

An Electron Diffraction Investigation of the Molecular Structure of Bicyclopropyl with Vibrational Amplitudes Calculated from Spectroscopic Data

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The molecular structure of bicyclopropyl has been reinvestigated by the gas electron diffraction method. Root mean square amplitudes of vibrations for various conformations have been calculated from spectroscopic data and the resulting u -values which are dependent on the dihedral angle of the central carbon carbon bond were applied in least squares refinements of the intensity data.

The results are in accordance with a conformation composition of about equal parts of *trans* and *gauche* conformers. The experimentally determined geometrical parameters are the following. $r(\text{C}-\text{H})$: 1.103 Å; $r(\text{C}_1-\text{C}_2)$: 1.499 Å; $r(\text{C}_2-\text{C}_3)$: 1.507 Å; $\angle \text{C}_1\text{C}_2\text{C}_3$: 120.9°; $\angle \text{H}_1\text{C}_1\text{C}_2$: 110.5°; $\angle \text{HCH}$: 110.5°; the *gauche* dihedral angle: 48.7°. The bond distances are given as $r_g(1)$ -values.

Bicyclopropyl was investigated in 1965 by Lüttke *et al.* using infrared and Raman spectroscopy. They found that the molecule assumes a centrosymmetric *trans* conformation in the solid state, while other conformations are in equilibrium with the *trans* conformation in liquid phase. Bastiansen and de Meijere¹ performed an electron diffraction investigation of the bicyclopropyl molecule in the gas phase at about the same time. They concluded that bicyclopropyl in gas phase exists both in *trans* and *gauche* conformations and that both conformers exhibit extended torsional motions around the central carbon carbon bond. At about the same time Eraker and Rømming² did an X-ray diffraction study of bicyclopropyl in the solid state and found the central CC bond length to be considerably smaller than the other CC bonds (1.487 Å *vs.* 1.501 Å and 1.510 Å). As Bastiansen and de Meijere did not distinguish the central CC bond from the other CC bonds and they also expressed doubts concerning the large torsional amplitude of the *trans* conformer, it was of interest to reinvestigate the molecular structure of bicyclopropyl.

EXPERIMENTAL PROCEDURE

The sample of bicyclopropyl used in the present investigation was provided by Professor W. Lüttke, Göttingen, Germany. The electron diffraction pattern from the gas was recorded on a Balzers Eldigraph KDG 2 at room temperature. Exposures were made at nozzle to photographic plate distances of 50 cm and 25 cm. Four apparently faultless plates were photometered and the data processed in the usual way.⁵ The resulting molecular intensity function extended from $s = 1.25 \text{ \AA}^{-1}$ to $s = 30.50 \text{ \AA}^{-1}$. $s = (4\pi/\lambda)\sin(\theta/2)$ where λ is the electron wavelength (determined by diffraction from gaseous CO_2) and θ is the diffraction angle.

In order to obtain intensity data at higher s -values, exposures were also made at the Oslo electron diffraction unit⁶ at a nozzle to photographic plate distance of about 19 cm. The additional experimental data gave intensity values out to $s = 44.0 \text{ \AA}^{-1}$. The modified experimental molecular intensity function is shown in Fig. 5. The intensity data in the outer s -range contain a large amount of noise.

Theoretical intensity functions were calculated from:

$$sM(s) = \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_C(s)|^2} \cos[\eta_i(s) - \eta_j(s)] \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2s^2)$$

The sum extends over all atom pairs i, j in the molecule. R_{ij} is the internuclear distance, u_{ij} the 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 functions were calculated by Fourier inversion of experimental and theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$.

