# The Molecular Structure of *trans*-Cyclooctene

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The molecular structure of *trans*-cyclooctene has been determined by gaseous electron diffraction. The molecule was found to have a twist conformation. The values of the principal bond distances ($r_a$), valence angles and dihedral angles ($\omega$) with estimated uncertainty of $2\sigma$ are: $r_{C=C} = 1.332$ Å (0.003), $r_{C_2-C_3} = 1.499$ Å (0.008), $r_{C_3-C_4} = 1.549$ Å (0.002), $r_{C_3-H} = 1.110$ Å (0.002), $\angle C=C-C = 121.9°$ (0.8), $\angle C_2C_3C_4 = 104.6°$ (0.4), $\angle C_3C_4C_5 = 113.8°$ (0.4), $\angle C_4C_5C_6 = 118.8°$ (0.6), $\angle C=C-H = 118.4°$ (2.0), $\angle HCH = 106.8°$ (1.7), $\omega(C=C) = 136.0°$ (0.4), $\omega(C_2-C_3) = -91.1°$ (0.8), $\omega(C_3-C_4) = 54.2°$ (1.0), $\omega(C_4-C_5) = -82.8°$ (0.6), $\omega(C_5-C_6) = 111.8°$ (1.0), $\omega(H-C=C-H) = 177.5°$ (11.2).

*trans*-Cyclooctene is a highly strained disymmetric molecule whose structure has been the subject of considerable discussion since the compound was first synthesized by Cope *et al.*[1] in 1953. X-Ray and NMR studies [2,3] on both metal complexes and the dibromocarbene adduct [4] allow the conclusion that the *trans*-cyclooctene molecule exists in a twist conformation. Theoretical calculations by Allinger [5,6] and by Ermer [7,8] support these observations. The only experimental determination of the structure of the free molecule (Gavin,[10] 1973) does, however, indicate that the molecule assumes a chair conformation. In the hope of elucidating this interesting structural problem it was decided to undertake a new electron diffraction study of the *trans*-cyclooctene molecule in the gas phase.

## EXPERIMENTAL

The sample of *trans*-cyclooctene used in the present study was kindly provided by Dr. Robert D. Bach, Wayne State University. The electron diffraction data were recorded on the Oslo electron diffraction unit [11] at two different nozzle-to-plate distances (480.78 and 200.78

mm). The exposures were made at room temperature and at an electron wavelength of 0.06458 Å.

Four plates from each of the two camera lengths were selected for analysis which was carried out in the usual way.[12] The range of data obtained from these distances were $1.500 \leq s \leq 18.750$ Å$^{-1}$ with data interval $\Delta s = 0.125$ Å$^{-1}$ and $7.25 \leq s \leq 41.25$ Å$^{-1}$ with $s = 0.25$ Å$^{-1}$ ($s = 4\pi\lambda^{-1} \sin\theta$ where $\lambda$ is the electron wavelength and $2\theta$ is the scattering angle).

The theoretical counterpart to the experimental molecular intensity function may be calculated as:

$$sM(s) = \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_C(s)|^2} \cos [\eta_i(s) - \eta_j(s)]$$

$$\sin (sr_{ij}) \exp (-\tfrac{1}{2}u_{ij}^2 s^2) r_{ij}^{-1}$$

The sum extends over all atom pairs i, j in the molecule. $r_{ij}$ represents an internuclear distance and $u_{ij}$ the corresponding root-mean-square amplitude of vibration. $f_j(s) = |f_j(s)| \exp [i\eta_j(s)]$ is the complex atomic scattering factor of atom j.

Radial distribution (RD) functions were calculated by Fourier inversion of the intensity functions after multiplication with the artificial damping function $\exp (-ks^2)$.

## STRUCTURE ANALYSES

All conformations that might be reasonably imagined for the *trans*-cyclooctene molecule, including twist and chair conformations, have $C_2$ symmetry. In addition to this obvious supposition, the following assumptions about the molecular structure were made: (a) equal $C_{sp^3} - C_{sp^3}$ bond lengths, (b) equal $C_{sp^3} - H$ bond lengths, (c) local $C_{2v}$ symmetry for $CH_2$ groups, and (d) equal $H - C - H$ valence angles.

