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

V. The Molecular Structure of 1,3-Cyclooctadiene

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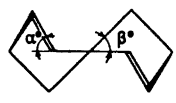
Gaseous 1,3-cyclooctadiene has been studied by the electron diffraction sector method. The molecule was found to have C_i symmetry. The angle between the two planar ethylene groups is 37.8° and minor oscillations around the equilibrium interplanar angle are probable. The experimentally determined geometrical parameters are the following: $r(C_1=C_2)$: 1.347 Å, $r(C_2-C_3)$: 1.475 Å, $r(C_4-C_5)$: 1.509 Å, $r(C_5-C_6)$: 1.542 Å, $r(C_1-H_1)$: 1.102 Å, $r(C_5-H_{14})$: 1.109 Å, $\angle C_1C_2C_3$: 129.0°, $\angle C_4C_5C_6$: 117.2°, $\angle C_5C_6C_7$: 105.9°, $\angle C_1C_2H_{10}$: 119.0°, $\angle C_4C_5H_{13}$: 110.5°. The bond distances are given as $r_g(1)$-values.

Cycloalkadienes of certain ring sizes (C_6, C_{10}, C_{14},...) have approximately strain free molecular structures when the two double bonds are diametrically placed.[1] Isomerisation of cyclooctadiene does, however, give almost quantitatively the conjugated isomer,[2] which therefore represents the most stable monocyclic C_8H_{12} configuration.

In 1954 Braude[3] considered the conformations of conjugated cycloalkadienes. Models showed that in order to attain a reasonable strainless structure the CC double bonds in 1,3-cyclooctadiene could not be coplanar. Ultra-violet absorption maximum for this molecule appeared at a lower wavelength (228 mμ) than for the C_5, C_6, and C_7 1,3-cycloalkadienes for which planar carbon skeletons were assumed. Braude therefore suggested a dihedral angle of 41° for the $=C-C=$ bond in 1,3-cyclooctadiene and an overall conformation as shown in formula (I).

I



II

UV-absorption measurements in 1958 by Merkel [4] confirmed that there is a fairly large angle between the planes defined by two planar ethylene groups.

Chen *et al.*[5] have discussed the conformations of some cyclic olefins on the basis of molecular polarisabilities. Their experimental results for 1,3-cyclooctadiene are in agreement with a non-planar conformation. They find that model (II) shown above with angles α and β approximately equal to 30° and 40°, respectively, are consistent with the experimental data. They do not discuss model (II) in detail, but it is obvious that in the suggested model either the individual CC double bonds are seriously twisted or the ring has a *trans, trans* conformation. Both these possibilities seem to be highly unreasonable.

NMR-spectra of 1,3-cyclooctadiene are also recorded,[6,7] but no further information concerning the molecular structure is reported in these studies.

EXPERIMENTAL PROCEDURE

The sample of 1,3-cyclooctadiene used in the present investigation was kindly provided by professor W. Lüttke, Göttingen, Germany. The 1,3-cyclooctadiene (in the following abbreviated to COD) molecule was studied by the sector electron diffraction method, using a modified s^3 sector. The photographs were taken in the usual way with the Oslo apparatus.[8] The nozzle temperature was approximately 50°C and the electron wave length 0.064849 Å, corresponding to an accelerating voltage of about 36 kV. Photographs were taken at two nozzle-to-plate distances, *i.e.* approximately 48 cm and 19 cm, respectively. Four plates were used for each distance. By connecting the data from two plates, one from each nozzle-to-plate distance, four experimental intensity curves were obtained. These curves covered the s range 1.25 $Å^{-1}$—46.00 $Å^{-1}$. Radial distribution (RD) curves were calculated from each of the intensity curves according to the formula

$$\sigma(r)/r = \int I(s)\ \exp(-ks^2)\sin(rs)\mathrm{d}s \qquad (1)$$

where k is an artificial damping constant. As the agreement between the four intensity curves and also between the four RD-curves was satisfactory, an average of the four intensity curves was applied in the structure analysis. The theoretical molecular intensities were calculated by the formula

