

The Molecular Structure of Bicyclo[4.1.0]-2-heptene, as Studied by the Gas Electron Diffraction Method

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The molecular structure of bicyclo[4.1.0]-2-heptene was studied by the gas electron diffraction method. Both possible conformers (see Fig. 1) were found to be present in a 70–30 % relationship, corresponding to an energy difference between the conformers of less than 1 kcal/mol. The conformation of the six-membered carbon ring was found to be approximately the same as in 1,3-cyclohexadiene.

A cyclopropylene group behaves in several ways like a carbon carbon double bond, for example with respect to ultraviolet absorption.¹ It is of interest to see how bond lengths and bond angles are affected when a cyclopropylene group is substituted for a CC double bond. The present investigation is part of our endeavour to study conjugated systems with cyclopropylene groups and/or CC double bonds.

EXPERIMENTAL PROCEDURE

The sample of bicyclo[4.1.0]-2-heptene used in the present investigation was synthesized from 1,3-cyclohexadiene and diazomethane² and was kindly provided by Professor W. Lüttke, Göttingen, Germany. The bicyclo[4.1.0]-2-heptene (in the following abbreviated to bicycloheptene or BCH) molecule was studied by the sector electron diffraction method, using a modified s^2 sector. The diffraction patterns were recorded in the usual way with the Oslo apparatus³ and yielded an experimental molecular intensity function from $s = 1.25 \text{ \AA}^{-1}$ to $s = 46.00 \text{ \AA}^{-1}$.

STRUCTURE ANALYSIS

Bicycloheptene can exist in two different conformations, which in the following are referred to as conformers A and B. They are presented in Fig. 1, which also shows the numbering of the atoms in the molecule. The corresponding bond lengths and bond angles were assumed to be the same in the two conformers.

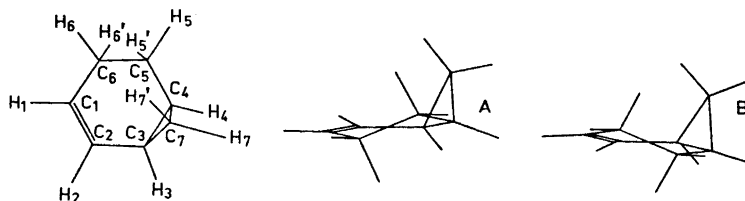


Fig. 1. Bicyclo[4.1.0]-2-heptene. Molecular models of the two possible conformers A and B.

Even with the assumption of equal CC bond lengths within the cyclopropylene group there are six different carbon carbon bond lengths in the molecule. It is not possible to refine all these independently in a least squares refinement of the molecular intensities. It was therefore assumed that there was a constant difference between $r(C_4-C_5)$ and $r(C_6-C_1)$. When this difference was systematically varied and other parameters were refined in a least squares adjustment process, the squared error sum had its minimum value when the difference between $r(C_4-C_5)$ and $r(C_6-C_1)$ was equal to zero. In the following refinements it was therefore assumed that $r(C_4-C_5) = r(C_6-C_1)$. It was also assumed that all carbon hydrogen distances were the same, that all CCH angles at C_5 and C_6 were equal to 109.5° , that the angles $\angle C_6C_1C_2$ and $\angle C_1C_2C_3$ were equal and also that $\angle C_2C_3C_4 = \angle C_3C_4C_5$.

When the assumptions mentioned above are applied, 15 parameters are necessary in order to describe a molecular model of bicycloheptene.

These are:

five bond distances: C-H, $C_1=C_2$, C_2-C_3 , C_3-C_4 , and C_6-C_1 ;

four bond angles: $\angle C_6C_1C_2$, $\angle C_2C_3C_4$, $\angle H_1C_1C_2$, and $\angle C_2C_3H_3$;

$\angle \alpha$: the angle between the $C_6C_1C_2$ and $C_2C_3C_4$ planes;

$\angle \gamma$: the angle between the $C_2C_3C_4C_5$ and $C_3C_4C_7$ planes;

$\angle \beta_5$: the $C_3C_4C_5H_5$ dihedral angle;

$\angle \beta_6$: the $C_2C_1C_6H_6$ dihedral angle; and

$\angle \rho$: the angle between the $C_2C_3C_4C_5$ and $H_3C_3C_4H_4$ planes.

The fifteenth parameter determines the conformation composition.