When these assumptions were applied, the geometry of a molecular model of *trans*-cyclo-
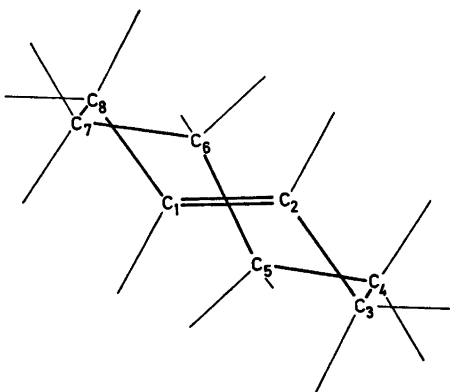
*Fig. 1.* *trans*-Cyclooctene. Molecular model which shows the numbering of the atoms.

octene could be completely defined by thirteen parameters. These were chosen as four bond lengths (C=C, $\overset{\diagdown}{\underset{\diagup}{C}}-\overset{\diagup}{\underset{\diagdown}{C}}-$, $-\overset{\diagdown}{\underset{\diagup}{C}}-\overset{\diagup}{\underset{\diagdown}{C}}-$, $-\overset{\diagdown}{\underset{\diagup}{C}}-H$), five valence angles ($\angle C=C-C$, $\angle C_2C_3C_4$, $\angle C_3C_4C_5$, $\angle C=C-H$, $\angle HCH$) and three dihedral angles (C−C=C−C, $C_1=C_2−C_3−C_4$, H−C=C−H). In addition the difference between the $C_3-H_3$ and $C_1-H_1$ distances were treated as a geometrical parameter.

The experimental radial distribution curve is shown in Fig. 3. The peaks at about 1.1 and 1.5 Å represent the carbon hydrogen and carbon carbon bond distances, respectively. The peak at about 2.15 Å contains contributions from non-bonded carbon hydrogen distances over one bond angle. The RD curve beyond 2.3 Å has seven more or less well resolved peaks that might be attributed to non-bonded carbon carbon distances across the ring. Since this region of the RD curve has so many well defined peaks, *trans*-cyclooctene must be a fairly rigid molecule. This hardly surprising observation is supported by the fact that it is possible to isolate optical isomers of the compound.

The structure of *trans*-cyclooctene was studied by least squares refinements of the molecular intensities. Both a twist and a chair model was studied in the early stages of the investigation. It became, however, soon evident that the twist model was clearly superior to the chair model. The following discussion does therefore only refer to the study of the twist

conformation of the *trans*-cyclooctene molecule.

In order to calculate a theoretical molecular intensity function for use in the least squares refinements it is necessary to assign values for the vibrational amplitudes (*u*-values) of all internuclear distances. Starting parameters for all the vibrational amplitudes were obtained by calculating these values from an assumed force field, using Gwinn's method.[13,14] In these calculations Allinger's [5] force constants were applied.

Some of the vibrational amplitudes could be determined experimentally. It was for example possible to obtain experimental *u*-values for all bond distances except for the $C_2-C_3$ and the $C_1-H_1$ bonds. The *u*-value for the $C_2-C_3$ bond was determined indirectly by varying this parameter systematically while the geometrical parameters and some of the *u*-values were refined by least squares. The lowest weighted square error sum was obtained for $u(C_2-C_3)$ equal to 0.0525 Å. This result seems reasonable compared to the experimental value of 0.0521 Å for $u(C_2-C_4)$. The calculated *u*-values for $C_2-C_3$ and $C_3-C_4$ are 0.0492 and 0.0491 Å.

When the theoretical RD curve based on the calculated *u*-values was compared with the experimental RD curve it was clearly seen that the theoretical curve was more smeared out and had fewer distinct features than the experimental curve. This observation indicated that the calculated vibrational amplitudes for the nonbonded distances were on an average too large.

