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# An Electron Diffraction Investigation of Gaseous *cis,cis*-Cyclodeca-1,6-diene

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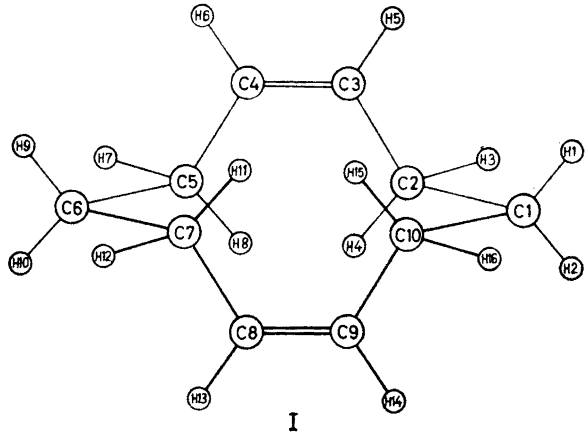
Gaseous *cis,cis*-cyclodeca-1,6-diene has been studied by electron diffraction. The compound was found to exist predominantly in the chair conformation (I) with $C_{2h}$ symmetry. The bond lengths are close to the normal values: $r_a$(C=C) = 1.326 (0.004) Å, $r_a$(–C–C–) = 1.534 (0.006) Å, and $r_a$(=C–C–) = 1.506 (0.006) Å. The CCC angles are 114.1 (0.5)° and 112.8 (0.3)°, while the C=C–C angles are rather large, namely 128.2 (0.3)°. The values in brackets are estimated standard deviations.

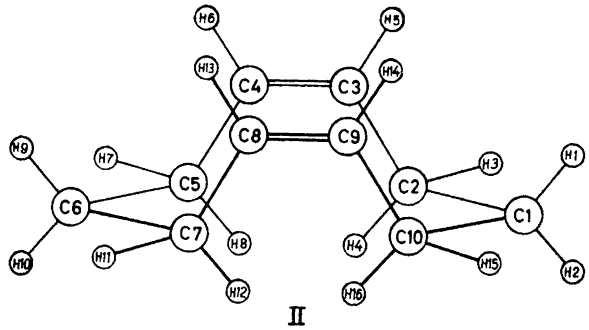
Cyclic hydrocarbons of certain ring sizes ($C_6$, $C_{10}$, $C_{14}$, . . .) with two double bonds have a strain free skeleton when the two double bonds are diametrically placed.[1] While isomerisation of cyclooctadiene gives almost quantitatively the conjugated isomer,[2] and isomerisation of cyclododecadiene gives a mixture of many isomers, the isomerisation of cyclodecadiene gives almost quantitatively the *cis,cis*-1,6-isomer. Dale and Moussebois[3] studied the *cis-trans* equilibria of cycloalkadienes

$$\overline{[(CH_2)_n-CH=CH-(CH_2)_n-CH=CH]}.$$

At room temperature they found almost exclusively the *cis,cis*-isomer when $n=3$ (10 ring atoms). The *cis,cis*-isomer was also predominant for $n=4$, while only a very small fraction of the *cis,cis*-isomer was obtained for larger rings ($n=5-9$). The model I (with symmetry $C_{2h}$), proposed for *cis,cis*-cyclodeca-1,6-diene by Grob and Schiess,[4] is strain free, and has reasonable non-bonded distances.[1] This fact is probably the reason for the preference of the *cis,cis*-isomer. The NMR spectrum supports also the assumption that the compound exists predominantly in the conformation I.[5,6] *cis,cis*-Cyclodeca-1,6-diene may be bond to metals [*e.g.* (*cis,cis*-cyclodeca-1,6-diene $RhCl)_2$], and the molecule is then probably in the conformation II.[7]




I




II

It should be possible by means of electron diffraction to decide if the molecule exists predominantly in the conformation I. Two other medium sized rings (cyclooctane and cyclotetradeca-1,8-diyne) have recently been studied by electron diffraction in Oslo.[8] In both cases it was found impossible to obtain satisfactory agreement between experimental and theoretical radial distribution curves with a single model of the molecule.

