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The Molecular Structure of Hexachloro-3,4-dimethylenecyclobutene

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The molecular structure of gaseous hexachloro-3,4-dimethylenecyclobutene has been investigated by electron diffraction. The molecule is found to be planar. The average value of the C—Cl distances is 1.695(6) Å. The carbon skeleton is almost unchanged from that of the unsubstituted hydrocarbon.

The main conclusions from the experimental study have been satisfactorily confirmed by an SCF-MO calculation including the π-electrons only.

The molecular structure of 3,4-dimethylenecyclobutene has previously been elucidated by an electron diffraction investigation.[1] The experimental results obtained were found to be in accordance with properties calculated by the ZDO approximation in the SCF theory.[2]

The aim of the present work is to study the geometric stability of the carbon skeleton of the perchlorinated derivative of the molecule. The main results from the electron diffraction study have been confirmed by semi-empirical calculations of the same kind as those used for the unsubstituted hydrocarbon. A sample of the compound was kindly given to me by Drs. E. D. Bergmann and I. Agranat of the Hebrew University of Jerusalem.

ELECTRON DIFFRACTION STUDIES

The electron scattering patterns were recorded on the Oslo electron diffraction unit [3] with a nozzle temperature of 140° and a nozzle-to-photographic plate distance of about 48 cm. Due to thermal instability of the compound, attempts at recordings at shorter distances were not successful, and the structure calculations were based on intensity data from one nozzle-to-plate distance only. The optical densities of four plates in the region $s = 1.375$ Å^{-1} to 19.75 Å^{-1} were measured at $\Delta s = 0.125$ Å^{-1} intervals, and the data were processed in the usual manner.[4]

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Theoretical intensity curves were calculated from the approximation

$$I^{ClCl}(s) = \sum \frac{|f_i(s)|\ |f_j(s)|}{|f_{Cl}(s)|^2} \cos[\eta_i(s) - \eta_j(s)] \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2) \quad (1)$$

The sum extends over all atomic pairs i, j in the molecule.

As usual, R_{ij} denotes the internuclear distance, u_{ij} the root mean square amplitude of vibration, and $f_i(s) = |f_i(s)| \exp[i\eta_i(s)]$ is the atomic scattering factor for atom i. For the carbon and chlorine atoms values from nonrelativistic Hartree-Fock calculations have been used.[5,6]

Radial distribution curves were calculated by Fourier inversions of experimental and theoretical intensity curves.

Because of the short intensity range in the data the constant k in the general formula for the radial distribution curve

$$RD = (2\pi)^{-\frac{1}{2}} \sum_{s=S_{min}}^{S_{max}} Im(s) \exp(-ks^2) \sin(rs)\Delta s \quad (2)$$

was put equal to 0.020.

The best agreement between experimental and theoretical curves was obtained by assuming the molecule to be planar. The carbon – carbon distances 1 – 2 and 2 – 3 were assumed to be 1.45 Å and the carbon – carbon distances 2 – 5 and 1 – 4 were assumed equal to 1.37 Å. The C – Cl bonds were assumed to be 1.69 Å, and a least squares refinement was carried out. For labelling of atoms, see Fig. 1.

Because of lack of intensity data at s-values above 20 Å^{-1} and strong scattering contribution from the six C – Cl distances, it was not possible to refine the C – C distances and the corresponding u-values. The external angles and the average C – Cl bond distance and corresponding u-value were refined.

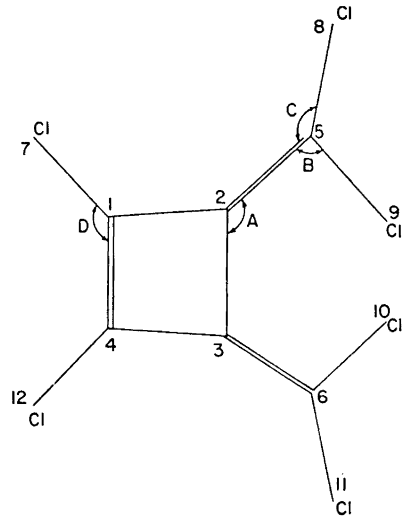

Fig. 1. Notation of atoms.

Table 1. Experimental and calculated distances in hexachloro-3,4-dimethylenecyclobutene. Calculated values for the unsubstituted hydrocarbon included for comparison.

Dist.	R(Å) exp	Stand. dev.	R calc.	R calc. for hydroc.
C_1-C_2	1.45		1.469	1.468
C_2-C_3			1.477	1.476
C_2-C_5	1.37		1.351	1.350
C_1-C_4			1.356	1.354
$(C-Cl)_{av.}$	1.695	0.006	1.721	

Table 2. Interbond angles from least squares refinement. For labelling of angles see Fig. 1.

Angle	Degrees	Stand. dev. (degr.)
A	134.4	0.9
B	127.4	1.9
C	118.7	1.5
D	134.9	0.9

The results are given in Tables 1 and 2. Other u-values were refined with the constraint that the u-values for all distances of one type and belonging to the same peak in the radial distribution curve are identical. The final results were used to calculate theoretical radial distribution curves, shown in Fig. 2. The final results for the experimental structure parameters are given in Table 1.

