

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

IV. The Molecular Structure of 1,3-Cyclohexadiene

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The molecular structure of 1,3-cyclohexadiene has been investigated using the gas electron diffraction sector method. The experimentally determined molecular parameters are the following:

| | | | |
|---------------------|---|----------------|---|
| $r_g(1)(C_1-H_1)$: | $1.099 \text{ \AA} \pm 0.004 \text{ \AA}$, | $u(C_1-H_1)$: | $0.079 \text{ \AA} \pm 0.003 \text{ \AA}$, |
| $r_g(1)(C_5-H_5)$: | $1.111 \text{ \AA} \pm 0.003 \text{ \AA}$, | $u(C_5-H_5)$: | $0.087 \text{ \AA} \pm 0.003 \text{ \AA}$, |
| $r_g(1)(C_1=C_2)$: | $1.348 \text{ \AA} \pm 0.001 \text{ \AA}$, | $u(C_1=C_2)$: | $0.046 \text{ \AA} \pm 0.001 \text{ \AA}$, |
| $r_g(1)(C_2-C_3)$: | $1.465 \text{ \AA} \pm 0.002 \text{ \AA}$, | $u(C_2-C_3)$: | $0.052 \text{ \AA} \pm 0.002 \text{ \AA}$, |
| $r_g(1)(C_4-C_5)$: | $1.519 \text{ \AA} \pm 0.001 \text{ \AA}$, | $u(C_4-C_5)$: | $0.048 \text{ \AA} \pm 0.001 \text{ \AA}$, |
| $r_g(1)(C_5-C_6)$: | $1.538 \text{ \AA} \pm 0.003 \text{ \AA}$, | $u(C_5-C_6)$: | $0.053 \text{ \AA} \pm 0.002 \text{ \AA}$, |

| | | | |
|----------------------|---------------------------------|--|------------------|
| $\angle C_1C_2C_3$: | $120.26^\circ \pm 0.23^\circ$, | $\angle C_3C_4C_5$: | 120.25° , |
| $\angle C_4C_5C_6$: | 110.88° , | $\angle C_1C_2H_2$ (assumed equal to $\angle C_2C_1H_1$): 118° . | |

The listed uncertainties are standard deviation values as resulting from least squares refinements of the molecular intensity data and systematic errors are therefore not included.

The experimental data are consistent with a molecule with two planar ethylene groups and a C_2C_3 torsional angle of 18° . Possible small distortions around the carbon carbon double bonds and a reduction in the given dihedral angle can, however, not be ruled out.

The molecular structure of 1,3-cyclohexadiene is of considerable interest to the structural chemist as well as to the biologist. The molecule presents several interesting structural problems, and to the biologist it is of importance as one of the component molecules which form larger molecules of chemical and biological interest.

From a structural point of view the distribution of bond lengths and valence angles and the conformation of the sixmembered carbon atom ring are interesting features.

Beckett and Mulley¹ suggested in 1955 as a result of chemical studies that the 1,3-cyclohexadiene ring in 9,10-dihydrophenanthrene is nonplanar. Ten years later Butcher² published a microwave spectroscopic investigation of the 1,3-cyclohexadiene molecule where he found a nonplanar conformation with a $17.5 \pm 2^\circ$ torsional angle between two planar ethylene groups. In order to achieve this result he assumed values for all bond lengths and valence angles in the molecule. His statement that the torsional angle is relatively independent of the assumptions made about the molecular parameters, is probably correct, but nevertheless it is of importance to undertake a complete structural analysis of the 1,3-cyclohexadiene molecule.

A microwave spectroscopic investigation by Luss *et al.*³ does not explicitly give the dihedral angle, but the authors state that their experimental data are in agreement with the structural conclusions presented by Butcher.

In 1966 the crystal and molecular structure of the antibiotic gliotoxin was studied by Beecham *et al.*⁴ They found a nonplanar 1,3-cyclohexadiene system in this molecule with a 14° dihedral angle between two planar ethylene groups.

When the present investigation was nearly completed the results from an electron diffraction study of 1,3-cyclohexadiene was published by Dallinga *et al.*⁵ As they could not determine unambiguously the complete structure of the molecule from diffraction data it was decided to finish and publish the structural results presented below.