It is reasonable to assume that the relative magnitudes between the calculated vibrational amplitudes were approximately correct. This problem was therefore studied by systematically reducing all calculated vibrational amplitudes of nonbonded distances by a certain procentage. For each set of *u*-values constructed in this way ordinary least squares refinements were carried out. The weighted squared error sum and most of the standard deviations of the refined parameters had fairly deep minima for a reduction of the calculated vibrational amplitudes of about 15 %. The reduced calculated vibrational amplitudes for the nonbonded distances were therefore applied in the following. In this connection it should be mentioned that when the *u*-value for the

*Table 1.* Final structural parameters and dependent distances obtained for *trans*-cyclooctene. Distances ($r_a$) and root-mean-square amplitudes ($u$) in Å, angles in degrees. $2\sigma$ are twice the standard deviations.

Bond distances

|  | $r_a$ | $2\sigma$ | $u$ | $2\sigma$ | $u^{calc.}$ |
|---|---|---|---|---|---|
| $C=C$ | 1.332 | 0.003 | 0.0337 | 0.0033 | 0.0408 |
| $C_2-C_3$ | 1.499 | 0.008 | (0.0525) |  | 0.0492 |
| $C_3-C_4$ | 1.549 | 0.002 | 0.0521 | 0.0022 | 0.0491 (av.) |
| $C_3-H_3$ | 1.110 | 0.002 | 0.0813 | 0.0023 | 0.0790 |
| $C_1-H_1$ | 1.103 |  | (0.0790) |  | 0.0790 |

Valence angles and dihedral angles

|  |  | $2\sigma$ |  |  | $2\sigma$ |
|---|---|---|---|---|---|
| $\angle C=C-C$ | 121.9 | 0.8 | $\omega(C-C=C-C)$ | 136.0 | 0.4 |
| $\angle C_2C_3C_4$ | 104.6 | 0.4 | $\omega(C_1=C_2-C_3-C_4)$ | $-91.1$ | 0.8 |
| $\angle C_3C_4C_5$ | 113.8 | 0.4 | $\omega(C_2-C_3-C_4-C_5)$ | $54.2^a$ | 1.0 |
| $\angle C_4C_5C_6$ | $118.8^a$ | 0.6 | $\omega(C_3-C_4-C_5-C_6)$ | $-82.8^a$ | 0.6 |
| $\angle C=C-H$ | 118.4 | 2.0 | $\omega(C_4-C_5-C_6-C_7)$ | $111.8^a$ | 1.0 |
| $\angle H-C-H$ | 106.8 | 1.7 | $\omega(H-C=C-H)$ | 177.5 | 11.2 |

Nonbonded CC distances

|  | $r_a$ | $2\sigma$ | $u^b$ |  | $r_a$ | $2\sigma$ | $u^b$ |
|---|---|---|---|---|---|---|---|
| $C_1C_7$ | 2.412 | 0.005 | 0.0658 | $C_1C_4$ | 3.193 | 0.006 | 0.0793 |
| $C_1C_3$ | 2.477 | 0.005 | 0.0645 | $C_3C_6$ | 3.450 | 0.006 | 0.0847 |
| $C_3C_5$ | 2.595 | 0.005 | 0.0665 | $C_3C_8$ | 3.752 | 0.008 | 0.0705 |
| $C_4C_6$ | 2.668 | 0.007 | 0.0682 | $C_4C_7$ | 3.784 | 0.007 | 0.0746 |
| $C_1C_6$ | 2.868 | 0.007 | 0.0752 | $C_3C_7$ | 4.052 | 0.005 | 0.0842 |
| $C_1C_5$ | 3.100 | 0.010 | 0.0853 |  |  |  |  |

*a* Dependent angle. *b* The applied vibrational amplitudes are those calculated from an assumed force field and then reduced by 15 %.
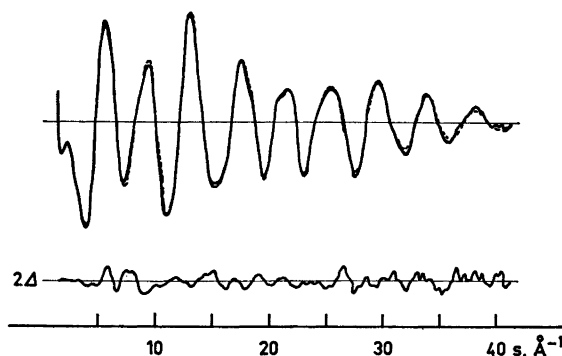


*Fig. 2. trans*-Cyclooctene. Experimental (———) and theoretical (– – –) molecular intensity functions. The scale of the difference curve is twice the scale of the intensities.