STRUCTURE ANALYSIS

A molecular model of bicyclopropyl is shown in Fig. 1 which also gives the numbering of the atoms. An experimental radial distribution function is presented in Fig. 6. The peak at 1.1 \AA corresponds to the C-H bond distances, while the peak at about 1.5 \AA contains contributions from the C-C bond distances. The peaks at about 2.2 \AA and about 2.6 \AA correspond to nonbonded distances between carbon and hydrogen atoms and between two carbon atoms over one bond angle, respectively. All these peaks contain contributions from distances that are independent of the dihedral angle at the central carbon-carbon bond. The conformation of the molecule must therefore be studied in the outer part ($r > 2.8 \text{ \AA}$) of the radial distribution function. In accordance with Bastiansen and de Meijere's results¹ refinements were first carried out on a model with a mixture of *trans* and *gauche* conformers with assumed torsional

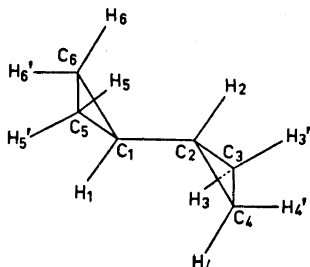


Fig. 1. Bicyclopropyl. Molecular model which shows the numbering of the atoms.

movements around the central CC bond. It was first assumed that both *trans* and *gauche* conformers had Gaussian distribution around equilibrium dihedral angles. In order to describe the torsional motions a series of molecular models with different dihedral angles was calculated. Each model was given weight in accordance with the assumption of a Gaussian distribution. The dihedral angle of the *trans* conformer is given by the symmetry of the molecule (180°), while the equilibrium *gauche* dihedral angle had to be determined. The computer (UNIVAC 1107) had a maximum storage capacity which made it possible to include fifteen single structures, and ten *trans* structures and five *gauche* structures were included in the following calculations.

If the carbon carbon bonds within the cyclopropyl groups are assumed to be the same and all carbon hydrogen bond lengths are assumed to be equal, the conformations and geometry of the bicyclopropyl molecule are determined by ten parameters. These include three bond lengths (C-H, C_1-C_2 , C_2-C_3), three bond angles ($\angle HCH$, $\angle C_1C_2H_2$, $\angle C_1C_2C_3$), the equilibrium *gauche* dihedral angle ($\angle \alpha$), the half widths of the *trans* and *gauche* Gaussian distributions ($\angle \beta$ and $\angle \delta$), and finally the relation between *trans* and *gauche* conformers.

In order to calculate theoretical intensity functions it is necessary to know the vibrational amplitudes (u_{ij}) in the molecule. At the beginning it was assumed that the u -value for a particular distance (e.g. C_3C_6) was independent of the C_1-C_2 dihedral angle and therefore the same in all fifteen single structures.

Preliminary u -values were assigned by using the results from Bastiansen and de Meijere's¹ study and experimental data obtained for other similar molecules.^{3,7-9}

The molecular structure was then refined by least squares calculations on the intensity data using a diagonal weight matrix.⁵ The half-widths of the *trans* and *gauche* Gaussian distributions and the parameter determining the conformation composition could not be refined in the least squares calculation. A combined trial and error and least squares method was therefore applied, in order to determine these parameters. The bond lengths and bond angles were refined in least squares calculations, while the other parameters were kept constant. In each run one of the constant parameters was changed slightly and in this way each of these were varied systematically in their expected range of values. The parameter in question was then determined on the criteria of minimum square error sum and smallest standard deviation values for the refined parameters. This method did not, however, give unambiguous results for the torsional motions around the *trans* conformation. Best correspondence between theoretical and experimental functions was obtained for remarkably large values of the *trans* torsional amplitude, but it was not possible to determine the halfwidth of the assumed Gaussian *trans* distribution accurately. The results based on this model showed that the distributions of *trans* and *gauche* conformers overlapped to a considerable extent. The results might therefore indicate that there were almost free rotation around the central carbon carbon bond in a remarkably large angle interval. This indication, however, did not agree with the potential curve that Bastiansen and de Meijere¹ calculated for the nonbonded hydrogen hydrogen interactions as functions of the C_1-C_2 dihedral angle. Their calculations gave a potential barrier of around 2 kcal/mol between *trans* and *gauche* conformations.