EXPERIMENTAL PROCEDURE

The sample of 1,3-cyclohexadiene used in the present investigation was kindly provided by professor W. Lüttke, Göttingen, Germany. The 1,3-cyclohexadiene molecule was studied by the sector electron diffraction method, using a modified s^2 sector. The electron diffraction intensity data were obtained with the Oslo diffraction camera.⁶

Diffraction photographs were taken at a nozzle temperature of about 17°C , applying an accelerating potential of approximately 35 kV. Four sets of plates were used, taken with nozzle-to-photographic plate distances of approximately 48 cm and 19 cm, respectively. The corresponding s ranges are approximately $1.25\text{--}20.00 \text{ \AA}^{-1}$ and $7.00\text{--}45.00 \text{ \AA}^{-1}$. The plates were photometered and corrected in the usual way.⁷

The corrected experimental intensities were modified by the function

$$\varphi(s) = |f(s)_C|^{-2}$$

where $f(s)_C$ represents nonrelativistic partial waves atomic scattering factors for carbon, computed for 35 keV electrons.⁸

The four sets of intensities for each nozzle-to-plate distance were averaged before experimental backgrounds were subtracted.

The experimental backgrounds were refined according to well established criteria and the overlap region averaged, yielding an experimental molecular intensity function, $M(s)$, from $s=1.25 \text{ \AA}^{-1}$ to $s=42.00 \text{ \AA}^{-1}$. The experimental $s \cdot M(s)$ function is shown in Fig. 4.

STRUCTURE DETERMINATION

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

Auto- and crosscorrelation power spectra⁹ for 1,3-cyclohexadiene were studied to find starting values for the bond distance parameters in the mole-

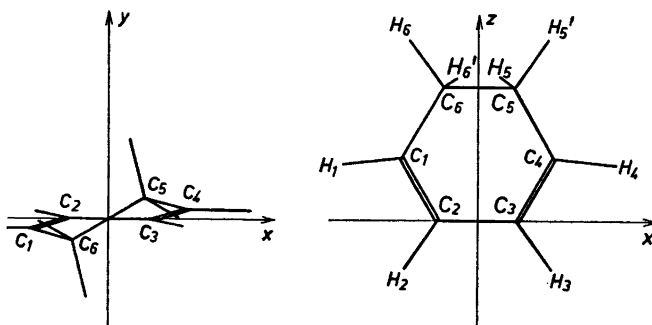


Fig. 1. 1,3-Cyclohexadiene. Molecular model which shows the numbering of the atoms.

cule. Sharpened radial distribution and autocorrelation power spectrum functions are shown in Figs. 2 and 3. In a case like this, with four different kinds of CC bonds within an r -range of 0.2 Å, one can not expect to obtain reliable high-precision bond parameters from the sharpened functions. But as these functions have higher resolution and are much more sensitive to changes in the molecular parameters than radial distribution functions, it is easier to deduce good starting values for the bond distance parameters from these functions. The following CC bond distance parameters were obtained from the sharpened functions: $C_1=C_2$: 1.348 Å, C_2-C_3 : 1.466 Å, C_4-C_5 : 1.519 Å, C_5-C_6 : 1.540 Å.

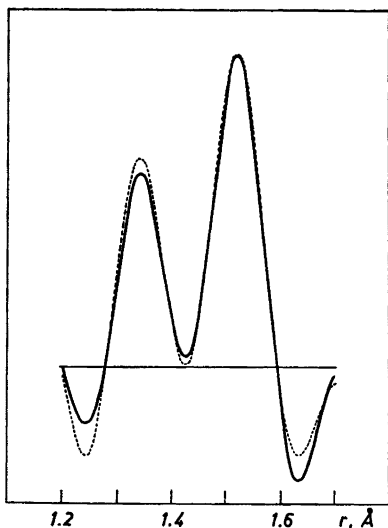


Fig. 2. 1,3-Cyclohexadiene. Experimental (—) and theoretical (---) sharpened radial distribution function. Modification function: $\sqrt{2\lambda} \exp(-\lambda(s_{\max}-s))$, $\lambda=0.04$.

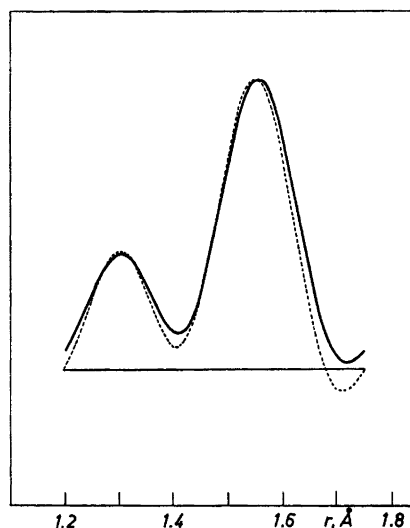


Fig. 3. 1,3-Cyclohexadiene. Experimental (—) and theoretical (---) autocorrelation power spectrum, $\lambda=0.04$.