It was not possible to vary all fifteen parameters simultaneously in the least squares refinements. The following procedure was therefore adopted. The parameters that did refine well (the bond distances, $\angle C_6C_1C_2$, $\angle C_2C_3C_4$, $\angle \alpha$, and $\angle \gamma$) were varied in a series of least squares refinements. The other parameters were kept constant throughout the procedure, but one of them was changed slightly in each run. In this way all the parameters that did not refine well in the least squares adjustments were studied systematically in the expected range for the parameter in question. Table 1 shows the results when the conformation composition was varied in the region 60–80 % of conformer A. The parameters that gave the smallest squared error sum and smallest standard deviation values were of course chosen as the experimental values.

The root-mean-square amplitudes of vibrations (u -values) could not be determined by the least squares method. The procedure described above was also applied for these cases, but did not give unambiguous results. The u -

Table 1. Bicyclo[4.1.0]-2-heptene. Results from least squares refinements of the molecular intensities when one parameter (here the conformation composition) is different in each run. The numbers in brackets are 100 × standard deviation values.

Parameter	Starting values	60 % A (see Fig. 1)	65 % A	70 % A	75 % A	80 % A
C ₁ —C ₂	1.3432 Å	1.3436 (.2122)	1.3437 (.2112)	1.3438 (.2116)	1.3439 (.2135)	1.3441 (.2167)
C ₂ —C ₃	1.4721 Å	1.4722 (.3238)	1.4725 (.3211)	1.4728 (.3205)	1.4730 (.3221)	1.4734 (.3257)
C ₃ —C ₄	1.5057 Å	1.5061 (.1655)	1.5062 (.1669)	1.5062 (.1696)	1.5063 (.1734)	1.5065 (.1778)
C ₅ —C ₆	1.5471 Å	1.5477 (.4685)	1.5472 (.4751)	1.5465 (.4848)	1.5457 (.4971)	1.5448 (.5105)
$\sum_1 W_1 d_i^2 \times 10^{-4}$		1.77	1.73	1.72	1.74	1.77
C—H:	1.1017		$\angle \beta_5^a$: 33.0°			
$\angle C_6C_1C_2$:	120.7°		$\angle \beta_6^a$: 29.0°			
$\angle C_5C_3C_4$:	120.2°		$\angle \rho^a$: 38.0°			
$\angle \alpha^a$:	15.4°		$\angle H_1C_1C_2$: 125.0°			
$\angle \gamma^a$:	77.0°		$\angle C_2C_3H_3$: 112.0°			

^a These angles are defined in Table 2.

values were therefore assigned by comparing experimental and theoretical radial distribution functions (RD-functions) and autocorrelation power spectra (APS-functions)⁴ and by comparing with experimentally obtained results for other, similar molecules.⁵⁻⁹

It turned out to be very difficult to arrive at an unambiguous conclusion concerning the molecular structure of bicyclo[4.1.0]-2-heptene. There appeared, not surprisingly, to be a high degree of coupling between the various CC bond lengths and accompanying amplitudes of vibrations. In the present case, with so many closely spaced bond distances, the correlation function and power spectra⁴ were not of much help either. The problem was particularly concerned with the C₂—C₃ and C₃—C₄ bond lengths and C₄—C₅ and C₅—C₆ bond lengths. The average value for each of these pairs was almost constant throughout the refinements but the magnitude of the individual bond lengths varied a good deal. The results obtained by the various least squares procedures were all through the investigation closely followed by studying radial distribution functions.

FINAL RESULTS

Bicyclo[4.1.0]-2-heptene may exist in two different conformations (see Fig. 1). Both conformers are found to be present in gas phase at room temperature.

The experimentally determined structural parameters are listed in Table 2. When the following assumptions are made: the corresponding bond lengths and bond angles are the same in the two conformers, $r(C_4-C_5) = r(C_6-C_1)$, $\angle C_6C_1C_2 = \angle C_1C_2C_3$, $\angle C_2C_3C_4 = \angle C_3C_4C_5$, all C—H bond lengths are the same and all CCH angles over an angle at C₅ and C₆ are equal to 109.5°, the molecular

Table 2. Bicyclo[4.1.0]-2-heptene. Experimentally determined molecular parameters and standard deviations values as resulting from least squares refinements of the molecular intensities.