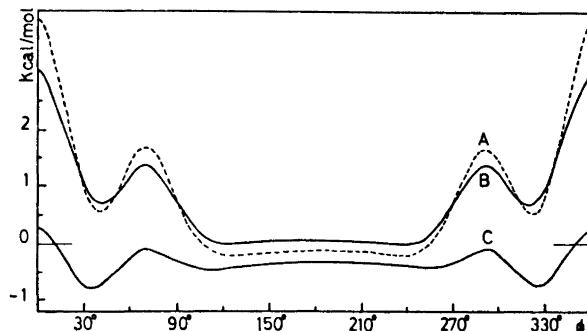


Fig. 2. Bicyclopropyl. Calculated van der Waals potential energy functions for the nonbonded interatomic interactions. Only contributions from distances that are dependent on the C_1-C_2 dihedral angle are included. Potential formulae according to: A, Jacob *et al.*,¹² B, Hendrickson,¹¹ C, Hill.¹⁰

To see if this picture changes when all nonbonded van der Waals interactions were included, the van der Waals potential function for the $H\dots H$, $C\dots H$, and $C\dots C$ nonbonded interactions were calculated according to Hill's¹⁰ formulae:

$$E_v = \varepsilon(-2.25\alpha^{-6} + 8.28 \times 10^5 \exp(-\alpha/0.0736))$$

$$\text{where } \alpha = r/(r_1^* + r_2^*), \quad r_H^* = 1.20 \text{ \AA}, \quad r_C^* = 1.70 \text{ \AA}$$

$$\varepsilon_{H\dots H} = 0.042 \text{ kcal/mol}, \quad \varepsilon_{C\dots H} = 0.067 \text{ kcal/mol}, \quad \varepsilon_{C\dots C} = 0.107 \text{ kcal/mol}.$$

Only nonbonded distances that are functions of the C_1-C_2 dihedral angle were included in the calculation. The resulting van der Waals potential energy function is shown in Fig. 2C. The potential barrier between *trans* and *gauche* conformations is here found to be only about 0.4 kcal/mol. The calculations also gave the lowest energy for *gauche* conformation, in contrast to the results obtained by Bastiansen and de Meijere.¹ Because of these discrepancies it was necessary to calculate the van der Waals potential function by other expressions than that given by Hill.¹⁰

Fig. 2, A and B, shows van der Waals potential energy functions calculated according to energy expressions given by Jacob *et al.*¹² and by Hendrickson.¹¹ The formulae given by Jacob *et al.*¹² are the following:

$$E_{H\dots H} = 6.591 \times 10^3 \exp(-4.08r) - 49.2/r^6$$

$$E_{C\dots H} = 4.471 \times 10^4 \exp(-2.04r)/r^6 - 124.9/r^6$$

$$E_{C\dots C} = 2.993 \times 10^5/r^{12} - 325.2/r^6$$

The expression for the $H\dots H$ interaction is approximately the same as that used by Bastiansen and de Meijere.¹

Hendrickson's¹¹ expressions for the van der Waals energy are:

$$E_{H\dots H} = 2.3 \times 10^3 \exp(-3.6r) - 49.2/r^6$$

$$E_{C\dots H} = 4.012 \times 10^3 \exp(-3.4r) - 125/r^6$$

$$E_{C\dots C} = 7.0 \times 10^3 \exp(-3.2r) - 325/r^6$$

The potential functions calculated by Jacob's and by Hendrickson's expressions (Fig. 2, A and B) were quite similar, but the energy barrier between *trans* and *gauche* conformations is somewhat lower when Hendrickson's energy formulae are employed.

The application of three different van der Waals energy expressions for calculation of the potential energy does therefore yield three different potential energy functions. If only the van der Waals contribution to the conformational energy is considered one should expect almost free rotation around the central CC bond according to Hill's¹⁰ formulae. Based on the other two potential functions one should expect a mixture of *gauche* and *trans* conformers with almost free rotation over a large range around *trans* conformation and also with torsional motions around *gauche* conformation.

If in addition the torsional conformational energy is considered, whose energy contribution may be expected to have minima at dihedral angles of 60°, 180°, and 300°, the maxima in the potential functions at about 75° and 285° will be somewhat reduced.

