An Electron Diffraction Investigation of the Molecular Structure of Bicyclo[2.2.0]hexane in the Vapour Phase

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The molecular structure of gaseous bicyclo[2.2.0]hexane has been determined from electron diffraction studies. The parameter values were obtained by least-square refinement applied on the molecular intensity curve assuming C_2-symmetry. The interatomic distances were found to be: $C_1 - C_4$ 1.577 (0.017) Å, $C_1 - C_2$ 1.557 (0.011) Å, $C_2 - C_3$ 1.542 (0.020) Å, and $(C - H)_{av}$ 1.113 (0.004) Å. The bond angle $\angle C_2 C_1 C_6$ is 113.5 (1.1)° and the puckering of each four-membered ring, defined as in cyclobutane, is 11.5 (1.8)°. The correspondence between experimental and theoretical autocorrelation power spectra computed for the bond distance region is shown to be satisfactory.

The carbon skeleton of cyclobutane is puckered. The angle β, defined as the angle between the two planes having the transannular distance in common, is reported to be 35°.[1] About the same value is found in dicyclobutyl where a carbon atom in one ring is bonded to a carbon atom in the other ring.[2]

Lately, the structures of two hydrocarbons with adjoined four-membered rings, *anti*-, and *syn*-tricyclo[4.2.0.0²,⁵]octane, have been investigated by electron diffraction.[3] In these molecules, where a central ring shares opposite carbon-carbon bonds with two other rings, the deviation from planarity of the carbon skeleton of each four-membered ring was determined to be considerably smaller than in cyclobutane itself. The puckering parameter, defined as in cyclobutane, was determined to be 8.0 (2.5)° for each ring in *anti*-tricyclo[4.2.0.0²,⁵]octane and 9.0 (2.6)° for each ring in *syn*-tricyclo[4.2.0.0²,⁵]-octane.

The carbon-carbon bond lengths determined in these compounds vary. In cyclobutane several $C - C$ bond lengths are reported, 1.568 ± 0.020 Å and 1.548 ± 0.003 Å, from electron-diffraction investigations [4,1] and 1.558 Å from a Raman spectroscopic investigation.[5] The newest electron-diffraction value, 1.548 Å, is reproduced in bicyclobutyl.[2] In *anti*- and *syn*-tricyclo(4.2.0.0²,⁵)-octane, however, the average $C - C$ bonds seem to be longer, 1.557 (0.002) Å and 1.566 (0.003) Å, respectively.[3]
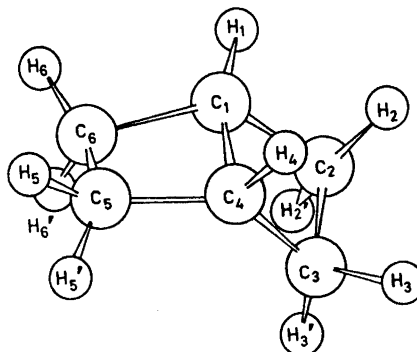
Fig. 1. Bicyclo[2.2.0]hexane.

Bicyclo[2.2.0]hexane, Fig. 1, is a compound with only two adjoined four-membered rings. It was therefore of interest to study the structure of this compound for comparison with the molecules investigated previously.

EXPERIMENTAL

Bicyclo[2.2.0]hexane was prepared by the mercury ($^3P_1$) sensitized isomerization of 1,5-hexadiene.[20] The material was separated by fractional distillation (b.p. 80°) and purified by passing twice through a gas chromatograph. The pure sample was free from infrared absorptions due to cyclohexene. Its refractive index was 1.4398 (25.5°C; D line).

The electron-diffraction diagrams were taken at the Oslo-apparatus [6] at nozzle-to-plate distances of 478.89 and 198.89 mm. During the experiment the sample of bicyclo-[2.2.0]hexane was maintained at a temperature of −10°C and the temperature at the nozzle was about 15°C. The wavelength of the electron beam determined from gold foil diffraction pattern and corrected by an experiment with CO_2, was 0.06458 Å. At each distance four apparently faultless plates were selected and the photometer traces derived from these were treated in the usual way [7] to give one averaged modified molecular intensity curve at each s-range considered. The curves were combined to give a single intensity curve extending from $s = 1.25$ Å^{-1} to $s = 42.25$ Å^{-1}. The intensity values were given in intervals of 0.125 Å^{-1} and 0.25 Å^{-1} below and above $s = 8.00$ Å^{-1}, respectively.