*Table 2. trans*-Cyclooctene. Results obtained in least-squares refinements of independent parameters when the $H-C=C-H$ dihedral angle ($\omega_{HH}$) is varied systematically. The standard deviations in brackets. Distances ($r_a$) and root-mean-square amplitudes ($u$) in Å, angles in degrees.

| Parameter | $\omega_{HH}$ 160° | 170° | 180° | 190° | 200° | 220° |
|---|---|---|---|---|---|---|
| $r(C=C)$ | 1.3322(18) | 1.3322(17) | 1.3320(17) | 1.3318(17) | 1.3318(17) | 1.3318(18) |
| $u(C=C)$ | 0.0339(17) | 0.0338(17) | 0.0337(16) | 0.0336(17) | 0.0334(17) | 0.0333(17) |
| $r(C_2-C_3)$ | 1.4989(39) | 1.4992(38) | 1.4988(36) | 1.4977(36) | 1.4967(35) | 1.4954(35) |
| $r(C_3-C_4)$ | 1.5491(10) | 1.5491(10) | 1.5492(9) | 1.5494(9) | 1.5495(9) | 1.5493(8) |
| $u(C_3-C_4)$ | 0.0518(12) | 0.0521(12) | 0.0521(11) | 0.0519(11) | 0.0517(11) | 0.0512(11) |
| $r(C-H)$ | 1.1097(12) | 1.1097(11) | 1.1096(11) | 1.1095(11) | 1.1095(12) | 1.1095(12) |
| $u(C-H)$ | 0.0810(12) | 0.0811(12) | 0.0813(11) | 0.0814(12) | 0.0814(12) | 0.0812(13) |
| $\angle C=C-C$ | 121.64(.46) | 121.74(.44) | 121.94(.42) | 122.15(.42) | 122.23(.43) | 122.17(.44) |
| $\angle C_2C_3C_4$ | 104.60(.22) | 104.60(.21) | 104.63(.21) | 104.72(.21) | 104.88(.22) | 105.39(.23) |
| $\angle C_3C_4C_5$ | 113.62(.20) | 113.69(.20) | 113.79(.20) | 113.87(.20) | 113.95(.21) | 114.33(.25) |
| $\angle HCH$ | 105.85(.92) | 106.46(.88) | 106.75(.86) | 106.69(.85) | 106.38(.85) | 104.90(.87) |
| $\angle C=C-H$ | 118.43(1.27) | 118.71(1.13) | 118.41(.99) | 117.68(.90) | 116.72(.83) | 115.06(.80) |
| $\omega(C-C=C-C)$ | 136.45(.43) | 136.25(.43) | 136.03(.44) | 135.98(.47) | 136.23(.49) | 136.97(.48) |
| $\omega(C=C-C-C)$ | −90.83(.40) | −90.92(.38) | −91.09(.37) | −91.36(.38) | −91.75(.40) | −92.93(.47) |
| $\sum_i w_i \Delta_i^2$ | 8.04 | 7.56 | 7.47 | 7.69 | 7.98 | 8.42 |

$C_3C_7$ distance, which appears as a fairly well isolated peak on the RD curve, is refined in least squares a value of 0.0840 Å is obtained, while 0.0842 Å corresponds to the reduced calculated $u$-value.

It was possible to refine all geometrical parameters simultaneously in the least squares calculations, except for the difference between the $C_3-H_3$ and $C_1-H_1$ bonds. This parameter

was determined by the combined trial and error/least squares procedure described above to be 0.007 Å. The final structural parameters obtained for *trans*-cyclooctene are listed in Table 1.