The obtained van der Waals potential energy curves combined with the difficulties in establishing a Gaussian distribution of the *trans* conformer in the molecular model studied made it reasonable to test other molecular models of bicyclopropyl with different conformation relations. In one of these models free rotation over a very wide range around *trans* conformation was assumed. The other model was based on a mixture of *trans* and *gauche* conformers. The latter was assumed to be Gaussian distributed around an equilibrium *gauche* dihedral angle, while the *trans* conformation distribution was assumed to be described by a potential well. This last model is in accordance with the results obtained by Bastiansen and de Meijere.¹

These two models were refined by least squares calculations, and the combined trial and error and least squares method was applied in order to study the distribution of the conformers and the conformation composition. The root mean square amplitudes of vibrations for the bond distances could be refined directly in the least squares calculations, while *u*-values for the nonbonded interatomic distances had to be assumed.

The correspondence between experimental and theoretical radial distribution functions were not satisfactory for $r > 2.8$ Å for results obtained for any one of the two models. There also appeared to be a high degree of coupling between the CC bond distances and the C₁C₂C₃ bond angle. In addition it was observed that the relation between the C₁-C₂ and C₂-C₃ bond lengths was dependent on several of the vibrational amplitudes for the nonbonded internuclear distances that could not be determined from the electron diffraction data. To arrive at an unambiguous conclusion about the molecular structure it was therefore necessary to obtain information about the root mean square amplitudes of vibrations for the nonbonded interatomic distances. It was not unreasonable to assume that some of the difficulties involved were due to invalidity of the assumption that the *u*-values were independent of the torsional motions around the central carbon carbon bond.

It is possible to calculate the molecular vibrational amplitudes if the frequencies of vibrations are known. Vibrational frequencies observed by de Meijere and Lüttke¹³ were applied in order to establish an approximate force

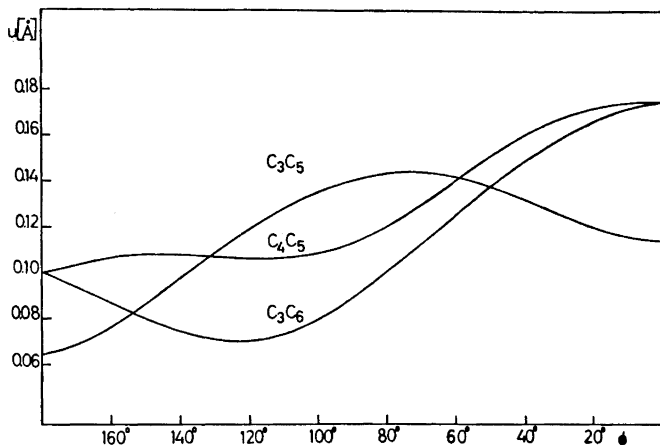


Fig. 3. Bicyclopropyl. Calculated root mean square amplitudes of vibration for the carbon carbon nonbonded interatomic distances that are dependent on the C_1-C_2 dihedral angle.

field for bicyclopropyl. This force field was then used to calculate the mean amplitudes of vibrations for the molecule. In the calculations it was assumed that the force constants for the vibrations were independent of the C_1-C_2 dihedral angle. This approximation is insignificant compared to the assumption made above about constant root mean square amplitudes of vibrations for distances that vary with the C_1-C_2 dihedral angle. We believe that the calculated mean amplitudes are quite reliable, as it is well known¹⁴ that even large errors in the force constants affect the calculated mean amplitudes to only minor extents. The results of the calculations are listed in Table 1, while Figs. 3 and 4 show calculated u -values for the carbon carbon distances and some of the carbon hydrogen distances, respectively, as functions of the C_1-C_2 dihedral angle. The figures demonstrate convincingly that the assumption about constant root mean square amplitudes for nonbonded distances that are conformation dependent is invalid.

The u -values for the bond distances determined by least squares refinements were in good agreement with those obtained in the calculation from spectroscopic data. The observed u -value for the C_2-C_3 distance from least square refinements is for example 0.0476 Å, while the spectroscopic calculations give 0.0485 for this parameter. The agreement for the other bond distances is of the same order of magnitude. The u -value for the C_1C_3 distances was also determined from the least squares calculations (0.0710 Å).