## EXPERIMENT AND THEORY

The sample of *cis,cis*-cyclodeca-1,6-diene was kindly supplied by Professor J. Dale at this university. The photographs were taken in the usual way with the Oslo apparatus.[9] The nozzle temperature was approximately 37°C, and the electron wave length 0.06474 Å, corresponding to an accelerating voltage of $\approx$36 kV. Photographs were taken at two nozzle-to-plate distances, *i.e.* approximately 48 cm and approximately 19 cm. 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—44.0 Å$^{-1}$, but only data for $s>2.0$ Å$^{-1}$ were applied. The interval in $s$ was 0.125 Å$^{-1}$ below $s=11$ Å$^{-1}$ and 0.25 Å$^{-1}$ above this value. The curves showed satisfactory agreement and so did the experimental radial distribution (RD) curves calculated from [10,11]

$$\sigma(r)/r = \int I(s) \exp(-ks^2) \sin(rs)ds \quad (1)$$

($k$ is an artificial damping constant.) The average of the four curves was therefore applied in the structure analysis. To test the reliability of the results refinements were also carried out on the separate curves.

The theoretical molecular intensity was calculated by the formula

$$I_{(k,l)}(s) = \text{const} \sum_{i \neq j} \sum g_{ij/kl}(s) \exp(-\tfrac{1}{2}u_{ij}{}^2 s^2) \sin(r_{ij}\, s)/r_{ij} \quad (2)$$

where

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

and $f_j = |f_j| \exp(i\eta_j)$ is the scattering amplitude of atom "j". The scattering amplitudes were calculated by the "phase amplitude method" described by Peacher and Wills,[12] using HF atomic potentials.[13]

Theoretical radial distribution functions were calculated by eqn. (1) where $I(s)$ then is the theoretical intensity (2).

## STRUCTURE ANALYSIS

Preliminary values for the bond distances and the bond angles were easily obtained from the experimental radial distribution curve (see Fig. 2). The model I was then refined by least-squares refinement.[14] In model I there is a twofold symmetry axis through $C_1$ and $C_6$ and a symmetry plane perpendicular to this axis ($C_{2h}$ symmetry). The HCH angles were assumed equal, and the H atoms in all the $CH_2$ groups were placed symmetrically with respect to the neighbouring C atoms. The Bastiansen-Morino shrinkage effect was neglected. The independent bond lengths and bond angles were:

Bond lengths: $C_1—C_2$, $C_2—C_3$, $C_3=C_4$, $C_1—H_1$, $C_3—H_5$

Bond angles: $\angle C_{10}C_1C_2$, $\angle C_1C_2C_3$, $\angle C_2C_3C_4$, $\angle C_4C_3H_5$, $\angle H_1C_1H_2$

These independent parameters seemed to refine, but the agreement between experimental and theoretical intensity values was not quite satisfactory. It was, of course, not possible to refine these parameters and all the root-mean-square amplitudes of vibration ($u$) simultaneously. The $u$ values were collected in groups, and all the $u$ values in a group were given the same shift. However, even then it seemed difficult to obtain satisfactory agreement.

A new program was written * in an attempt to overcome this difficulty.

* The program was written by one of us (H.M.S.) in collaboration with cand.real. Reidar Stølevik.

This program calculates the quantity

$$S = \sum W_s(I_s^{obs} - \text{Scale} \times I_s^{theor})^2 \quad (4)$$

for a given parameter set. ($W_s$ is the weight on the observation $s$, and the sum is over all the observations.) One of the parameters is then given a suitable shift, and the sum $S$ is again calculated and compared to the first value of $S$. If the new value is smaller than the previous one, the parameter may be given a new shift in the same direction; if it is greater, a shift in the opposite direction is tried. The program will treat a second parameter in the same way when the minimum for the first parameter has been found, or when the parameter has been given the maximum number of shifts specified by the user.

In the present case we were mainly interested in improving the $u$ values for the non-bonded distances, especially for the long CH distances. The sum $S$ (eqn. (4)) was considerably reduced after sufficient refinement cycles. Most of the $u$ values were then reasonable, though a few appeared to be definitely too high or too low. The unreasonable $u$ values were adjusted to more likely values and the least-squares refinement continued. An additional reduction of $S$ was then obtained. Various refinements with different number of parameters were tried. The results * in the Tables 1 and 2 were obtained refining

*Table 1.* Results for bond lengths, the corresponding $u$ values and for the bond angles.
The results have been obtained by least-squares refinement, assuming that the molecule has the conformation I, and applying eqn. (2). The distances may be denoted by $r_a$ [15] which is identical to $r_g(1)$ in Bartell's notation.[16]
The standard deviations are in some cases greater than the values obtained in the least-squares calculation. The uncertainty in the wave length, the correlation between the parameter and $u$ values refined in groups or assumed, and the variation in the results obtained from the four observed intensity curves, have been taken into account.