Even if the standard deviation of the $H-C=C-H$ dihedral angle ($\omega_{HH}$) is as large as 5.6° it might seem surprising that it is possible at all to determine this parameter in

*Table 3.* Correlation matrix for

| $C=C$ | $C_2-C_3$ | $C_3-C_4$ | $\angle C-C=C$ | $\angle C_2C_3C_4$ | $\omega(1=2)$ | $\omega(2-3)$ | $\angle C_3C_4C_5$ |
|---|---|---|---|---|---|---|---|
| *b* | | | | | | | |
| 0.0017 | 0.0037 | 0.0009 | 0.445 | 0.212 | 0.450 | 0.395 | 0.204 |
| 1.000 | 0.565 | −0.479 | −0.623 | −0.340 | −0.447 | 0.390 | 0.236 |
| | 1.000 | −0.836 | −0.818 | −0.589 | −0.578 | 0.564 | 0.351 |
| | | 1.000 | 0.670 | 0.432 | 0.454 | −0.392 | −0.420 |
| | | | | 0.416 | 0.779 | −0.616 | −0.182 |
| | | | | 1.000 | 0.450 | −0.721 | 0.024 |
| | | | | | 1.000 | −0.314 | −0.292 |
| | | | | | | 1.000 | −0.384 |
| | | | | | | | 1.000 |

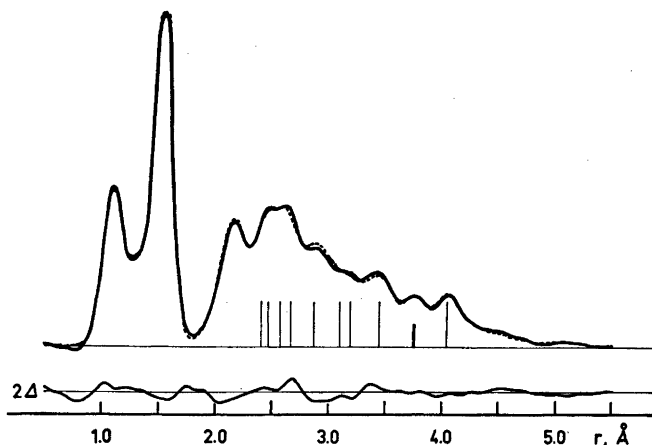*a* Distances ($r$) and root-mean-square amplitudes ($u$) in Å, angles in degrees. *b* Standard deviations from

*Fig. 3. trans*-Cyclooctene. Experimental (——) and theoretical (— — —) radial distribution curves. Artificial damping constant $k = 0.0015$ Å². The scale of the difference curve is twice the scale of the RD-curves. The vertical bars indicate the positions of the CC nonbonded distances.

the least squares refinements. As this dihedral angle is very important for the discussion of the structural implications in connection with the CC double bond, the parameter was also studied by a different approach. $\omega_{HH}$ was varied systematically between 160 and 220° while the other geometrical parameters were refined by least squares. Coplanar sigma bonds at each of the unsaturated carbon atoms would correspond

to $\omega_{HH}$ equal to 244° (see Fig. 4). The results are presented in Table 2, and they strongly support the observed value of 177.5° for $\omega_{HH}$.

The theoretical intensity and radial distribution functions calculated from the final parameters for *trans*-cyclooctene (Table 1), are shown in Figs. 2 and 3 together with their experimental counterparts. Table 3 gives the correlation matrix for the parameters of the molecule.