In the further refinements the experimentally obtained u -values for C-H, C_1-C_2 , C_2-C_3 , and C_1C_3 distances were applied while the spectroscopically calculated vibrational amplitudes were used for the other interatomic distances. Introduction of the calculated varying vibrational amplitudes led to striking improvements in the least squares calculations for the model with a

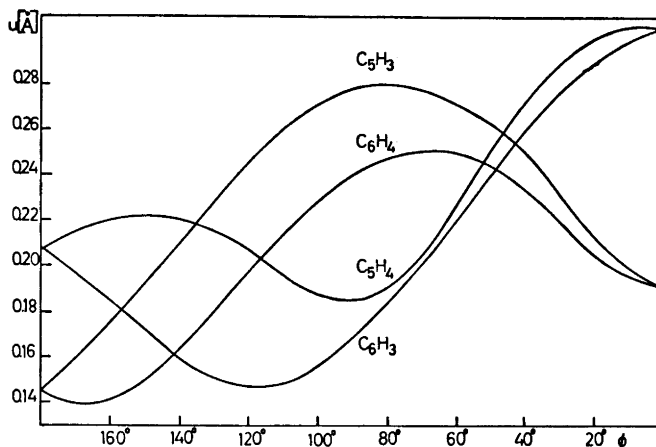


Fig. 4. Bicyclopropyl. Calculated root mean square amplitudes of vibration for some of the carbon hydrogen nonbonded interatomic distances that are dependent on the C_1-C_2 dihedral angle.

mixture of *trans* and *gauche* conformations. The agreement between experimental and theoretical radial distribution functions for $r > 2.8$ Å was also very much better in this case. At this stage it could be clearly decided that a model including only the *trans* conformer, but with a large freedom of torsional motion around *trans* conformation, was inferior to the one with a mixture of *gauche* and *trans* conformers and was therefore rejected.

It was also at this stage necessary to apply the combined trial and error/least squares method in order to determine the conformation composition, the half-width of the Gaussian distribution around *gauche* conformation ($\angle \delta$), the extension of the torsional well around *trans* position and $\angle H_1C_1C_2$. Table 2 shows the results from least squares refinements when the conformation composition is varied systematically.

FINAL RESULTS

Bicyclopropyl is found to exist as a conformation mixture at room temperature with about 47.5 % *trans* conformer and about 52.5 % *gauche* conformer. The *trans* contribution is distributed in a large region ($\pm 100^\circ$) around the equilibrium *trans* dihedral angle and the governing potential may be approximated as a square well. The *gauche* contribution may be described as a Gaussian distribution around an equilibrium *gauche* dihedral angle of 48.7° . The root mean square amplitudes of vibrations in the molecule are calculated from spectroscopic data for increments in the C_1-C_2 dihedral angle of 15° , and are listed in Table 1. Some of the calculated u -values are shown in Figs. 2 and 3 as functions of the C_1-C_2 dihedral angle.

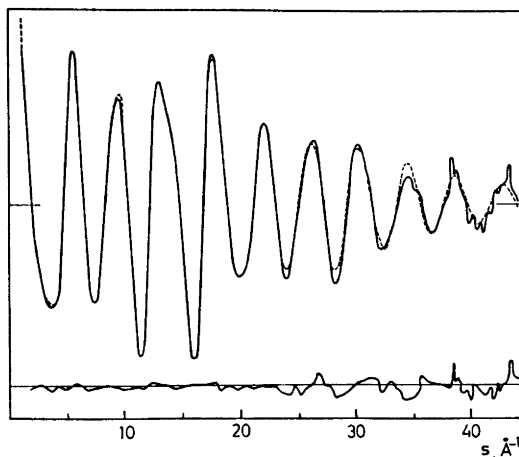


Fig. 5. Bicyclopropyl. Experimental (—) and theoretical (---) molecular intensity functions and the differences between them.