$$sM(s) = \text{const} \sum_{i \neq j}\sum g_{ij,kl}(s)\ \exp(u_{ij}^2 s^2/2)\ \sin(sr_{ij})/r_{ij} \qquad (2)$$

where

$$g_{ij,kl}(s) = \frac{|f_i(s)| \cdot |f_j(s)|}{|f_k(s)| \cdot |f_l(s)|}\ \cos(\eta_i(s) - \eta_j(s)) \qquad (3)$$

and $f(s) = |f(s)| \exp(i\eta(s))$ is the scattering amplitude of an individual atom. The scattering amplitudes were calculated by the "phase-amplitude method" described by Peacher and Wills,[10] using HF atomic potentials.[11]

STRUCTURE DETERMINATION

Preliminary values for the bond distances were obtained from auto- and crosscorrelation power spectra.[12] It was considerably more difficult to get preliminary values for the bond angles and dihedral angles.

Fig. 1 shows a molecular model of 1,3-cyclooctadiene where also the numbering of the atoms is given.

It was not possible to study the COD molecular structure by least squares refinements on the intensity data until a fairly good molecular model had

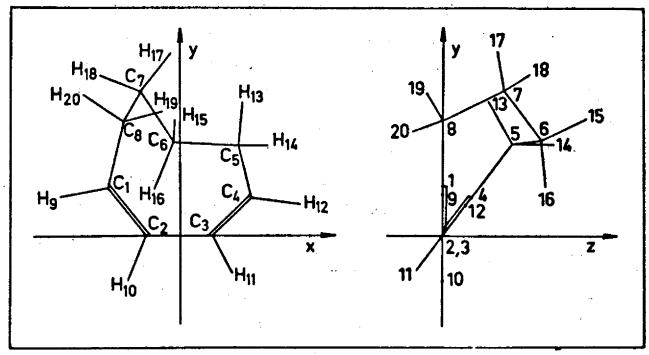


Fig. 1. 1,3-Cyclooctadiene. Molecular model which shows the numbering of the atoms.

been obtained. An inspection of the experimental RD curve reveals beyond doubt that the molecule has no symmetry elements and therefore belongs to the C_i symmetry group.

If it is assumed that $\angle C_1C_2C_3 = \angle C_2C_3C_4$ and $\angle C_8C_1C_2 = \angle C_3C_4C_5$ and that the bonds around each ethylenic group are coplanar, the carbon skeleton may be defined by the CC bond distances, four CC bond angles ($\angle C_2C_3C_4$, $\angle C_3C_4C_5$, $\angle C_4C_5C_6$, $\angle C_1C_8C_7$), the interplanar angle ($\angle \beta$) and one dihedral angle (either the C_8-C_1 or the C_5-C_4 dihedral angle). If the C_8-C_1 dihedral angle is chosen as a parameter, the other dihedral angle may be calculated by fitting the correct value for the C_6-C_7 bond distance.

If the various angle parameters and especially the interplanar angle β are not carefully chosen, it is not possible to solve this last problem. But if a solution exists, there will be two values for the C_5-C_4 dihedral angle that give the right answer. They correspond to *endo* and *exo* position of carbon atom No. 6, respectively. In a rather early stage of the investigation it was possible to rule out the possibility of a conformation corresponding to *exo* position of carbon atom No. 6.

In the beginning of this investigation the determinations of bond angles and dihedral angles were based on the study of radial distribution curves, but a peculiarity has been noticed for medium-sized cyclic hydrocarbons. For some molecules of this category many different parameter combinations give fairly good fit between theoretical and experimental RD curves and therefore make it difficult to determine the various parameters with high precision. For other medium-sized cyclic hydrocarbons it is very difficult to find a molecular model at all whose theoretical radial distribution curve is in satisfactory agreement with the experimental RD curve. 1,3-Cyclooctadiene belongs to the latter category of molecules. It was difficult to fit a theoretical model to the experimental RD function in the region from $r = 2.4$ Å to $r = 4.0$ Å.