parameters of *trans*-cyclooctene.[a]

| C—H | ∠HCH | ∠C=C—H | $\omega(H_1C_1C_2H_2)$ | $u(C=C)$ | $u(C_3-C_4)$ | $u(C-H)$ |
|---|---|---|---|---|---|---|
| 0.1131 | 0.875 | 1.025 | 5.651 | 0.0016 | 0.0011 | 0.0012 |
| 0.191 | 0.257 | − 0.046 | − 0.092 | 0.113 | 0.452 | 0.182 |
| 0.130 | 0.254 | 0.062 | − 0.129 | 0.207 | 0.860 | 0.065 |
| − 0.097 | − 0.093 | − 0.035 | 0.124 | − 0.159 | − 0.672 | − 0.009 |
| − 0.127 | − 0.354 | − 0.135 | 0.280 | − 0.178 | − 0.690 | − 0.082 |
| − 0.021 | − 0.365 | − 0.006 | 0.124 | − 0.116 | − 0.554 | − 0.096 |
| − 0.079 | − 0.317 | − 0.149 | 0.209 | − 0.126 | − 0.491 | − 0.073 |
| 0.045 | 0.382 | 0.003 | − 0.302 | 0.119 | 0.521 | 0.092 |
| 0.093 | − 0.089 | − 0.096 | 0.190 | 0.060 | 0.279 | 0.016 |
| 1.000 | 0.354 | − 0.085 | − 0.50 | − 0.068 | 0.100 | 0.037 |
| | 1.000 | 0.154 | 0.163 | 0.002 | 0.300 | 0.168 |
| | | 1.000 | 0.014 | 0.049 | − 0.002 | − 0.065 |
| | | | 1.000 | − 0.043 | − 0.060 | 0.056 |
| | | | | 1.000 | 0.038 | − 0.086 |
| | | | | | 1.000 | 0.157 |
| | | | | | | 1.000 |

least squares.

DISCUSSION

In Table 4 the geometrical parameters determined for *trans*-cyclooctene in the present study are compared with other structural results obtained for this molecule. All the other data refer to theoretical calculations of structure parameters, except those in the last column which are Gavin's [10] electron diffraction data for the twist conformation. Gavin concludes that the molecule apparently assumes a chair conformation but the only parameters that differ noticeably in his determination of the two conformations, are $\angle C_3C_4C_5$ (chair: 110.9°), $\angle C_4C_5C_6$ (115.3°) and $\omega(C-C=C-C)$ (157.7°).

The present study concludes that the *trans*-cyclooctene assumes a twist conformation. This observation is in agreement with most investigations concerning this molecule and its derivatives.[2-8] The only reported indication of another conformation is Gavin's [10] electron diffraction study. Ermer [8] suggested that possibly Gavin might have had a *trans*-cyclooctene sample which was prepared under non-equilibrium conditions and consisting primarily of the

chair conformation. The barrier separating the chair and twist conformations will probably be sufficiently high (*ca*. $125-150$ kJ mol$^{-1}$) to prevent rapid interconversion at room temperature. Even if this should be true, there are several inconsistencies between Gavin's results and those calculated for a chair model.[8] They will, however, not be discussed here.

The correspondence between the results obtained for *trans*-cyclooctene in the present study and those calculated by Allinger [6] and by Ermer [8] is remarkably good. The structural parameters show that the strain in the molecule is distributed among the valence angles, torsional angles and the double bond.

Allinger's [5] calculated structure for *trans*-cyclooctene was the first one to indicate a substantial rehybridization of the unsaturated carbon atoms in the ring. Locating the hydrogens in toward the ring, which constitutes a rehybridization of the olefinic carbons, will reduce the angle between the *p* orbitals and thus increase the overlap. The present experimental results confirm Allinger's predictions concerning the structural features in connection

*Table 4.* Comparison of results obtained for the structure of *trans*-cyclooctene. The numbers in brackets are standard deviations as resulting from least squares refinements. Distances are given in Å and angles in degrees.