Table 1. 1,3-Cyclohexadiene. Experimentally determined interatomic distances, root-mean square amplitudes of vibrations and bond angles. The standard deviations are results of least squares refinements of the molecular intensity data.

| Distance | $r_g(1)$, Å | $\Delta r_g(1)$, Å | u , Å | Δu , Å |
|---|--------------------|---------------------|--------------------|--------------------|
| C ₁ -H ₁ | 1.099 ₀ | 0.003 ₅ | 0.079 ₃ | 0.002 ₈ |
| C ₅ -H ₅ | 1.110 ₇ | 0.003 ₂ | 0.087 ₀ | 0.003 ₂ |
| C ₁ =C ₂ | 1.348 ₁ | 0.000 ₈ | 0.046 ₂ | 0.000 ₇ |
| C ₂ -C ₃ | 1.464 ₈ | 0.002 ₀ | 0.052 ₅ | 0.001 ₈ |
| C ₄ -C ₅ | 1.518 ₇ | 0.001 ₁ | 0.048 ₄ | 0.000 ₉ |
| C ₅ -C ₆ | 1.538 ₄ | 0.002 ₅ | 0.052 ₉ | 0.001 ₉ |
| C ₁ C ₃ | 2.439 ₉ | | 0.065 | |
| C ₃ C ₅ | 2.487 ₃ | | 0.065 | |
| C ₁ C ₆ | 2.517 ₆ | | 0.065 | |
| C ₂ C ₅ | 2.851 ₇ | | 0.070 | |
| C ₁ C ₄ | 2.846 ₇ | | 0.070 | |
| \angle C ₁ C ₄ C ₃ : | 120.26 ± 0.23° | | | |
| \angle C ₃ C ₄ C ₅ : | 120.25° | | | |
| \angle C ₄ C ₁ C ₆ : | 110.88° | | | |
| \angle C ₁ C ₂ H ₂ ≈ \angle C ₃ C ₁ H ₁ : | 118° | | | |
| \angle C ₄ C ₅ H ₅ : | 110.8° | | | |

Angle of distortion around C₂-C₃, $\angle \beta = 17.96 \pm 0.12^\circ$.

The molecular structure was refined by a least squares analysis of the molecular intensity data and all through the analyses the results were controlled by comparing the theoretical and experimental radial distribution functions.

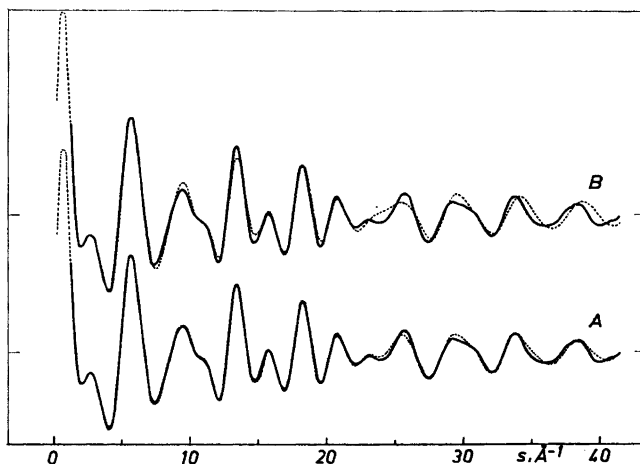


Fig. 4. 1,3-Cyclohexadiene. Comparison of the experimental (—) and two theoretical (---) molecular intensity functions. A: The present results, B: Dallinga's results.

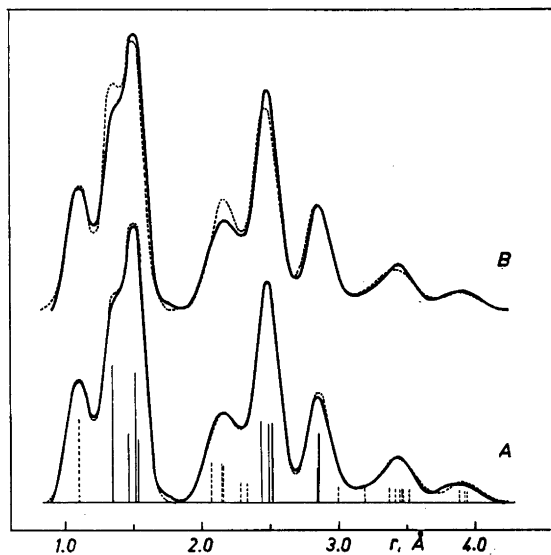


Fig. 5. 1,3-Cyclohexadiene. Comparison of the experimental (—) and two theoretical (---) radial distribution functions ($k=0.0009$). A: The present results, B: Dallinga's results.

