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The Single and Double Bonds Between sp^2-Hybridized Carbon Atoms, as Studied by the Gas Electron Diffraction Method.

VIII. The Molecular Structure of 1,3-Cycloheptadiene

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The molecular structure of 1,3-cycloheptadiene has been investigated by the gas electron diffraction sector method. The molecule was found to have C_s symmetry with all but one of the carbon atoms being coplanar. The experimentally determined geometrical parameters are the following. $r(C_1=C_2)$: 1.347 Å; $r(C_2-C_3)$: 1.445 Å; (C_4-C_5): 1.509 Å; $r(C_5-C_6)$: 1.522 Å; $r(C_1-H_1)$: 1.092 Å; $r(C_5-H_5)$: 1.102 Å; $\angle C_1C_2C_3=\angle C_7C_1C_2$: 129.1°; $\angle H_2C_2C_1$: 117.5°. The bond distances are given as $r_g(1)$-values. The angle between the $C_4C_5C_7C_1$ and $C_5C_6C_7$ planes was found to be 63.9°.

1,3-Cycloheptadiene was first synthesized by Willstätter[1] in 1901. The ultraviolet absorption spectrum of the compound was determined in 1950 by Pesch and Friess.[2] The spectrum showed a broad absorption band with one maximum ($\lambda_{max}=248$ mμ, log $\varepsilon=3.87$). The same result was also obtained by Hafner and Rellesmann[3] for a hexane solution of the compound. The result is typical for conjugated dienes.[4–6] Based on a discussion of UV-spectra Braude[7] concluded that the CC double bonds in 1,3-cycloheptadiene must be coplanar. This conclusion does not carry too much weight, though, as he also concluded that 1,3-cyclohexadiene has a planar carbon skeleton, while later investigations[8–10] have shown that this molecule has a dihedral angle of about 18° between two planar ethylene groups.

1,3-Cycloheptadiene was studied by Chiang and Bauer[11] in 1966. Their vapour phase electron diffraction results showed the double bonds to be coplanar. Crews[12] recently reported a ^{1}H nuclear magnetic resonance analysis of 1,3-cycloheptadiene. His results are not in accord with a C_s structure in which all but one of the carbon atoms are coplanar. His data indicate a distorted tub conformation of C_2 symmetry.

EXPERIMENTAL PROCEDURE

The sample of 1,3-cycloheptadiene used in the present investigation was kindly provided by professor W. Lüttke, Göttingen, Germany. The 1,3-cycloheptadiene (in the following sometimes abbreviated CHD) molecule was studied by the sector electron diffraction method, using an s^3 sector. The photographs were taken at room temperature in the usual way with a Balzers Eldigraph KDG-2 in Oslo.[13] The data were treated in the usual way [14] and an experimental intensity function in the region $s = 1.25 - 29.50$ Å^{-1} was obtained.

STRUCTURE ANALYSIS

Before one can hope to get convergence when the molecular intensities are adjusted to the experimental intensities using the least squares method, it is necessary to know approximate values for the bond distances and also to have reasonable estimates for the various angle parameters. This preliminary information was obtained by comparing experimental and theoretical radial distribution functions (RD-functions) and – for the bond distances – autocorrelation power spectra (APS-functions).[17] Starting values for the vibrational amplitudes (u-values) were partly obtained from the power spectra and partly by applying experimentally obtained results for similar molecules.[8,11,18,19]

In the present investigation three different molecular models for 1,3-cycloheptadiene were studied. One model, which is shown in Fig. 1, has a twofold symmetry axis bisecting $r(C_2-C_3)$. This model with a fairly large angle between the $C_7C_1C_2$ and $C_2C_3C_4$ planes, has C_2 symmetry. If this angle is sufficiently small the C_2 symmetry is destroyed and this situation represents the second model. In the third model all but one of the carbon atoms are coplanar and the model corresponds to C_s-symmetry (see Fig. 2).

The experimental radial distribution function was not compatible with a molecular model with C_2 symmetry and this case was therefore ruled out.

The other two models were studied by least squares refinements of the intensity data. The second model gave a C_2-C_3 dihedral angle that was not significantly different from zero. This model was therefore virtually equal to the third model, and in the following only the refinements based on this latter model are discussed.

As the least squares refinements gave no significant difference in the angles $\angle C_2C_3C_4$ and $\angle C_3C_4C_5$, these angles were assumed to be equal. It was

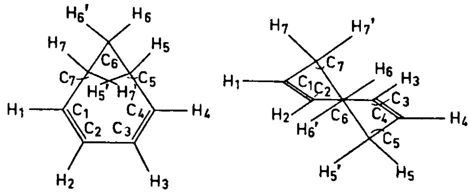

Fig. 1. 1,3-Cycloheptadiene. Molecular model with C_2 symmetry.