MOLECULAR ORBITAL CALCULATIONS

The procedure applied in these calculations has been presented in detail previously.[7-9] The parameters appropriate to the carbon-carbon bond have

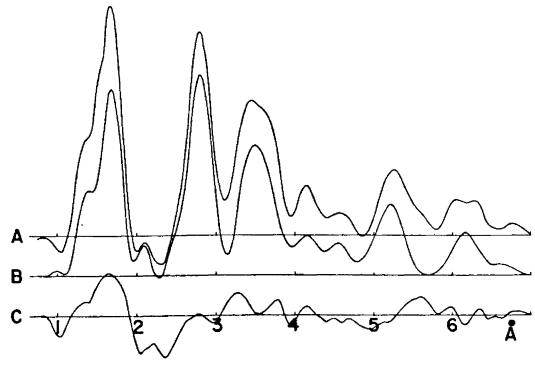

Fig. 2. Radial distribution curves. A, experimental; B, theoretical; C, A−B.

been taken from a paper by Roos and Skancke,[7] and for the chlorine-carbon bond parameters evaluated by Grabe [9] have been used. Her paper, however, does not give a relation between bond order and bond length for the C – Cl bond. All the molecules chosen for the parameterization have bond lengths very close to 1.718 Å, and also her calculated bond orders varied very little, between 0.14 and 0.18.

For the carbon-carbon bond, the relation $R_{\mu\nu} = 1.517 - 0.18\ p_{\mu\nu}$ has been successfully used in previous papers. $p_{\mu\nu}$ is here the bond order between neighboring atoms μ and ν as calculated by this parameterization scheme. The constant 0.18, the slope of the bond distance to bond order graph, seems to change little when one atom is a hetero atom. If we assume the value 0.18 also for the chlorine-carbon bond, and use the experimental bond distance for *o*-dichlorobenzene and 1,2,4,5-tetrachlorobenzene which are both determined to 1.717 Å ± 0.005 Å,[10] and the calculated bond order 0.150, we obtain the relation

$$R_{\mu\nu} = 1.744 - 0.18\ p_{\mu\nu} \quad (3)$$

By using the experimental bond distance [11] and calculated bond order for *cis*-1,2-dichloroethylene, however, one arrives at a relation

$$R_{\mu\nu} = 1.755 - 0.18\ p_{\mu\nu} \quad (4)$$

The CCCl bond angles of the benzene derivatives are 120°, and the corresponding angle for *cis*-1,2-dichloroethylene is 121°33′, so the difference can hardly be explained as due to hybridization. Eqn. (3) based upon benzene derivative data are used in the present work to calculate C–Cl bond distances from bond orders, but the uncertainty at this point should be kept in mind.

RESULTS AND DISCUSSION

Table 1 gives the bond distances of the molecule. In spite of the rather poor resolution of the radial distribution function the experimental results show a planar molecule with a strongly alternating ring system similar to the one in the unsubstituted hydrocarbon. This conclusion is confirmed by the molecular orbital calculations.

The difference between the experimental and the theoretical value for the C–Cl bond is hard to explain. Partly it may be ascribed to the uncertainty in the bond order to bond distance relationship for the C – Cl bond. The bond orders for the C–Cl bonds in this molecule were all equal to 0.132 as compared to about 0.15 for the molecules chosen for the parameterization. This should indicate a C–Cl distance larger than 1.718 Å for the molecule investigated here. Because of the strong contribution from this distance in the radial distribution curve (see Fig. 1) its experimental value should be quite reliable.

In Table 3 the calculated π-electron charges are compared with those in the hydrocarbons.[2] It is seen that the chlorine atoms increase the electron density in the ring, while atoms 5 and 6 have reduced atomic net charges as compared to the hydrocarbon.

The experimental UV spectrum of the molecule recorded in *n*-heptane solution [12,13] is given in Table 4. This shows two pronounced absorption maxima,

Table 3. Calculated π-electron atomic charges in hexachloro-3,4-dimethylenecyclobutene (I), and in the substituted hydrocarbon (II). For labelling of atoms see Fig 1.

Atom No.	I	II
1	1.017	0.988
2	0.994	0.878
5	1.045	1.132
7	1.982	
8	1.981	
9	1.981	

Table 4. Calculated and observed electronic transitions in hexachloro-3,4-dimethylenecyclobutene. Frequencies in cm^{-1}.

$\nu_{calc.}$	$\nu_{obs.}$	$f_{calc.}$	$\log E_{obs.}$
37 000	34 700	0.15	
38 300	35 700	0.0	
47 000	39 700	0.82	4.5
48 000	41 700	0.84	4.56

one at about 35 000 cm^{-1} and one at about 40 000 cm^{-1}. Both peaks exhibit fine structure. By a comparison to the calculated counterparts, the experimental transition at 41 700 cm^{-1} ($\log E = 4.56$) has to be assigned to the calculated strong transition at 48 000 cm^{-1}. The close-lying transition of 39 700 ($\log E = 4.5$) must correspond to the calculated value of 47 000 cm^{-1}. As a shoulder on this dominating double peak are two transitions at 34 700 cm^{-1} and 35 700 cm^{-1}, respectively. These are most likely related to the calculated values of 37 000 cm^{-1} and 38 300 cm^{-1}. The experimental intensities of these weak transitions are very uncertain.

The discrepancies between experimental and calculated values for the strong transitions may partly be due to solvent shifts.

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