Distance	Mult.	$r_g(1)$, Å	$\delta(r_g(1))$, Å	u , Å
C-H	10	1.1017	0.0020	0.0805
C ₁ =C ₂	1	1.3438	0.0024	0.0440
C ₂ -C ₃	1	1.4728	0.0045	0.0520
C ₃ -C ₄	3	1.5062	0.0019	0.0480
C ₆ -C ₁	2	1.5465	0.0075	0.0520
C ₅ -C ₆ ^a	1	1.5542		0.0520
Angles	Degrees	δ		
$\angle C_6C_1C_2$	120.7°	0.2°		
$\angle C_1C_2C_3$				
$\angle C_2C_3C_4$	120.2°	0.2°		
$\angle C_3C_4C_5$				
$\angle \alpha^b$	15.4°	0.5°		
$\angle \gamma^c$	77.0°	0.9°		
$\angle \beta_5^d$	33.0°	ϵ		
$\angle \beta_6^d$	29.0°	ϵ		
$\angle \rho^f$	38.0°	ϵ		
$\angle H_1C_1C_2$	125.0°	ϵ		
$\angle C_2C_3H_3$	112.0°	ϵ		
$\angle C_4C_5C_6^h$	109.4°			
$\angle C_5C_6C_1^h$	117.0°			

Conformation composition: 70 % A, 30 % B (see Fig. 1).

^a C₅-C₆ is a dependent parameter. ^b $\angle \alpha$ is the angle between the C₆C₁C₂ and C₂C₃C₄ planes. ^c $\angle \gamma$ is the angle between the C₂C₃C₄C₅ and C₃C₄C₅C₆ planes. ^d $\angle \beta_5$ is the C₃C₄C₅H₅ dihedral angle. ^e $\angle \beta_6$ is the C₂C₃C₄H₆ dihedral angle. ^f $\angle \rho$ is the angle between the C₂C₃C₄C₅ and H₂C₃C₄H₄ planes. ^g It is not possible to give standard deviation values for these angles (see text). ^h These angles are calculated from independently determined molecular parameters.

geometry is described by 15 parameters, including one that governs the conformation composition. It was not possible to vary all parameters simultaneously in least squares refinements of the molecular intensity data. The parameters that are listed with standard deviation values in Table 2 were refined by a normal least squares procedure, while the other were determined by a combined trial and error/least squares method (see Structure Analysis).

The experimental molecular intensity function is shown in Fig. 2 together with the theoretical $sM(s)$ -function calculated from the parameters presented in Table 2. The corresponding experimental and theoretical radial distribution curves with artificial damping constant, $k=0.0015$, are presented in Fig. 3.

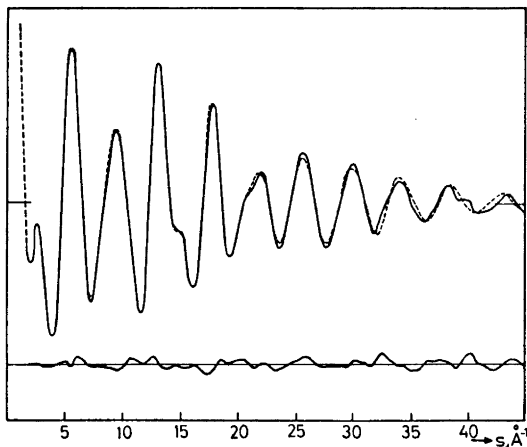


Fig. 2. Bicyclo[4.1.0]-2-heptene. Experimental (—) and theoretical (---) molecular intensity functions and the difference between the two.

DISCUSSION

From Fig. 3 is seen that there are fairly large discrepancies between experimental and theoretical RD-functions in the region around $r = 3.1 \text{ \AA}$. These discrepancies were present in all the various models that were tested during the investigation. These difficulties might be caused by invalidity of some of the assumptions made about the structure of the molecule, but they might also be due to uncertainties in the experimental material.

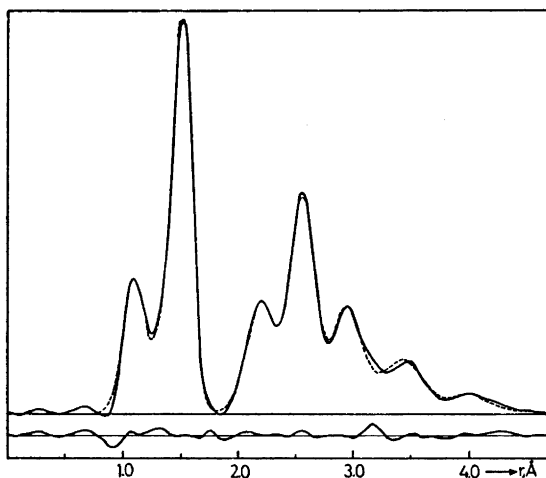


Fig. 3. Bicyclo[4.1.0]-2-heptene. Experimental (—) and theoretical (---) radial distribution functions. Artificial damping constant $k = 0.0015 \text{ \AA}^2$.