| Distance type | $r$ (Å) | $u$ (Å) |
|---|---|---|
| $C_1-C_2$ | 1.534 (0.006) | 0.060 (0.004) |
| $C_2-C_3$ | 1.506 (0.006) | |
| $C_3=C_4$ | 1.326 (0.004) | 0.033 (0.005) |
| $C_3-H_5$ | 1.102 (0.012) | 0.080 (0.005) |
| $C_1-H_1$ | 1.112 (0.004) | |
| | degrees | |
| $\angle C_{10}C_1C_2$ | 114.1 (0.6) | |
| $\angle C_1C_2C_3$ | 112.8 (0.3) | |
| $\angle C_2C_3C_4$ | 128.2 (0.3) | |
| $\angle C_4C_3H_5$ | 116.6 (1.0) | |
| $\angle H_1C_1H_2$ | 105.6 (1.0) | |

* In this laboratory the wave length has usually been determined by means of a gold foil. Recent calibrations using $CO_2$ gave slightly (about 0.2 %) smaller values. The results given here have been obtained using the value from the investigation of $CO_2$.

five bond lengths, five bond angles, and altogether eleven $u$ parameters. The independent bond distances (with the corresponding $u$ values) and bond angles are given in Table 1. Additional (dependent) distances and $u$ values are given in Table 2. Fig. 1 shows the experimental molecular intensity (curve A) and the corresponding theoretical curve (B) calculated according to eqn. (2) with the parameters given in the Tables 1 and 2. The dashed curve gives the difference between the curves A and B.

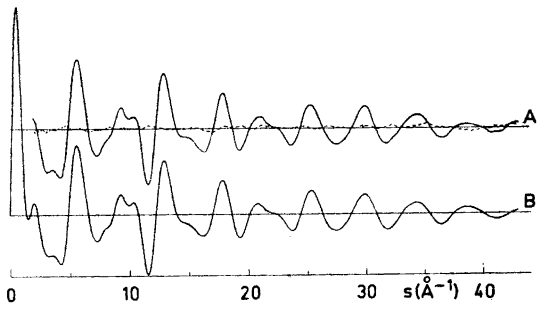



*Fig. 1.* Experimental (A) and theoretical (B) modified molecular intensity curves. The dashed curve shows the difference between the curves A and B.

*Table 2.* Some non-bonded (dependent) distances and the corresponding $u$ values. All C···C distances, the C···H distances less than 3.0 Å, and the H···H distances less than 2.50 Å are included. $u$ values for which standard deviations are given, were refined. The standard deviations in this table have been taken directly from the least-squares refinement.

| Distance type | $r$ (Å) | $u$ (Å) | Distance type | $r$ (Å) | $u$ (Å) |
|---|---|---|---|---|---|
| $C_1\cdots C_3$ | 2.532 | 0.066 (0.004) | $C_3\cdots H_6$ | 2.068 | |
| $C_2\cdots C_{10}$ | 2.574 | | $C_3\cdots H_3$ | 2.150 | 0.116 (0.012) |
| $C_2\cdots C_4$ | 2.548 | 0.099 (0.005) | $C_2\cdots H_1$ | 2.170 | |
| $C_2\cdots C_9$ | 3.061 | 0.099 (0.006) | $C_1\cdots H_3$ | 2.175 | |
| $C_2\cdots C_5$ | 3.187 | 0.090 (0.011) | $C_2\cdots H_5$ | 2.213 | |
| $C_1\cdots C_4$ | 3.584 | 0.110 (0.005) | $C_2\cdots H_8$ | 2.766 | 0.120 |
| $C_2\cdots C_8$ | 3.687 | | $C_3\cdots H_8$ | 2.700 | |
| $C_3\cdots C_9$ | 3.628 | 0.156 (0.005) | $C_3\cdots H_{15}$ | 2.761 | 0.153 |
| $C_3\cdots C_8$ | 3.865 | | $C_3\cdots H_1$ | 2.816 | |
| $C_2\cdots C_7$ | 4.096 | | $C_2\cdots H_{15}$ | 2.861 | 0.125 |
| $C_1\cdots C_5$ | 4.222 | 0.141 (0.016) | $C_1\cdots H_5$ | 2.901 | 0.125 |
| $C_1\cdots C_6$ | 4.855 | | | | |
| | | | $H_1\cdots H_2$ | 1.78 | |
| | | | $H_4\cdots H_8$ | 2.02 | |
| | | | $H_5\cdots H_6$ | 2.32 | |
| | | | $H_1\cdots H_3$ | 2.49 | |

