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An Electron Diffraction Investigation of the Molecular Structure of *cis*-3,4-Dichlorocyclobutene-1

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The structure of *cis*-3,4-dichlorocyclobutene-1 in the gaseous state was studied. The parameters obtained by the electron diffraction method, applying a least squares procedure, are listed in Table 1.

EXPERIMENTAL WORK AND CALCULATION PROCEDURE

The electron-diffraction technique has been applied to study the molecular structure of *cis*-3,4-dichlorocyclobutene-1 (Fig. 1). The electron diffraction intensity data were obtained with the Oslo electron diffraction camera [1] using two different nozzle-to-plate distances, *viz.* 48 and 19 cm, and room temperature. The usual procedure was followed and phase shift effects were neglected.[2] An experimental background was subtracted in order to obtain the molecular intensity curve. As the diffraction photographs were rather dark, three different blackness corrections were tried, and the results analysed with the usual procedure including least squares refinements. In Fig. 2 the experimental molecular intensity curve is shown, using the medium blackness correction. In Fig. 3 the corresponding radial distribution curve is reproduced. An "envelope" was subtracted and an artificial damping factor of $\exp(-0.0015s^2)$ was used.

The experimental radial distribution curve was studied and the data thus obtained were used for the starting model in least squares refinements.

INTERPRETATION OF THE EXPERIMENTAL RESULTS

In spite of considerable difference between the three blackness corrections the geometry parameters did not differ significantly taking the standard deviations into account. The variation caused by different blackness corrections was in the order of 0.02 Å for the longer C—C bond distance and 0.01 Å

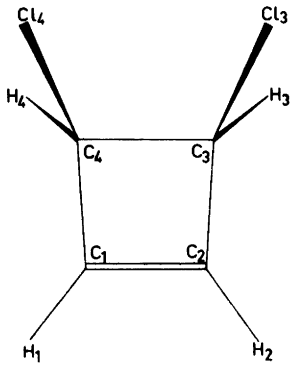

Fig. 1. Numbering of the atoms in the *cis*-3,4-dichlorocyclobutene-1.

for the double bond, while the medium C—C bond distance and the C—Cl bond distance varied only a few thousandths of an Å. For vibrational parameters (u values) variations were larger, but in any case the u value for the double bond was found much lower than according to general experience. Particularly the lowest blackness correction lead to unreasonable small u values. Furthermore, the application of the lowest blackness correction caused great difficulties in fitting together intensity contributions obtained by different diffraction distances. When the medium blackness correction was applied, these difficulties disappeared and the u values seemed more reasonable, though they are definitely uncertain.

The molecule model was assumed to be symmetrical, and the ring to be planar. In the refinement procedure the u values of the two different C—C

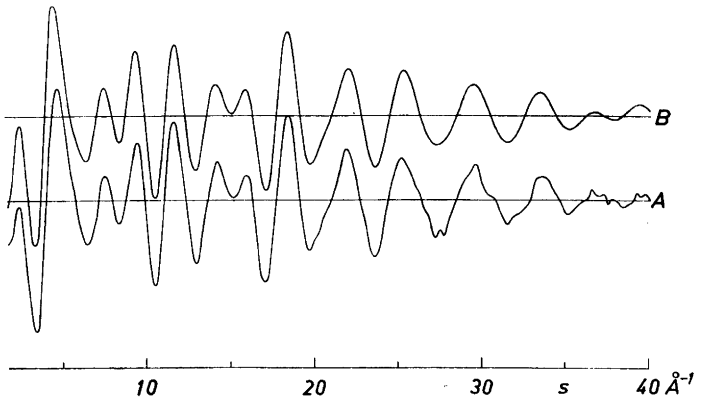

Fig. 2. Experimental (A) and theoretical (B) intensity curve for *cis*-3,4-dichlorocyclobutene-1.

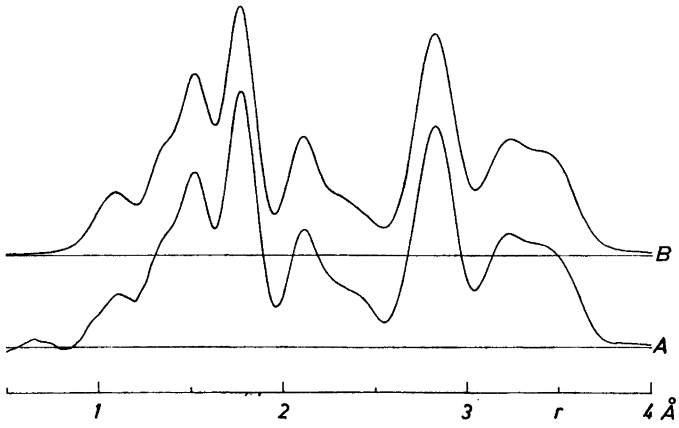

Fig. 3. Experimental (A) and theoretical (B) radial distribution curve for *cis*-3,4-dichlorocyclobutene-1.

single bonds were assumed to be equal. The same was done for the two different C···Cl distances through one angle. Though this assumption is not entirely correct, it does not influence the final geometric parameters significantly. The u values for the longer distances were not refined, the values were taken from general experience with other chlorohydrocarbons. This rather arbitrary choice may seem somewhat dubious, but we know from the study of the application of least squares in electron diffraction that the geometry parameters are unsignificantly affected by the u values of the longer distances. The theoretical intensity and radial distribution curves of the final model are included in Figs. 2 and 3, respectively. The structure parameters and their standard deviations as obtained by the least squares programme are shown in Table 1.

Table 1. Geometrical and vibrational parameters for *cis*-3,4-dichlorocyclobutene-1 obtained by least squares refinement. (The u value is the root-mean-square amplitude of vibration).

	r (Å)	Stand. dev. for r (Å)	u (Å)	Stand. dev. for u (Å)
C_1-C_2	1.349	0.006	0.035	0.008
C_2-C_3	1.505	0.004	0.040	0.009
C_3-C_4	1.583	0.013	0.040	0.009
C_4-Cl_4	1.771	0.002	0.054	0.003
C—H	1.09	—	0.134	0.025
C_1-Cl_4	2.782	0.008	0.079	0.007
C_3-Cl_4	2.865	0.008	0.079	0.007

Angle $C_1-C_4-Cl_4 = 166.0°$ Angle $C_3-C_4-Cl_4 = 117.2°$

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