Because of the large number of angle parameters in the COD molecule it was necessary to systematize the search for the correct molecular structure. A computer program was written for this purpose. In the program the parameters were varied systematically, one by one, over a reasonable range while

all the others were kept constant. For each parameter combination all the interatomic distances were calculated, and a theoretical radial distribution curve was calculated in the 2.4 – 4.0 Å r-region. The sum of the differences and the sum of the squared differences between theoretical and experimental RD curves were calculated for all models. The theoretical RD curves corresponding to the parameter combinations that gave fairly low values for the sums discussed above, were plotted along with the experimental RD curve.

Using the procedure described above close to a hundred different theoretical RD curves were plotted and studied, but none of these showed a similarity to the experimental RD curve that could be judged as nearly satisfactory.

Some information could, however, be deduced from the systematic study of bond angles and dihedral angles. 1) All the C – C = C angles were very nearly the same and close to 129°. 2) Even if the angles $\angle C_4C_5C_6$ and $\angle C_7C_8C_1$ were varied independently, best results were obtained when they were equal and close to 117°. 3) The interplanar angle was slightly below 40°.

It may seem surprising that it was not possible to get satisfactory agreement between theoretical and experimental data when so many parameters were fairly well determined. Using the information about the bond distances from the correlation spectra and the angle parameters from the systematic study described above, all the carbon atoms except C_6 and C_7 may be located. When $\angle C_4C_5C_6$ and $C_7C_8C_1$ are known, two out of three additional parameters are necessary to locate atoms C_6 and C_7, namely the $C_6 - C_7$ bond distance and the $C_7 - C_8$ and $C_4 - C_5$ dihedral angles, respectively. A preliminary value for the bond distance was known from the correlation spectra.

The real difficulty accordingly was connected with the dihedral angles. A systematic study like the one described above was not meaningful in this case as unacceptable bond angles at C_6 and C_7 were very easily obtained. For example if $\angle C_5C_6C_7$ were tetrahedral (109.5°), the other angle, $\angle C_6C_7C_8$, often came out as low as about 80°.

It was finally decided that the only possibility of keeping the bond angles at C_6 and C_7 under control was to fit the two dihedral angles so that $\angle C_5C_6C_7$ and $\angle C_6C_7C_8$ were kept equal. When this restriction was imposed, much better results were obtained, and the molecular model was soon good enough to be refined by least squares adjustment of the molecular intensity function.

The parameters discussed above describe the carbon skeleton of the COD molecule. If all the C = C – H angles are assumed to be equal and the same assumption is made about the C – C – H angles, these two angle parameters are necessary to determine the positions of the hydrogen atoms. In addition, two dihedral angle parameters are also necessary to locate the H_{15}, H_{16} atom pair and the H_{17},H_{18} atom pair.

The least squares refinement program requires a subprogram that calculates the coordinates of the different atoms in the molecule. With the assumptions made above about the bond angles and based on experimental evidence, the rigid COD molecule may be calculated from 12 parameters.

In the present case it is not surprising that it is impossible to vary all parameters simultaneously in the least squares refinements. The parameters that could not be reliably varied in the least squares program, were determined in the following way: Several least squares programs were run simultaneously.

Table 1. 1,3-Cyclooctadiene. Results from least squares intensity data refinements when one parameter (here $\angle C_4C_5C_6$) is different for each run. The numbers in brackets are 100 × the standard deviations.

Parameter	Start value	Run No.: I	II	$\angle C_4C_5C_6$ III	IV	V	VI
		116.6°	116.8°	117.0°	117.2°	117.4°	117.6°
C–H	1.1038 Å	1.1015(.3766)	1.1018(.3741)	1.1021(.3727)	1.1024(.3719)	1.1027(.3727)	1.1029(.3740)
C=C	1.3484 Å	1.3471(.1444)	1.3470(.1435)	1.3470(.1430)	1.3470(.1427)	1.3470(.1432)	1.3470(.1437)
$C-C_3$	1.4730 Å						
$C-C_5$	1.5100 Å						
$C-C_6$	1.5430 Å	1.5409(.1527)	1.5409(.1518)	1.5410(.1513)	1.5410(.1510)	1.5410(.1516)	1.5410(.1526)
C=C–C	129°						
$C_4C_5C_6$							
β	37.8°						
ϑH15	30°						
C=C–H	119°						
C–C–H	110.5°						
ϑH17	−30°						
$V_i\Delta_i^2 \times 10^{-3}$		1.45	1.44	1.43	1.42	1.44	1.45

