The Molecular Structure of 3,4-Dimethylenecyclobutene

ANNE SKANCKE

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

The molecular structure of 3,4-dimethylenecyclobutene has been determined by means of the electron diffraction method. The molecule, which is planar, exhibits a pronounced single-bond double-bond structure. The carbon-carbon bond distances found are: $C_1-C_2=1.488\pm0.009$ Å, $C_2-C_3=1.516\pm0.020$ Å, $C_1-C_4=1.357\pm0.005$ Å, $C_2-C_5=1.335\pm0.003$ Å. The average value for the $C-H$ bond distances is 1.098 ± 0.005 Å.

The molecule 3,4-dimethylenecyclobutene, a cyclic isomer of benzene, has recently been synthesized,[1] and some of its properties have been reported. The central point in the discussion of its properties is whether the molecule contains some of the aromatic character of benzene, or has an olefine structure with alternating bond distances.

Structure analyses of a series of molecules containing four-membered rings have been carried out, and abnormal bond distances have been reported. In this way the hybridization of these strained systems may be elucidated. As an example, the *peri*-bonds in biphenylene are found to be 1.514 Å,[2] a value which is considerably larger than a normal aromatic $C-C$ bond. This circumstance has been discussed in previous papers.[3,4]

To the author's knowledge no complete structure determination has been carried through for 3,4-dimethylenecyclobutene. Spectroscopic studies in the infrared region [1,5] indicate an olefine character, and NMR studies [5,6] show
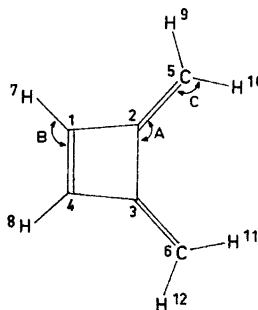

Fig. 1. Numbering of the atoms in 3,4-dimethylenecyclobutene.

the presence of exomethylene groups, indicating also an alteration in bonds. Furthermore, microwave spectrum investigations indicate that the molecule is planar, and measurements of the Stark effect give a dipole moment of 0.618±0.011 D.[7]

In a previous paper,[8] a semi-empirical SCF—MO calculation has been carried through, using the Pariser-Parr-Pople approximation. The resulting bond distances show a pronounced single bond-double bond structure irrespective of the chosen starting model for the evaluation of the necessary semi-empirical parameters.

An electron diffraction investigation of the molecule has now been carried through. A comparison of experimental and theoretical results is presented, and an attempt is made to correlate results with those obtained for other four-membered ring systems.

EXPERIMENTAL

A sample of 3,4-dimethylenecyclobutene was generously given by Professor W. D. Huntsman, Ohio University.

The electron scattering pattern was recorded at room temperature. Exposures were made with two nozzle-plate distances, 48 cm and 19 cm, giving a total recorded intensity from $s=1$ Å^{-1} to $s=42.75$ Å^{-1}. Four plates from each distance were photometered, and intensities read off at $\Delta s=0.125$ Å^{-1} for $s<7$ Å^{-1}, and $\Delta s=0.250$ Å^{-1} for $s>7$ Å^{-1}. The data were processed in the usual manner,[9] and the resulting final intensity curve is shown in Fig. 2A.

Theoretical intensity curves were calculated from the formula

$$I_{\mathrm{M}}(s) = \mathrm{const} \sum_{i \neq j} \frac{|f_i(s)| \; |f_j(s)|}{(f_{\mathrm{C}}(s))^2} \; \frac{\sin(R_{ij}s)}{R_{ij}} \; \exp(-\tfrac{1}{2}u^2{}_{ij}s^2) \tag{1}$$
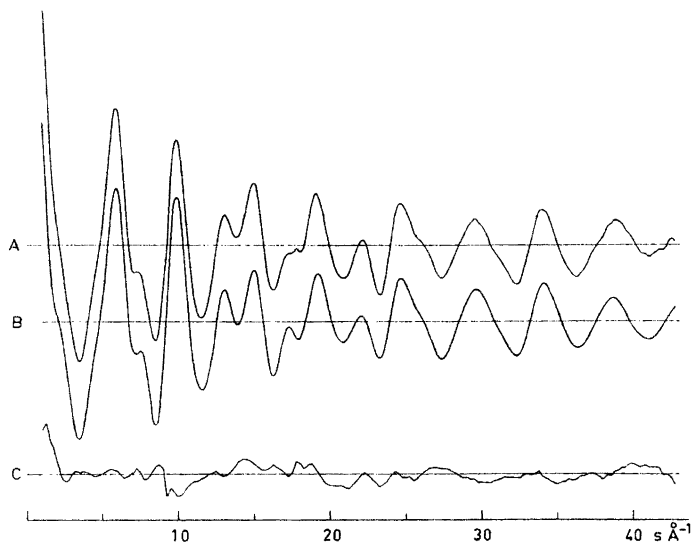

