long bonds about 1.43 Å. The transannular bond was assumed to be 1.48 Å. The u values were taken from experience with benzene and naphthalene (unpublished results from this laboratory). These 20 starting models refined to only two groups of models. The various models in one or the other of these groups are
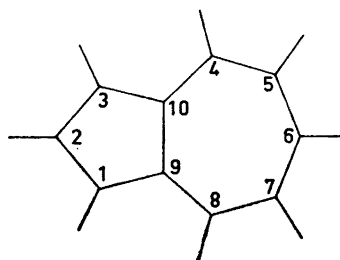

Fig. 3. The azulene molecule.

not quite identical but very similar. The two main remaining models have the following specifications (for numbering of the atoms see Fig. 3):

    Model 1: bonds 2—3,   10—4,   5—6 are "short"
              bonds 3—10, 4—5,   are "long"
    Model 2: bonds 3—10, 4—10, 4—5 are "short"
              bonds 2—3,   5—6,   are "long"

The short distances are in the range of 1.37 to 1.40 Å and the long distances from 1.41 to 1.44 Å.

In the subsequent application of least squares refinement, groups of parameters were kept constant, while other parameters were refined. Usually u values were kept constant, while geometrical parameters were refined, followed by the reverse procedure until no appreciable change occurred. From that point on geometrical and vibrational parameters were refined simultaneously, choosing the u values in groups, for example all the u values of the C—C bond distances equal. The hydrogen positions were not refined. During this refinement the two types of models converged to one and the same model, the parameters of which are given in Table 1.

The corresponding theoretical intensity curve and radial distribution curve are given in Figs. 1 and 2, respectively. The standard deviations as obtained directly from the least squares calculations are included in the table. We know [8] that these standard deviations are often too small, but aside from a possible scale error they are in this case not too unlikely. Of course there are strong correlations between the various parameters, a fact that was studied on the correlation matrix. One obvious type of correlation is that an increase of one bond distance leads to a decrease of other bond distances. It appears, and is also well understood, that a refinement in which the u values are kept constant will lead to smaller standard deviations than a refinement where the geometrical and vibrational parameters are varied simultaneously. In Table 2 a set of u values obtained by this procedure is presented and compared with the corresponding values for benzene.

Though the assumption of a symmetrical molecule undoubtedly seems to be reasonable, the unsymmetric models could not be ruled out, neither by our investigation nor by general structural chemical arguments. It seems obvious that satisfactory agreement can be obtained also with an unsymmetric model though only very limited work on unsymmetric models was actually carried out. However, we feel that in case of a system with alternating long and short bonds in the periphery of the molecule only a difference of 0.02 to 0.05 Å in the bond lengths should be possible. This is already indicated by the width of the C—C bond peak in the radial distribution curve.

The shrinkage effect has not been taken into consideration. According to results of Cyvin et al. on similar systems [9] small effects on the bond lengths may be expected. However, it is unlikely that the inclusion of shrinkage would change the result substantially, and the essential result seems to hold, namely the finding of the nearly equal peripheral bond lengths and the somewhat longer transannular bond.

Table 1. Geometrical parameters for azulene.

Distances	M.O.[3]	Valence bond[4]	X-ray (Robertson et al.[1])	st. errors	X-ray (Hanson[2])	mean	st. errors	Electron diffraction value	st. errors
C_1-C_2	1.406	1.48	1.425	0.032	1.387	1.394	0.004	1.399	0.009
C_2-C_3		1.35	1.363	0.027	1.398				
C_1-C_9	1.411	1.35	1.459	0.024	1.395	1.398	0.004	1.418	0.010
C_3-C_{10}		1.48	1.378	0.019	1.404				
C_8-C_9	1.412	1.48	1.369	0.007	1.392	1.391	0.004	1.383	0.008
C_4-C_{10}		1.35	1.395	0.005	1.390				
C_7-C_8	1.405	1.35	1.440	0.021	1.402	1.400	0.004	1.406	0.016
C_4-C_5		1.48	1.337	0.034	1.393				
C_6-C_7	1.407	1.48	1.422	0.026	1.397	1.392	0.005	1.403	0.014
C_5-C_6		1.35	1.337	0.035	1.391				
C_9-C_{10}	1.459	1.50	1.483	0.004	1.498	1.498	0.004	1.501	0.005
$C-H$								1.085	

Angles					X-ray (Hanson[2])			value	st.dev.
$C_9-C_{10}-C_3$					106.44			106.2°	0.5°
					106.19				
$C_9-C_{10}-C_4$					127.15			128.6°	0.6°
					127.67				
$C_{10}-C_4-C_5$					129.20			127.3°	1.3°
					128.42				

Table 2. Average vibrational parameters (*u* values). Comparison with results from benzene.

Distances	Azulene	Benzene
C_1-C_2	0.0486	0.0455
C_1-C_3	0.054	0.054
C_5-C_{10}	0.057	0.054
C_6-C_{10}	0.078	0.062
$C-H$	0.090	0.073

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