The parameters for the molecular model that gave maximum correspondence between experimental and theoretical molecular intensity and radial distribution functions are listed in Table 1. The theoretical molecular intensity function ($sM(s)$) and radial distribution (R.D.) function for this model are shown in Figs. 4 and 5 along with their experimental counterparts.

All the C=C—H angles were assumed to be equal, but even with this restriction the C=C—H angle could not be accurately determined. The smallest nonbonded carbon hydrogen distances all contribute to the peak at about 2.15 Å in the radial distribution function and when the C=C—H angle is kept within $118 \pm 4^\circ$ the contribution from the smallest CH nonbonded distances to the $sM(s)$ - and R.D. functions is practically independent of the magnitude of this angle. It can easily be verified that for example the distance between the atoms C_1 and H_4 is extremely insensitive to changes in the C=C—H angles as long as it is kept within the limits given above. It is therefore not surprising that it was not possible to determine the exact positions of the hydrogen atoms 1, 2, 3, and 4 in the present study.

The least squares refinement program makes use of a subprogram that calculates the dependent distances in the molecule as functions of the independent ones. It is often necessary to make certain assumptions about the molecular model in order to perform this task. The results presented in Table 1 are based on a molecular model where planar ethylene groups are assumed. The restriction of planarity of each of the ethylene groups was later relaxed and distortions around the carbon carbon double bonds were allowed. This extra motional freedom did not essentially improve the results but it did not

worsen them either. Very nearly the same molecular intensity function and radial distribution function is obtained for a molecular model where the nonplanarity is accounted for by an approximately 18° dihedral angle between planar ethylene groups as for a model where the distortions are distributed among the C_2-C_3 single bond and the two CC double bonds. On basis of the present electron diffraction investigation possible minor distortions around the CC double bonds can therefore not be ruled out.

FINAL RESULTS

The final molecular parameters for 1,3-cyclohexadiene are listed in Table 1. The molecule is found to have a nonplanar conformation of the carbon atom ring. The experimental data are consistent with a molecule with two planar ethylene groups and a C_2C_3 torsional angle of approximately 18° . The experimental material does not rule out the possibility that the nonplanarity of the molecule may be caused by the combined effects of minor distortions (maximum 10°) around the carbon carbon double bonds and a reduced torsional angle ($\angle\beta$) around the C_2-C_3 bond.

The theoretical molecular intensity function based on the parameters listed in Table 1 is shown in Fig. 4 which also shows the experimental $sM(s)$ function. The corresponding theoretical and experimental radial distribution functions are presented in Fig. 5. The solid and dotted bars represent relative contributions from carbon carbon and carbon hydrogen interatomic distances, respectively.

DISCUSSION OF THE RESULTS

The distribution of carbon carbon bond distances in the 1,3-cyclohexadiene molecule appears to be very reasonable when compared to similar internuclear distances in related molecules. Especially can be mentioned that the carbon carbon double and single bond distances in the conjugated system of carbon atoms in this molecule within the error of the method are the same as the electron diffraction values determined for 1,3-butadiene (C=C: 1.344 Å, C—C: 1.467 Å).

The nonplanarity of the 1,3-cyclohexadiene ring found in microwave and other investigations¹⁻⁵ has been confirmed. Neither the spectroscopic² nor the electron diffraction measurements are sensitive to slight deviations from planarity of the ethylene groups. Nonplanar ethylene groups have recently been observed in other molecules (1,3,5-*cis*-hexatriene,¹⁴ 2-butene¹⁵). Even if the present data are consistent with each ethylene group being planar, the possibility of the nonplanarity being caused by combined distortions around the C_2-C_3 single bond and the two CC double bonds can not be ruled out.

The deviation from planarity of the carbon atom ring is probably a result of two factors. According to the present study all the carbon carbon valence angles have "normal" values. If the ring were planar there would be angle strain in the molecule. The average deviation from "strainfree" carbon carbon

Table 2. Comparison of the present results with the electron diffraction results obtained by Dallinga *et al.*⁵ for the molecular structure of 1,3-cyclohexadiene.