Table 2. 1,3-Cyclooctadiene. Experimentally determined bond lengths, the corresponding amplitudes of vibrations (u-values), the bond angles and estimated error limits.

Distance	$r_g(1)$, Å	$\Delta r_g(1)$, Å	u, Å
$C_1=C_2$ (2)	1.3474	0.005	0.0455
C_2-C_3 (1)	1.4750	0.010	0.0536
C_4-C_5 (2)	1.5090	0.005	0.0515
C_5-C_6 (3)	1.5422	0.005	0.0519
C_1-H_1 (4)	1.1021	0.010	0.0770
C_5-H_{14} (8)	1.1088	0.010	0.0800
Angles	**Degrees**	Δ	
$\angle C_1C_2C_3$	129.0	0.5	
$\angle C_4C_5C_6$	117.2	0.5	
$\angle C_5C_6C_7$	105.9		
$\angle\beta$	37.8	1.0	
$\angle C_1C_2H_{10}$	119.0	1.0	
$\angle C_4C_5H_{13}$	110.5	1.0	

The numbers in brackets in column one are the multiplicities of the distances.

In all the runs all parameters were identical except the one being studied which had a fixed value that was slightly different in each run. In each run a few parameters that refined nicely were varied, and the standard deviations of these parameters and the squared error sum was studied as a function of the parameter that was different for each run. Table 1 is arbitrarily chosen among the tables constructed in this way and illustrates the results obtained by this method.

Table 3. 1,3-Cyclooctadiene. The CC nonbonded distances and corresponding u-values.

Distance	$r_g(1)$, Å	u, Å
C_5C_7 (2)	2.4612	
C_3C_7 (2)	2.5480	0.0620
C_3C_5 (2)	2.5791	
C_4C_8 (2)	2.6044	
C_1C_8 (1)	2.7708	0.0950
C_5C_8 (1)	3.0234	0.0700
C_3C_8 (1)	3.0304	0.0950
C_2C_8 (1)	3.1023	0.0700
C_3C_8 (2)	3.2254	0.0900
C_1C_4 (1)	3.2426	0.0700
C_4C_8 (2)	3.3839	0.0900
C_2C_7 (1)	3.4410	
C_4C_7 (1)	3.4723	0.0950
C_2C_7 (1)	3.8017	

The root-mean-square amplitudes of vibrations (u-values) for the bond distances refined well in the least squares adjustment and the results are presented in Table 2 which also gives the final geometrical parameters for 1,3-cyclooctadiene. The resulting u-values for the bond distances are reasonable except for the C_2-C_3 distance where the u-value probably is too high. The u-value for the smallest CH nonbonded distance was determined by the combined trial and error and least squares method described above and was found to be 0.1025 Å. The u-values for the nonbonded CC distances were obtained in the same way, and the results were in all cases closely followed on the radial distribution curve. The results for the nonbonded CC distances are presented in Table 3.

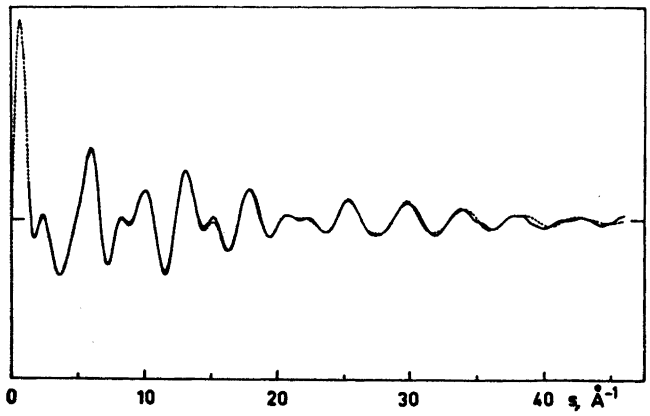


Fig. 2. 1,3-Cyclooctadiene. Experimental (———) and theoretical (— — —) molecular intensity functions.