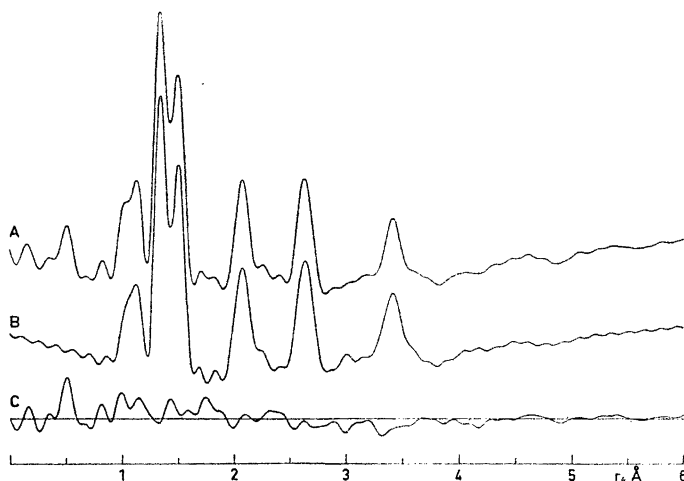*Fig. 2.* Experimental (A) and theoretical (B) intensity curve for 3,4-dimethylenecyclobutene. C=A−B.

Fig. 3. Experimental (A) and theoretical (B) RD curve for 3,4-dimethylenecyclobutene.
C=A—B.

where the sum extends over all atom pairs i,j in the molecule. R_{ij} denotes the internuclear distance, u_{ij} the root mean square amplitude of vibration, and $f_i(s)$ is the atomic form factor for atom i.

Radial distribution (RD) curves were obtained by Fourier inversion of the experimental and theoretical intensity curves.

The constant k in the general formula for the radial distribution curve

$$RD = \frac{1}{\sqrt{2\pi}} \sum_{s=S_{min}}^{S_{max}} I_M(s) \exp(-ks^2) \sin(sr) \Delta s \qquad (2)$$

was put equal to 0.

Fig. 3 A shows the experimental RD curve. The splitting into two peaks with maxima at about 1.36 Å and 1.50 Å unambiguously reveals the alteration of C—C bond lengths, and settles the question of olefinic or aromatic character.

As a first attempt, a theoretical RD curve was calculated with C—C bond lengths of 1.36 Å and 1.48 Å. The exomethylene groups were taken to bisect the external angles of the ring, and so were the C—H bonds at atoms 1 and 4. The angles within the methylene groups were assumed to be equal to 120°. The molecule was assumed to be planar, an assumption strongly supported by the above mentioned microwave investigation. This model gave a fairly good reproduction of the experimental curve, and a least squares refinement could then be carried out.

The least squares refinement gave as a first result a splitting of the single bonds and double bonds into four different C—C bond distances, and a further study of these bond distances was done by calculating sharpened radial distribution functions in the region $R = 1.0 - 2.0$ Å. The sharpened radial distribution function was calculated according to the formula

$$SRD = \sqrt{2\alpha} \sum_{s=S_{min}}^{S_{max}} I_M(s) \exp[-\alpha(S_{max}-s)] \sin(sr) \Delta s \qquad (3)$$

where α, the anti-damping constant, was put equal to 0.035. The best fit to the experimental curve was obtained using the following distances: $C_1 - C_2 = 1.49$ Å, $C_2 - C_3 = 1.52$ Å, $C_1 - C_4 = 1.36$ Å and $C_2 - C_5 = 1.34$ Å. For notation of atoms and angles, see Fig. 1.
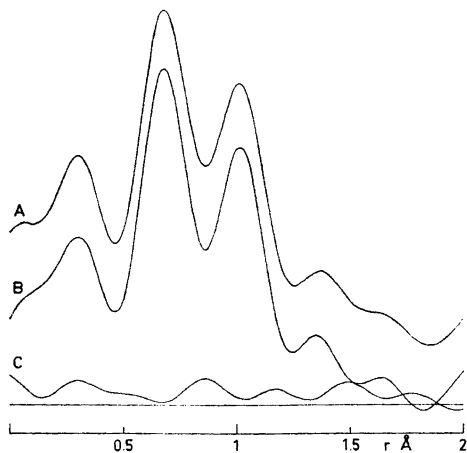
Fig. 4. Experimental (A) and theoretical (B) SRD curve for 3,4-dimethylenecyclo-butene. C=A−B.