The experimentally determined parameters for bicyclopropyl are presented in Table 3. Fig. 5 shows the experimental molecular intensity function together with the theoretical $sM(s)$ -function calculated from the parameters listed in Tables 1 and 3. The corresponding radial distribution functions are shown in Fig. 6.

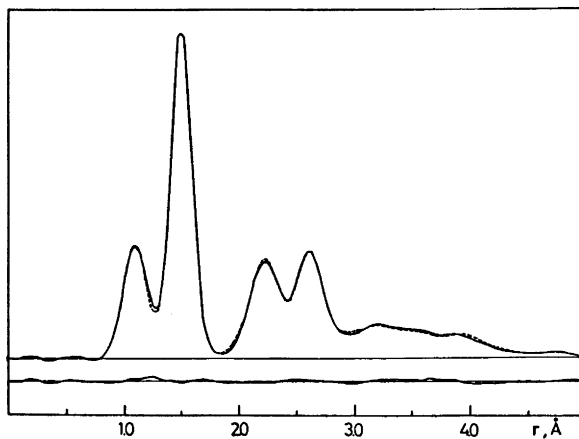


Fig. 6. Bicyclopropyl. Experimental (—) and theoretical (---) radial distribution functions and the differences between them.

Table 1. Bicyclopopyl. Vibrational amplitudes (μ -values), calculated from spectroscopic data as functions of the central torsional angle.

	C_3C_6	C_4C_5	C_3C_5	C_5H_2	C_4H_2	C_3H_2'	C_4H_2	C_5H_4'	C_5H_3'	C_6H_4'	C_6H_3'	C_4H_3	C_5H_4	C_5H_3	C_6H_4	C_6H_3
<i>trans</i>	0.0998	0.0998	0.0632	0.1954	0.1954	0.1536	0.1536	0.1536	0.1281	0.1281	0.2074	0.2074	0.2074	0.1458	0.1458	0.1458
168°	0.0923	0.1037	0.0676	0.1970	0.1900	0.1496	0.1496	0.1565	0.1172	0.1417	0.1952	0.1952	0.2161	0.1613	0.1613	0.1385
157°	0.0849	0.1067	0.0782	0.1964	0.1811	0.1449	0.1449	0.1586	0.1109	0.1544	0.1809	0.1809	0.2212	0.1803	0.1803	0.1420
146°	0.0777	0.1078	0.0909	0.1942	0.1716	0.1397	0.1397	0.1605	0.1093	0.1650	0.1664	0.1664	0.2219	0.2003	0.2003	0.1544
135°	0.0719	0.1075	0.1037	0.1898	0.1640	0.1338	0.1338	0.1630	0.1115	0.1731	0.1544	0.1544	0.2180	0.2199	0.2199	0.1716
124°	0.0694	0.1066	0.1159	0.1830	0.1597	0.1282	0.1282	0.1667	0.1168	0.1792	0.1474	0.1474	0.2099	0.2389	0.2389	0.1910
113°	0.0714	0.1064	0.1265	0.1737	0.1583	0.1229	0.1229	0.1717	0.1243	0.1823	0.1471	0.1471	0.1990	0.2554	0.2554	0.2098
102°	0.0782	0.1082	0.1349	0.1624	0.1590	0.1189	0.1189	0.1777	0.1329	0.1839	0.1542	0.1542	0.1889	0.2685	0.2685	0.2264
91°	0.0887	0.1132	0.1409	0.1500	0.1603	0.1170	0.1170	0.1842	0.1417	0.1828	0.1677	0.1677	0.1848	0.2776	0.2776	0.2396
80°	0.1016	0.1215	0.1441	0.1371	0.1609	0.1179	0.1179	0.1910	0.1498	0.1799	0.1858	0.1858	0.1913	0.2816	0.2816	0.2483
60°	0.1268	0.1420	0.1427	0.1158	0.1580	0.1267	0.1267	0.1988	0.1611	0.1717	0.2192	0.2192	0.2286	0.2708	0.2708	0.2495
45°	0.1450	0.1578	0.1357	0.1054	0.1512	0.1391	0.1391	0.2013	0.1657	0.1660	0.2525	0.2525	0.2633	0.2564	0.2564	0.2388
30°	0.1601	0.1698	0.1266	0.1020	0.1411	0.1535	0.1535	0.1990	0.1670	0.1623	0.2773	0.2773	0.2903	0.2303	0.2303	0.2191
15°	0.1710	0.1764	0.1185	0.1063	0.1288	0.1683	0.1683	0.1923	0.1657	0.1615	0.2960	0.2960	0.3046	0.2042	0.2042	0.1989
<i>cis</i>	0.1768	0.1768	0.1151	0.1163	0.1163	0.1817	0.1817	0.1817	0.1632	0.1632	0.3059	0.3059	0.3059	0.1913	0.1913	0.1913