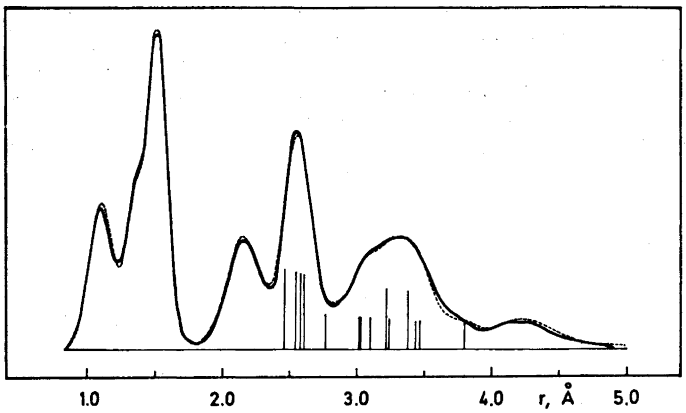


Fig. 3. 1,3-Cyclooctadiene. Experimental (———) and theoretical (— — —) radial distribution functions. $k=0.0009$. The solid bars represent relative contributions from CC nonbonded distances.

The theoretical molecular intensity function ($sM(s)$) and radial distribution function based on the parameters given in Tables 2 and 3 are shown in Figs. 2 and 3 along with their experimental counterparts. The solid bars in Fig. 3 represent relative contributions from the CC nonbonded interatomic. distances. The overall correspondence between the theoretical and experimental curves is very satisfactory. From Table 3 it will be seen that all the CC nonbonded distances where C_6 and C_7 are involved, except C_3C_6, have fairly large u-values (0.0950 Å). This corresponds to what could be expected if there are minor oscillations around the equilibrium interplanar angle ($\angle\beta$) 37.8°. Dreiding models also reveal that the C_3C_6 distance is the only one of those discussed that does not change considerably with a change in $\angle\beta$. An oscillation around the equilibrium interplanar angles does also explain why the region around 3.8 Å on the RD curve, where C_3C_7 is the only contributing CC distance, does not show as good correspondence with the experimental RD curve as the other r-regions.

Table 4. Torsion angles in the 1,3-cyclooctadiene ring system.

Bond	Torsion angle	Staggered conformation	Deviation
1—2	0		
2—3	−37.8	−60	22.2
3—4	0		
4—5	−18.2	0	18.2
5—6	+75.2	+60	15.2
6—7	−77.5	−60	17.5
7—8	−32.3	−60	27.7
8—1	+79.7	+120	40.3

The torsion (dihedral) angles in the 1,3-cyclooctadiene ring are presented in Table 4. The dihedral angles are given according to the IUPAC nomenclature.[13] As a torsional angle in this system is defined as the angle between projected bonds along a C–C single bond, the minimum torsional energy conformations have different torsional angles when both carbon atoms are sp^3 hybridized (minimum torsional strain for $\theta = 60°$ or 180°) and when one is sp^3 and the other sp^2 hybridized (minimum torsional strain for $\theta = 0°$ or 120°). In Table 4, column 3, the torsional angles corresponding to the nearest torsional strain minima are given and column 4 gives the deviation between the values in columns 2 and 3. In a carbon ring system like the one being studied it is obviously impossible to avoid torsional strain. From Table 4, column 4, it is seen that the torsional strain in the molecule is fairly well distributed along the different C–C bonds, except for the $C_8 - C_1$ bond where the torsional angle deviates 40° from the nearest staggered conformation. An inspection of Dreiding models indicates that a release in torsional strain along the $C_8 - C_1$ bond imposes a considerable increase in torsional strain along other CC bonds. The results therefore seem to be reasonable.