| Parameter | Dallinga's results | Present study | Differences |
|---|--------------------|-------------------|-----------------|
| C ₁ =C ₂ | 1.339 ± 0.001 Å | 1.3481 ± 0.0008 Å | +0.009 (0.0) |
| C ₂ -C ₃ | 1.468 ± 0.008 Å | 1.4648 ± 0.0020 Å | -0.003 (-0.013) |
| C ₄ -C ₅ | 1.494 ± 0.017 Å | 1.5187 ± 0.0011 Å | +0.025 (+0.015) |
| C ₅ -C ₆ | 1.510 ± 0.032 Å | 1.5384 ± 0.0025 Å | +0.027 (+0.018) |
| ∠C ₁ C ₂ C ₃ | 121.6 ± 1.0° | 120.26° | -1.3° |
| ∠C ₃ C ₄ C ₅ | 118.2 ± 0.7° | 120.25° | +2.0° |
| ∠C ₄ C ₅ C ₆ | 111.5 ± 0.5° | 110.88° | -0.6° |
| torsional angle, θ | 17° | 17.96° | +1.0° |

valence angles would, however, be less than 3.5°, and it is unlikely that the cease in angle strain by a nonplanar conformation is the solely responsible factor. The interaction of the nonbonded hydrogen atoms in the two methylene groups is probably an equally important factor. The hydrogen atoms are eclipsed in the planar conformation, while the present study gives a C₅-C₆ dihedral angle of approximately 46°. The hydrogen interactions would be minimized for a 60° C₅-C₆ dihedral angle if the carbon valences were strictly tetrahedral.

The deviations between Dallinga's⁵ electron diffraction results for 1,3-cyclohexadiene and those from the present study has to be commented. The most important parameters determined in the two investigations are summarized in Table 2. It should be pointed out that the structural parameters given by Dallinga are not consistent. If the C₅-C₆ bond length is calculated from the other parameters given in Table 2, column 2, a value of 1.5456 Å is obtained. If instead the dihedral angle is calculated from the given bond length and valence angle parameters, the angle is found to be 15.1°. This inconsistency in the given parameter list is probably not too serious as the standard deviation for the important C₅-C₆ bond length (0.032 Å) is of the same order of magnitude as the difference between the calculated value of 1.5456 Å and the listed value of 1.510 Å.

Theoretical $sM(s)$ - and R.D. functions for Dallinga's model have been calculated and are shown in Figs. 4 B and 5 B together with the corresponding experimental data from the present investigation.

Dallinga's CC bond distances are on an average smaller than those of the present investigation, and a possible scale factor between the two sets of data caused by uncertainties in the electron wavelength of one or both investigations can not be ruled out. The CC double bond distance is most accurately determined in both studies, and if this bond is taken to be the same in both sets of parameters, the scale factor will be 1.0068. If this scale factor is applied, the differences between the two sets of CC bond distances will be those given in brackets in Table 2. The discrepancies between the results for the C₄-C₅ and C₅-C₆ bonds are reduced while the correspondence between the C₂-C₃ distance determinations is diminished. Dallinga stated that he was not able

to determine with certainty even the relative order of the C_4-C_5 and C_5-C_6 bond lengths, and it has therefore no purpose to discuss the different results for these parameters. The correspondence between the results for the $C_1=C_2$ and C_2-C_3 bonds is acceptable.

Finally it should be added that a dihedral angle of 18° for 1,3-cyclohexadiene corresponds very well with the optical rotatory dispersion results by Charney *et al.*¹¹⁻¹³ for homoannular twisted dienes.

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REFERENCES

1. Beckett, A. H. and Mulley, B. H. *Chem. Ind. (London)* **1955** 146.
2. Butcher, S. S. *J. Chem. Phys.* **42** (1965) 1830.
3. Luss, G. and Harmony, M. D. *J. Chem. Phys.* **43** (1965) 3768.
4. Beecham, A. F., Fridrichsons, J. and Mathieson, A. McL. *Tetrahedron Letters* **27** (1966) 3131.
5. Dallinga, G. and Toneman, L. H. *J. Mol. Struct.* **1** (1967-68) 11.
6. Bastiansen, O., Hassel, O. and Risberg, F. *Acta Chem. Scand.* **9** (1955) 232.
7. Bastiansen, O. and Skancke, P. N. *Advan. Chem. Phys.* **3** (1960) 323.
8. Peacher, J. L. and Wills, J. G. *J. Chem. Phys.* **46** (1967) 4809.
9. Trætteberg, M. and Bonham, R. A. *J. Chem. Phys.* **42** (1965) 587.
10. Haugen, W. and Trætteberg, M. *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, p. 113.
11. Weiss, U., Ziffer, H. and Charney, E. *Tetrahedron* **21** (1965) 3105.
12. Charney, E., Ziffer, H. and Weiss, U. *Tetrahedron* **21** (1965) 3121.
13. Charney, E. *Tetrahedron* **21** (1965) 3127.
14. Trætteberg, M. *Acta Chem. Scand.* **22** (1968) 2294.
15. Haaland, A. *Private communication.*

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