|  | Present study | Allinger [5] | Ermer [7] | Buemi [8] | Gavin [9] |
|---|---|---|---|---|---|
| **Bond distances** |  |  |  |  |  |
| $C=C$ | 1.3321(17) | 1.3376 | 1.338 | (1.331) [a] | 1.363(8) |
| $C_2-C_3$ | 1.4990(38) | 1.4990 | 1.504 | (1.505) [a] | (1.538) [b] |
| $C_3-C_4$ | 1.5491( 9) | 1.5462 | 1.541 | (1.533) [a] | 1.538(3) |
| $Csp^3-H$ | 1.1096(11) | 1.0998 | 1.107 |  | 1.107(2) |
| **Valence angles** |  |  |  |  |  |
| $\angle C=C-C$ | 121.9(.4) | 118.9 | 117.9 | 117.5 | 114.9(3.6) |
| $\angle C_2C_3C_4$ | 104.6(.2) | 104.0 | 106.4 | 98.0 | 101.3(2.0) |
| $\angle C_3C_4C_5$ | 113.8(.2) | 116.5 | 115.0 | 108.8 | 115.9(2.5) |
| $\angle C_4C_5C_6$ | 118.8(.3) | 119.7 | 117.0 | 114.5 | 107.7(3.0) |
| $\angle C=C-H$ | 118.4(1.0) | 120.5 | 121.9 |  |  |
| $\angle H-C-H$ | 106.75(.86) | 104.5 | 108.0 |  | 114(2.0) |
| **Dihedral angles** |  |  |  |  |  |
| $C=C$ | 136.0(.2) | 145.0 | 138.0 | $-163.0$ | 134.6(6.5) |
| $C_2-C_3$ | $-91.1(.4)$ | $-92.6$ | $-87.0$ | $+64.0$ |  |
| $C_3-C_4$ | 54.2(.5) | 46.4 | 50.0 | $+32.7$ |  |
| $C_4-C_5$ | $-82.8(.3)$ | $-76.7$ | $-80.6$ | $-96.4$ |  |
| $C_5-C_6$ | 111.8(.5) | 110.9 | 114.8 | $+115.2$ |  |
| $H-C=C-H$ | 177.5(5.6) | 170.4 | 177.6 |  |  |

[a] Assumed values. [b] Assumed equal to $C_3-C_4$.

with the double bond.

Evidence supporting the indicated rehybridization of the unsaturated carbon atoms is also found in the 0.8 D dipole moment of *trans*-cyclooctene,[15] as compared to the quite normal 0.4 D moment of the *cis* isomer.

Based on the parameters presented in Table 1, the angle between the $p$ orbitals is found to be about 20°, which should result in a reduction in the overlap between these orbitals of about 12 %. It might therefore seem surprising that the $C = C$ bond is found to be slightly, but not significantly shorter than in ethylene. If, however, the hybridization of the orbitals extending from the carbon atoms of the double bond is roughly evaluated, based on the observed valence angles, the orbitals making up the $C_1 - C_2$ sigma bond are found to have about 36.4 % $s$-character ($sp^{1.74}$ orbitals). An estimate of the expected shortening in a $\sigma$ bond when going from $sp^2$ to $sp^{1.74}$ orbitals is found to be somewhat larger than the expected increase because of non-parallell $p$-orbitals. The observed CC double bond length seems therefore to be reasonable.

The discussion above weighs heavily on the exact location of the hydrogen atoms at the $C = C$ bond. Even when the large error of $\omega_{HH}$ (see Fig. 4) is taken into account the present study shows beyond doubt that the discussed hydrogen atoms really are bent in towards the ring. It would, however, be of great interest to obtain more experimental information concerning this important structural detail. Substituting methyl groups for the two hydrogens in question will probably not cause any drastic structural changes at the un-
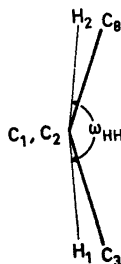
saturated carbon atoms as no serious additional steric strain is expected for the dimethyl derivative. An electron diffraction study of 1,8-dimethyl-*trans*-cyclooctene is therefore being planned.

There are not many reported data that are suitable for comparison with the amplitudes of vibrations determined in this study. Gavin[10] has determined the $u$-values for the non-bonded CC distances to be 0.130 Å for $r < 3.45$ Å, 0.120 Å for $r = 3.45$ Å and 0.090 Å for $r > 3.45$ Å. These amplitudes are almost an order of magnitude larger than those found in the present study, and they are not compatible with the experimental radial distribution curve. His reported $u$-values for the bond distances are, however, not very different from those determined here.

*Fig. 4. trans*-Cyclooctene. A projection of the dihedral angles at the carbon carbon double bond.

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