A possible small deviation from coplanarity of the individual CC double bonds could not be detected. There is, however, no reason to expect significantly distorted double bonds as that would involve a decrease in the interplanar angle β.

FINAL RESULTS

The 1,3-cyclooctadiene molecule is shown to have C_i symmetry in the free state. The molecular parameters are listed in Table 2. Table 3 presents the CC nonbonded distances in the molecule, and Table 4 gives the dihedral angles in the carbon ring system. The experimental data are consistent with a molecule containing two planar conjugated ethylenic groups and with an interplanar angle of 37.8°. There are probably minor oscillations around the equilibrium interplanar angle.

The theoretical molecular intensity function based on the parameters listed in Table 2, is shown in Fig. 2 which also shows the experimental $sM(s)$ function. The corresponding theoretical and experimental radial distribution functions are presented in Fig. 3. The solid bars represent relative contributions from the CC nonbonded interatomic distances and may be identified from Table 3.

The error limits listed in Table 2, column 3, include estimates of experimental errors due to the various measured quantities and uncertainties in the observed parameters due to random errors in the molecular intensity function.

DISCUSSION OF THE RESULTS

The molecular structure of 1,3-cyclooctadiene may be compared with the structural results for 1,3-cyclohexadiene and 1,3-cycloheptadiene, and the most important structural parameters for the three molecules are listed in Table 5. The 1,3-cyclohexadiene results are from the present research series [14] and the 1,3-cycloheptadiene data are taken from Bauer's [15] electron diffrac-

Table 5. Molecular parameters for conjugated 1,3-cycloalkadienes.

Parameter	C_6H_8[a]	C_7H_{10}[b]	C_8H_{12}[c]
$C_1=C_2$	1.3481 Å	1.35 Å	1.3474 Å
C_2-C_3	1.4648 Å	1.48 Å	1.4750 Å
C_4-C_5	1.5187 Å	1.54 Å	1.5090 Å
C_5-C_6	1.5384 Å	1.55 Å	1.5422 Å
$\angle C=C-C$	120.3°	129°	129.0°
interplanar angle, $\angle\beta$	18°	0°	37.8°

[a] Ref. 14
[b] Ref. 15
[c] Present study

tion study. The bond lengths agree well in the two cyclic 1,3-alkadienes studied in this laboratory when the difference in strain in the two molecules is taken into account.

The results for the interplanar angles in the three cases are not as surprising as they might appear at first sight. If the two double bonds in C_6H_8 were coplanar, the two methylene groups would be eclipsed. In C_7H_{10}, however, it is possible to have coplanar CC double bonds and at the same time reasonable dihedral angles. But coplanarity of the CC double bonds will have to be attained at the expense of increased $C=C-C$ angles. In the COD molecule there are many reasons why coplanarity of the double bonds is energetically unfavourable. Several torsional angles would be highly unfavourable and so would the $H_{13}H_{19}$ repulsion. The experimentally determined value for the interplanar angle seems to be very reasonable.

The $C=C-C$ angle is quite large (129°). It is, however, the same result as obtained for 1,3-cycloheptadiene, and the result is also comparable to the same kind of angle in *cis,cis*-1,6-cyclodecadiene [16] (128.2°). $\angle C_4C_5C_6$ (117.2°) is comparable to the CC bond angle found in cyclooctane [17] (116.5°).

The $C_5C_6C_7$ angle is surprisingly small (105.9°). The problem of locating the C_6 and C_7 atoms and simultaneously give the CC bond angles at C_6 and C_7 is, however, very complicated, and both the $C_4C_5C_6$ angle and the torsional angles are involved. If $\angle C_4C_5C_6$ were decreased, the closure of the ring would require the CC bond angles at C_6 and C_7 to decrease also. The interdependence of these angles combined with the torsional angle problem probably explains why $\angle C_4C_5C_6$ is quite large and $\angle C_5C_6C_7$ is quite small.

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