Table 2. Bicyclopentyl. Results obtained by least squares refinements of the molecular intensities when one parameter (here the conformation composition) is different for each run. The numbers in brackets are $100 \times$ standard deviation values.

Parameter	Starting value	40 % A ^a	45 % A	47.5 % A	50 % A	55 % A
C-H	1.1030 Å	1.1035(.1968)	1.1034(.1960)	1.1034(.1960)	1.1033(.1961)	1.1032(.1971)
C ₂ -C ₃	1.5080 Å	1.5089(.0482)	1.5088(.0480)	1.5088(.0480)	1.5088(.0480)	1.5088(.0482)
$\angle C_1C_2C_3$	121.50°	121.59(20.83)	121.58(20.82)	121.58(20.86)	121.58(20.94)	121.58(21.17)
$\angle \sigma^b$	40.00°	46.25(614.8)	41.89(843.4)	40.20(906.4)	39.33(942.5)	38.67(1027.3)
$\angle HCH$	115.90°	115.96(94.82)	115.92(94.42)	115.90(94.37)	115.87(94.42)	115.82(95.00)
$w(C-H)$	0.0765 Å	0.0766(.1677)	0.0766(.1671)	0.0766(.1670)	0.0766(.1671)	0.0766(.1679)
$w(C_2-C_3)$	0.0470 Å	0.0471(.0603)	0.0471(.0601)	0.0471(0.0600)	0.0471(.0601)	0.0470(.0604)
$w(C_1C_3)$	0.0710 Å	0.0710(.1861)	0.0710(.1854)	0.0710(.1853)	0.0710(.1854)	0.0709(.1863)
$\sum_1 W_i 4I_i^2 \times 10^{-3}$		3.59	3.57	3.56	3.57	3.60
C ₁ -C ₂ : 1.4787 Å	$\angle \delta^b$ 15.0°	$\angle \beta^b \pm 100.0^\circ$	$\angle H_1C_1C_2$: 111.0°			

^a A denotes *trans* conformation.

^b The angles are defined in Table 3.

Table 3. Bicyclopropyl. Experimentally determined molecular parameters and standard deviation values, as resulting from least squares refinements of the molecular intensities.

Distance	Mult.	$r_g(1)$, Å	$\sigma(r_g(1))$, Å	u , Å	$\sigma(u)$, Å
C-H	10	1.1034	0.0020	0.0766	0.0017
C ₁ -C ₂	1	1.4993	0.0156	0.0485	
C ₂ -C ₃	6	1.5069	0.0026	0.0476	0.0007

Angles	Degrees	σ
$\angle C_1C_2C_3$	129.89°	1.0°
$\angle H_1C_1C_2$	110.5°	^a
$\angle \alpha^b$	48.74°	7.3°
$\angle H_3C_3H_3'$	116.14°	0.9°
$\angle \beta^c$	$\pm 100.0^\circ$	^a
$\angle \delta^d$	15.0°	^a

47.5 % A (*trans* conformation).
 52.5 % B (*gauche* conformation).

^a No standard deviation values can be given for these angles (see text). ^b $\angle \alpha$ represents the angle corresponding to the *gauche* potential minimum. ^c $\angle \beta$ gives the extension of the torsional well around *trans* conformation. ^d $\angle \delta$ represents the root-mean-square amplitude for Gaussian distribution in *gauche* conformation.