The model II (with $C_{2v}$ symmetry) was also considered. The angle $\theta$ between the planes through the atoms $C_1C_2C_{10}$ (or $C_6C_5C_7$) and through $C_2C_5C_7C_{10}$

was refined as an additional parameter. The best agreement was obtained for $\theta=0.1°$ with a standard deviation of 1.2°. The sum $S$ was about 21 % higher for this model than for model I. Hamilton's $R$ factor test [17] may be applied to decide if this difference is significant. We find $R=(S_{II}/S_I)^{\frac{1}{2}}=1.099$. However, there are some difficulties in applying the test. First, we have used a diagonal weight matrix in the least-squares calculations. Because of the correlation between the intensity data this may be a rather poor approximation.[18] Secondly, it may be argued about the dimension of the hypothesis. We have refined 22 * parameters and have 211 observations. With the $R$ ratio given above it is found that model II may be rejected at the 0.01 significance level if the dimension of the hypothesis is less than about 20. The number of C···C and C···H distances that are different in the two models if all the independent distances and angles (Table 1) are identical, *i.e.* eight, seems to be an upper limit to the dimension. According to this test model II may thus be rejected at a very low significance level. However, with little experience in applying this test in electron diffraction, the result must be used with care. Therefore both models were refined using the four experimental intensity curve separately. $S_{II}$ was found greater than $S_I$ in all cases.

## DISCUSSION

This investigation indicates strongly that *cis,cis*-cyclodeca-1,6-diene exists predominantly in the conformation I. The $R$ factor test described above provides one of the reasons for this conclusion in spite of the uncertainties connected with this test.

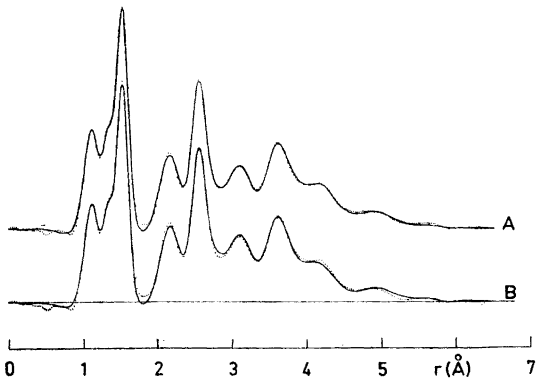



*Fig. 2.* Radial distribution curves ($k=0.0015$ Å$^2$). The full line curve A shows the theoretical intensity corresponding to the refined model I, and the full line curve B corresponds to the refined model II. The two dotted curves are identical and have been calculated from the experimental intensity curve shown in Fig. 1.

* One more parameter (the angle $\theta$) was actually refined in model II. If $\theta$ is different from zero in model I the symmetry is no longer $C_{2h}$. $\theta$ was not refined in model I, partly because of the excellent agreement obtained with $\theta=0$, and partly since two of the distances of the type $C_3H_{15}$ would become unlikely small if $\theta$ was considerably different from zero.

Fig. 2 shows experimental and theoretical radial distribution curves. The agreement between experimental and theoretical curves is seen to be better for model I than for model II. To draw conclusions from these curves, it is necessary to bear in mind that the zero line in the experimental RD curve is subject to uncertainties. Because of the lack of data below $s=2.0$ Å$^{-1}$, one must either draw the zero line (an envelope) in the experimental RD curve [10] or use theoretical data for the lowest $s$ values. Errors in the background in the inner part of the intensity curve (where it may be difficult to draw the background) may be compensated for by slowly varying modifications of the envelope. However, it is seen from Fig. 2 that the experimental curve will not fit the theoretical curve calculated for model II even after a reasonable envelope change.

In Fig. 2B we see that the theoretical curve (full line) is slightly above the experimental curve around 3 Å and slightly below around 4 Å. The reason for this becomes clear when the refined values of the distances of the types $C_3\cdots C_9$ and $C_3\cdots C_8$ are considered:

| | Model I | | Model II | |
|---|---|---|---|---|
| | $r$ | $u$ | $r$ | $u$ |
| $C_3\cdots C_9$ | 3.63 | 0.156 | 2.82 | 0.49 |
| $C_3\cdots C_8$ | 3.87 | | 3.12 | |

Thus in model II there are contributions around 3 Å which do not fit the experimental data. The best agreement is then obtained by giving the distances large $u$ values. The contributions to the radial distribution curve are then very broad Gaussian peaks.