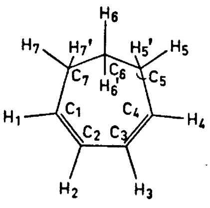

Fig. 2. 1,3-Cycloheptadiene. "Semiplanar" molecular model with C_s symmetry.

further assumed that $\angle C_4C_5H_5 = \angle C_4C_5H_5' = \angle H_6C_6H_6' = 109.5°$. When the root mean square amplitudes of vibrations (u-values) were kept constant and the above mentioned and chemically reasonable assumptions were applied, it was possible to refine all independent bond length parameters and angle parameters simultaneously in the least squares adjustments. It was not possible, however, to determine the u-values by this method. These parameters were therefore assigned by comparing theoretical and experimental RD- and APS-functions.

FINAL RESULTS

The experimentally determined structural parameters for 1,3-cycloheptadiene are presented in Table 1. The conjugated diene system is found to assume a planar *cis* equilibrium conformation and the molecule as a whole is observed to have approximately C_s symmetry. Fig. 3 shows the theoretical and experimental molecular intensity functions ($sM(s)$-functions) and the difference between the two functions, while Fig. 4 shows the corresponding radial distribution functions.

Table 1. 1,3-Cycloheptadiene. Experimentally determined molecular parameters and corresponding standard deviation values, as determined by the least squares method.

Distances	Mult.	$r_g(1)$, Å	$\delta(r_g(1))$, Å	u, Å
C_1-H_1	4	1.0922	0.0027	0.0750
C_2-C_3	1	1.4498	0.0064	0.0500
$C_1=C_2$	2	1.3465	0.0023	0.0410
C_4-C_5	2	1.5092	0.0083	0.0500
C_5-C_6	2	1.5218	0.0079	0.0500
C_5-H_5	6	1.1022		0.0750

Angles	Degrees	σ	Angles	Degrees
$\angle C_1C_2C_3$ $\angle C_7C_1C_2$	129.1	0.1	$\angle C_4C_5C_6$ [b]	114.0
$\angle H_2C_2C_1$	117.5	4.9	$\angle C_5C_5C_7$ [b]	113.0
$\angle \delta$ [a]	63.9	1.2	$\angle C_6C_5C_7$ [b]	24.1

[a] $\angle \delta$ is the angle between the planes $C_4C_5C_7C_6$ and $C_5C_6C_7$. [b] Angles calculated from independently determined molecular parameters.

DISCUSSION

From Table 1 it is seen that the 1,3-cycloheptadiene molecule possesses considerable angle strain. It is fully possible to have normal bond angles in the molecule, but in this case there will be a relatively large angle between the

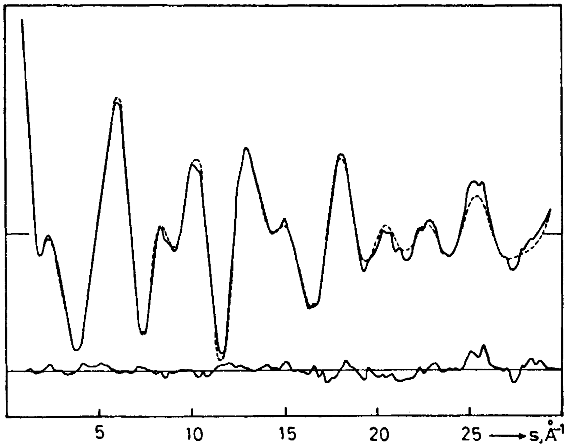

Fig. 3. 1,3-Cycloheptadiene. Experimental (———) and theoretical (– – –) molecular intensity functions with difference curve.

$C_7C_1C_2C_3$ and $C_2C_3C_4C_5$ planes and accordingly considerably reduced conjugation between the CC double bonds. Such a conformation corresponds to model 1 discussed above. For this model the atom H_5' (see Fig. 1) will be very close to the π-orbital at C_1 and the atom H_7' similarly close to the C_4 π-orbital. There will also be considerable torsional strain as the bonds at C_4-C_5 and C_1-C_7 will be approximately eclipsed, while the "semi-planar" model (see Fig. 2) has dihedral angles for C_4-C_5 and C_1-C_7 of about 24°.