DISCUSSION

From Fig. 6 it will be seen that there are still small discrepancies between theoretical and experimental radial distribution functions for large r values. One possible reason is the assumption that the C₁C₂C₃ bond angle is independent of the C₁-C₂ dihedral angle. This assumption is probably not valid. It is also possible that the assumption about a Gaussian potential around an equilibrium *gauche* conformation is not quite valid and that another potential function in this case would give better agreement. These uncertainties will, however, not affect the general conclusions drawn about the bicyclopropyl molecular structure.

The molecular parameters from three different studies are compared in Table 4 which also lists the relevant parameters from the study of *cis* and *trans* isomers of tricyclo[5.1.0.0^{2,4}]-octane. The X-ray study of bicyclopropyl gave a central carbon carbon bond length (1.478 Å) that was significantly smaller than those within the cyclopropyl groups (1.501 Å and 1.510 Å). Similar results were also obtained for the tricyclo[5.1.0.0^{2,4}]octane isomers (*cis*: 1.454 Å vs. 1.513 Å, *trans*: 1.440 Å vs. 1.509 Å). The central CC bond in bicyclopropyl is found to be smaller than those in the cyclopropyl groups also in the present study. When the error limits are considered they can, however, not be claimed to be significantly different.

The determination of the conformation composition is in good agreement with what could be expected from calculations of van der Waals conforma-

Table 4. Comparison of the structural parameters for bicyclopropyl obtained in the present study (A) with those from Bastiansen and de Meijere's electron diffraction study (B) and from Eraker and Rømming's X-ray investigation (C). Molecular parameters for *trans*- (D) and *cis*-tricyclo[5.1.0.0^{2,4}]octane (E) are also listed.

Parameter	A ^a	B ^b	C ^c	D ^d	E ^d
C ₁ -C ₂	1.499 Å	1.517 Å	1.487 Å	1.440 Å	1.454 Å
C ₂ -C ₃	1.507 Å	1.517 Å	1.501 Å	1.509 Å	1.513 Å
C ₃ -C ₄	1.507 Å	1.517 Å	1.510 Å	1.509 Å	1.513 Å
C-H	1.103 Å	1.094 Å	1.010 Å	1.111 Å	1.108 Å
∠C ₁ C ₂ C ₃	120.9°	120.5°	120.0°	120.0°	120.9°
∠HCH	116.1°	117.3°	113.0°	117.7°	(117.2°)
∠C ₂ C ₁ H ₁	110.5°	115.2°	113.0°	115.5°	(115.5°)
∠δ ^e	15°				
∠β ^e	± 100°	± 80°			
∠α ^e	48.7°	38°			

^a This work. ^b Ref. 1. ^c Ref. 2. ^d Ref. 3. ^e For definition of the angles, see Table 3.

tional energies according to formulae given by Hendrickson¹¹ and by Jacob *et al.*¹²

The results for the conformation composition are also in accordance with results obtained for vinylcyclopropane,⁷ where a conformation composition at 75 ± 6 % *trans* and 25 ± 6 % *gauche* was determined. The electron diffraction investigation of cyclopropyl carboxaldehyde gave, however, as results that the gas was a mixture of about equal amounts of *cis* and *trans* conformers.

Even with an estimated uncertainty in the conformation composition of about 5 % it is obvious that the *trans* conformation has somewhat lower energy than the *gauche* conformation. The difference is small though (probably less than 0.5 kcal/mol).

Acknowledgement. The authors are grateful to Professor W. Lüttke, Göttingen, Germany, for donation of the bicyclopropyl sample that was used in the present investigation. They are also greatly indebted to Mr. Kristen Brendhaugen who made all the electron diffraction diagrams. Sincere thanks are due to Professor S. J. Cyvin for making his programs for calculations of vibrational amplitudes from spectroscopic data available to the authors. Financial support from *Norges almenvitenskapelige forskningsråd* is gratefully acknowledged.

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Received April 20, 1972.