One might be surprised that two models as different as the conformations I and II give rather similar RD curves. One reason is that the number of parameters is quite large. It is therefore important to inspect the results to see if any of the parameters have refined to unreasonable values. The value given above for the $C_3\cdots C_9$ distance in model II (2.82 Å) indicates that considerable repulsion between the double bonds must occur in a molecule in this conformation. (The "half-thickness" of an aromatic molecule is usually considered to be 1.7—1.8 Å.)

We feel that the evidence mentioned is sufficient to conclude that *cis,cis*-cyclodeca-1,6-diene exists predominantly in conformation I. It is, of course, impossible to exclude a small amount of conformation II.

Model I was in the introduction described as strain free. The torsional strain (Pitzer strain) for the bonds must certainly be small. With the actual parameters (Table 1) the torsional angle around for example the $C_1—C_2$ bond is found to be 58.2°.

$\angle C_1C_3C_3$ is almost equal to the CCC angles found in propane [19] (112.4°) and in butane (112.2° [20] or 112.4° [21]). $\angle C_{10}C_1C_2$ is slightly larger, but still smaller than the CCC angle found in cyclooctane [8] (116.5°). However, $\angle C_2C_3C_4$ is quite large. This must be due to the short distances of the type $H_4\cdots H_8$.

These distances are certainly considerably less than 2.40 Å even though the value given in Table 2 (2.02 Å) is rather uncertain since it depends on the assumptions concerning the $CH_2$ groups (see p. 1497). The value for $\angle C_2C_3C_4$ (128.2°) may be compared to the CCC angles found in *cis*- and *trans*-2-butene [22]

| | |
|---|---|
| *cis*-2-butene | 125.2° |
| *trans*-2-butene | 123.7° |

However, in *cis*-2-butene some of the strain seems to be relieved by a small tilt of the methyl groups or by a small twist around the double bond.[22]

The lengths of the CC single bonds are quite normal (Table 1), but the C=C bond is slightly shorter than usual, though it is not certain that the difference is real.

## REFERENCES


1. Dale, J. *Angew. Chem. Intern. Ed.* **5** (1966) 1000; *Angew. Chem.* **78** (1966) 1070.
2. Devaprabhakara, D., Gardenas, G. G. and Gardener, P. D. *J. Am. Chem. Soc.* **85** (1963) 1553.
3. Dale, J. and Moussebois, C. *J. Chem. Soc.* **1966 C** 264.
4. Grob, C. A. and Schiess, P. W. *Helv. Chim. Acta* **47** (1964) 558.
5. Dale, J., Ekeland, T. and Schaug, J. *Chem. Commun.* **1968** 1477.
6. Roberts, B. H., Vollmer, J. J. and Servis, K. L. *J. Am. Chem. Soc.* **90** (1968) 5264.
7. Trebellas, J. C., Olechowski, J. R., Jonassen, H. B. and Moore D. W. *J. Organomet. Chem.* **9** (1967) 153.
8. Almenningen, A., Bastiansen, O. and Jensen, H. *Acta Chem. Scand.* **20** (1966) 2689.
9. Bastiansen, O., Hassel, O. and Risberg, F. *Acta Chem. Scand.* **9** (1955) 232.
10. Bastiansen, O. and Skancke, P. N. *Advan. Chem. Phys.* **3** (1960) 323.
11. Seip, H. M. In *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, p. 25.
12. Peacher, J. L. and Wills, J. G. *J. Chem. Phys.* **46** (1967) 4809.
13. Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* **40** (1964) 1686.
14. Almenningen, A., Bastiansen, O., Seip, R. and Seip, H. M. *Acta Chem. Scand.* **18** (1964) 2115.
15. Kuchitsu, K. *Bull. Chem. Soc. Japan* **40** (1967) 498.
16. Bartell, L. S. *J. Chem. Phys.* **23** (1955) 1219.
17. Hamilton, W. C. *Acta Cryst.* **18** (1965) 502.
18. Murata, Y. and Morino, Y. *Acta Cryst.* **20** (1966) 605.
19. Lide, D. R. *J. Chem. Phys.* **33** (1960) 1514.
20. Kuchitsu, K. *Bull. Chem. Soc. Japan* **32** (1959) 748.
21. Bonham, R. A. and Bartell, L. S. *J. Am. Chem. Soc.* **81** (1959) 3491.
22. Almenningen, A., Anfinsen, I. M. and Haaland, A. *To be published.*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