These bond distances were used as input data for further least squares refinements. During the refinement no bisecting of external angles was assumed. The internuclear distances and the angles A, B, and C were first refined keeping the u-values constant, and all parameters were finally refined until the convergence limit was reached. Since it proved to be impossible to refine all the u-values independently, the C−C and C−H u-values were refined with the constraint that the u-values for all distances of one type belonging to the same peak in the radial distribution curve, are identical. The H−H u-values were not refined. The final results were used to calculate theoretical intensity, RD and SRD functions (Figs. 2−4).

RESULTS AND DISCUSSION

The bond lengths and u-values resulting from the least squares refinement are listed in Table 1. The u-values for the non-bonded distances are not given in the table, because of their large standard deviations. The comparatively large uncertainty in these values will, however, not influence the values for the geometrical parameters significantly.

The table shows four different C−C bond distances although the standard deviation of distance C_2—C_3 is rather large, and the observed difference between the distances C_1—C_2 and C_2—C_3 is within the error limit.

Table 1. Bond distances and root mean square vibrational amplitudes as obtained from least squares refinements.

Dist.	r (Å)	Stand.dev. for r (Å)	u (Å)	Stand.dev. for u (Å)	$r_{\text{calc.}}$ (Å)
C_1—C_2	1.488	0.009	0.052	0.004	1.468
C_2—C_3	1.516	0.020	0.052	0.004	1.476
C_1—C_4	1.357	0.005	0.042	0.003	1.354
C_2—C_5	1.335	0.003	0.042	0.003	1.350
(C—H)$_{\text{av.}}$	1.098	0.005	0.072	0.004	

Table 2. Angles in degrees from least squares refinements.

Angle	Degrees	Stand.dev.(degr.)
A	135.7	1.4
B	131.5	1.4
C	121.2	1.0

The distance C_1-C_4 may be compared to the double bond in cyclobutene, which has been reported in a paper by Goldish et al.[10] to 1.325 ± 0.046 Å. The large standard error taken into account, this is in agreement with the value 1.357 ± 0.005 Å found in the present investigation. Furthermore, this bond may be compared to the double bond in cis-3,4-dichlorocyclobutene, which has been determined to 1.349 ± 0.006 Å [11] in good agreement with the present work. The C—C single bonds of the chloro-substituted molecule are, however, found to be considerably longer than the single bonds of the molecule studied here. This circumstance may be ascribed to the difference in hybridization between the two compounds, and in part also to the repulsion between the two chlorine atoms.

The C_2-C_5 bond should have an environment quite similar to the C—C bond in ethylene, and in fact excellent agreement is found between these two distances. The most recent determination of this distance in ethylene is 1.336 ± 0.001 Å,[12] compared to the C_2-C_5 bond of 1.335 ± 0.003 Å.

The formal single bonds C_1-C_2 and C_2-C_3 have lengths comparable to values found for corresponding bonds in the four-membered ring of 1-cyclo-hexenyl-1-cyclobutene-dione.[13] The agreement between our value for C_1-C_2 (1.488 Å) and the value reported for the corresponding bond in the dione (1.486 Å) is almost complete, whereas the discrepancy between the values found for the other single bond, is somewhat larger. This difference which is hardly significant, may be interpreted in terms of the presence of heteroatoms.

Another unsaturated pure hydrocarbon containing a four-membered ring is biphenylene, for which rather accurate measurements are available.[2] The formal single bonds linking the hexagonal rings are reported to be 1.514 Å, a value which is in close agreement with our result.

The calculated R-values referred to in Table 1 are based on bond orders obtained by a SCF study recently published.[8] The main conclusion reached in the theoretical work, a pronounced single-bond double-bond alteration, is in complete agreement with the present findings. Furthermore, it is worth noticing that the predicted differences between the two single and the two double bonds, respectively, are qualitatively confirmed by the present results. In view of the uncertainties in both sets of values, a closer examination of these differences seems, however, to be unrealistic.

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