The structural parameters for 1,3-cyclohexadiene, bicycloheptene and *cis*- and *trans*-tricyclo[5.1.0.0^{2,4}]-octane are compared in Table 3. These molecules are six-membered alicyclic compounds with two conjugated double bonds, one double bond and one cyclopropylene group in conjugation and two conjugated cyclopropylene groups, respectively. The angles $\angle C_1C_2C_3$ and $\angle C_3C_4C_5$ are found to be nearly the same in the three compounds. This is also approximately true for $\angle \alpha$. The conformation of the six-membered ring in 1,3-cyclohexadiene is therefore approximately unchanged when one or both of the carbon carbon double bonds are substituted by cyclopropylene groups.





Table 3. Bicyclo[4.1.0]-2-heptene. Comparison of structural parameters with results obtained for 1,3-cyclohexadiene^a (C₆H₈) and *cis* and *trans* isomers of tricyclo[5.1.0.0^{2,4}]-octane^b (C₈H₁₂).

Parameter	C ₆ H ₈ ^a	C ₇ H ₁₀ ^b	C ₈ H ₁₂ ^c (<i>trans</i>)	C ₈ H ₁₂ ^c (<i>cis</i>)
C ₁ =C ₂	1.348 Å	1.344 Å		
C ₂ -C ₃	1.465 Å	1.473 Å	1.440 Å	1.454 Å
C ₃ -C ₄		1.506 Å	1.509 Å	1.513 Å
C ₄ -C ₅ ^f		1.547 Å	1.561 Å	1.559 Å
C ₅ -C ₁ ^f	1.519 Å	1.547 Å		
C ₅ -C ₆	1.538 Å	1.554 Å	1.561 Å	1.559 Å
$\angle C_1C_2C_3$	120.26°	120.7°	122.4°	122.0°
$\angle C_3C_4C_5$	120.25°	120.2°	122.4°	122.0°
$\angle \alpha$ ^d	17.96°	15.4°	16.2°	18.3°
$\angle \gamma$ ^e		77.0°	71.5°	70.0°

^a Ref. 5. ^b This work. ^c Ref. 7. ^d $\angle \alpha$ is the angle between the C₆C₁C₂ and C₂C₃C₄ planes. ^e $\angle \gamma$ is the angle between the C₂C₃C₄C₅ and C₃C₄C₅C₆ planes. ^f $r(C_4-C_5)$ and $r(C_5-C_1)$ assumed equal in C₇H₁₀.

Even though the uncertainties in the obtained values for $r(C_2-C_3)$ and $r(C_5-C_1)$ in bicycloheptene are relatively large, it will be seen from Table 2 that $r(C_2-C_3)$ is significantly smaller than $r(C_5-C_1)$. The observed decrease

Table 4. Comparison of carbon carbon bond lengths in vinylcyclopropane (A), cyclopropylcarboxaldehyde (B), bullvalene (C), and bicyclo[4.1.0]-2-heptene (D).

				
	A ^a	B ^b	C ^c	D ^d
C ₁ =C ₂	1.334 Å		1.347 Å	1.344 Å
C ₂ -C ₃	1.475 Å	1.507 Å ^e	1.466 Å	1.473 Å
C ₃ -C ₄	1.522 Å	1.507 Å ^e	1.544 Å	1.506 Å

^a Ref. 7. ^b Ref. 8. ^c Ref. 9. ^d This work. ^e Average value.

in the C₂–C₃ single bond length may be explained by the state of hybridization of the carbon atoms involved.

The present results are in accordance with observed UV-spectra for compounds with cyclopropylene groups and carbon carbon double bonds in conjugation.¹

From Table 2 it will be seen that the bicycloheptene molecule exists in two conformations with about 70 % of conformer A (see Fig. 1) and about 30 % of conformer B. The uncertainty in the percentage is estimated to 5–10 %, and the obtained results are in accordance with an energy difference of less than 1 kcal/mol between the two conformers.

Acknowledgement. The authors are greatly indebted to Professor W. Lüttke who provided the sample of bicyclo[4.1.0]-2-heptene and who also originally suggested the present research study. They also express their sincere gratitude to Mr. Kristen Brendhaugen who skilfully made all the electron diffraction diagrams. Professor Otto Bastiansen and the electron diffraction group in Oslo are thanked for many services. Financial support from *Norges almenvitenskapelige forskningsråd* is gratefully acknowledged.

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Received April 20, 1972.