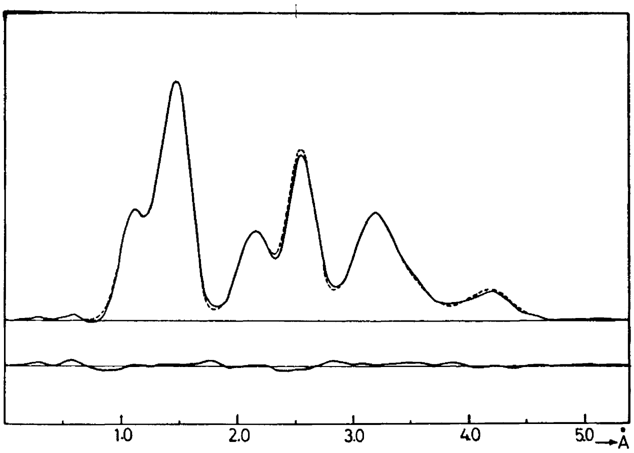

Fig. 4. 1,3-Cycloheptadiene. Experimental (———) and theoretical (– – –) radia distribution functions and difference curve. Artificial damping constant $k=0.0036$ Å^2.

Since the molecule in the present investigation is found to have a "semi-planar" structure, where all but one of the carbon atoms are coplanar, one may conclude that the mentioned repulsions between the π-orbitals and the hydrogen atoms, the higher torsional strain energy together with less conjugation of the π-orbitals correspond to higher conformational strain energy than those due to the angle strain in the "semi-planar" molecule with C_s symmetry. There are good reasons to believe that the reduced torsional energy in the "semi-planar" model is more important than the conjugation effect. In the 1,3-cyclohexadiene molecule the planar conformation has maximum torsional energy and maximum overlap between the C_2 and C_3 π-orbitals. Electron diffraction structure studies [8–10] showed that the molecule has a non-planar carbon skeleton, which means that loss in conjugation is less important than the reduced torsional strain. It is difficult to evaluate the importance of the repulsions between the π-orbitals and the hydrogen atoms in determining the conformation. Chiang and Bauer [11] claim that this repulsion is the decisive effect why a "semi-planar" molecule is energetically most favorable. They did, however, not consider the contribution from torsional strain in the molecule.

In Table 2 the most important structural parameters for 1,3-cycloheptadiene obtained in the present study are compared with those determined by Chiang and Bauer.[11] There is good agreement between the $C-H$ and $C_1=C_2$ bond lengths in the two investigations, while the present study gives considerably shorter C_2-C_3, C_4-C_5, and C_5-C_6 bond lengths. The average bond length in Chiang and Bauer's study is a good deal greater than that found in the present work. This might indicate a wave length error in one or both of the studies. The CC double bond length, which is one of the most accurately determined parameter, is, however, the same in the two studies. This explanation does therefore not seem very likely.

It is of interest to compare the results obtained for 1,3-cycloheptadiene with experimental data for other conjugated cycloalkadienes. Table 3 shows that the C_2-C_3 bond length for 1,3-cycloheptadiene is found to be somewhat

Table 2. 1,3-Cycloheptadiene. Comparison of the present results with those from Chiang and Bauer's earlier electron diffraction study.[11] The presented error limits for this work are 2.5 times the standard deviations from the least squares refinements.[15]

Parameter	Chiang and Bauer's results	This work
C_1-H_1	1.09 ± 0.02 Å	1.092 ± 0.007 Å
C_2-C_3	1.48 ± 0.01 Å	1.450 ± 0.015 Å
$C_1=C_2$	1.35 ± 0.01 Å	1.347 ± 0.006 Å
C_4-C_5	1.54 ± 0.01 Å	1.509 ± 0.020 Å
C_5-C_6	1.55 ± 0.01 Å	1.522 ± 0.020 Å
$\angle C_1C_2C_3$ $\angle C_7C_1C_2$	129 ± 2°	129.1 ± 0.3°
$\angle \delta$ [a]	72.8°	63.9 ± 3.0°

[a] $\angle \delta$ is the angle between the $C_5C_6C_7$ plane and the plane of the other carbon atoms.

Table 3. Experimentally determined molecular parameters for conjugated 1,3-cycloalkadienes.

Parameter	C_6H_8 [a]	C_7H_{10} [b]	C_8H_{12} [c]
$C_1=C_2$	1.348 Å	1.347 Å	1.347 Å
C_2-C_3	1.465 Å	1.450 Å	1.475 Å
C_4-C_5	1.519 Å	1.509 Å	1.509 Å
C_5-C_6	1.538 Å	1.522 Å	1.542 Å
$\angle C=C-C$	120.3°	129.1°	129.0°
$\angle \beta$ [d]	18.0°	0°	37.8°

[a] Ref. 8. [b] The present study. [c] Ref. 16. [d] $\angle \beta$ defines the angle between planar ethylene groups.

shorter than the corresponding bond length in 1,3-cyclohexadiene[8] and 1,3-cyclooctadiene.[16] The uncertainty in this parameter is, however, of the order of magnitude of ± 0.015 Å for all these three molecules and the discussed bond lengths are therefore not significantly different. The other CC bond lengths presented in Table 3 are also the same in the three molecules when the error of the method is taken into account.

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