Preliminary values for the structure parameters were obtained from the observed radial distribution (RD) curves.[8] The distances and angles were refined by a least-squares procedure applied to the observed molecular intensity curve, a diagonal weight matrix being used.[9−11] The scattering amplitudes and phases used in the theoretical equation
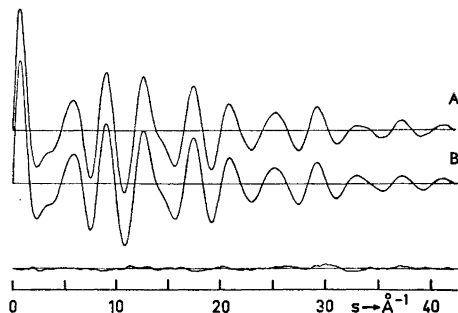

Fig. 2. Bicyclo[2.2.0]hexane. Experimental (A) and theoretical (B) intensity curves.
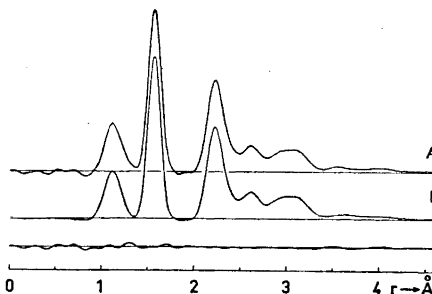

Fig. 3. Bicyclo[2.2.0]hexane. Experimental (A) and theoretical (B) radial distribution, curves, $k = 0.0009$ Å.

Table 1. Structure parameters obtained by least-squares refinement on the intensity data. Distances (r_a[18]-values) and mean amplitudes of vibration (u) in Å, angles in degrees. The standard deviation given in parentheses have been corrected to take into account data correlation [19] and have also been increased to include the uncertainty arising from error in the electron wavelength.[8]

Distances		r		u	
C_1-C_2	1.557	(0.011)			
C_1-C_4	1.577	(0.017)	0.052	(0.002)	
C_2-C_3	1.542	(0.020)			
$C_1\cdots C_3$	2.198	(0.004)	0.061	(0.003)	
$C_2\cdots C_4$	2.604	(0.008)	0.069	(0.007)	
$C_2\cdots C_6$	2.910	(0.016)	0.087	(0.022)	
$C_3\cdots C_5$	3.117	(0.013)			
$(C-H)_{av}$	1.113	(0.004)	0.077	(0.004)	
$C_1\cdots H_2$	2.276	(0.012)	0.111		
$C_1\cdots H_4$	2.480	(0.047)	0.082		
$C_3\cdots H_4$	2.253	(0.023)			
$C_1\cdots H_3$	3.079	(0.015)			
$C_1\cdots H_3'$	2.950	(0.018)	0.141		
$C_2\cdots H_4$	3.087	(0.024)			
$C_6\cdots H_4$	3.180	(0.011)			
$C_2\cdots H_6$	3.529	(0.010)	0.150		
$C_3\cdots H_5$	3.582	(0.009)			
$C_2\cdots H_6'$	2.739	(0.027)	0.080		
$C_3\cdots H_5'$	2.813	(0.028)			
$C_2\cdots H_5$	3.152	(0.039)			
$C_2\cdots H_5'$	3.986	(0.012)	0.150		
$C_3\cdots H_6$	4.105	(0.011)			
$C_3\cdots H_6'$	3.610	(0.033)			

Angles		
$\angle C_2C_1C_6$	113.5	(1.1)
ϕ*	8.1	(1.3)
$\angle C_2C_1H_1$	114.0	(2.1)
$\angle C_4C_1H_1$	133.8	(5.3)
$\angle C_1C_2H_2$	115.9	(1.0)
$\angle HCH$	105.3	(3.6)

*ϕ is defined as the angle between the bonds C_1-C_4 and C_2-C_3 in the xz-plane.

were calculated by the method described by Peacher and Wills,[12] using HF atomic potentials.[13]

In Fig. 2 the theoretical molecular intensity curve based on the final parameters (listed in Table 1) is compared with the corresponding experimental curve.

STRUCTURE ANALYSIS

An experimental RD curve is shown in Fig. 3. The peaks at about 1.1 Å and 1.55 Å represent the $C-H$ and $C-C$ bond distances, respectively. The third peak contains contribution from the non-bonded diagonal distances in each four-membered ring, while the fourth peak mainly is caused by the $C_2\cdots C_6$ and $C_3\cdots C_5$ distances. The long carbon-carbon distances contribute to the next broad peak, the shape of the peak indicates that these distances are different, *i.e.* the carbon skeleton of the four-membered rings must be puckered.

Only the average bond distances could be obtained from the RD curves and no attempts were made to separate the carbon-carbon bond distances in the first cycles of the least-squares refinement. C_2-symmetry was assumed, it was also assumed that the CCC angle bisector bisects the plane HCH at carbon atoms C_2, C_3, C_5, and C_6. The six geometrical parameters, $(C-C)_{av}$, $(C-H)_{av}$, $\angle C_2 C_1 C_6$, the angle between the bonds $C_1 - C_4$ and $C_2 - C_3$ in the xz-plane * (ϕ), $\angle C_1 C_4 H_4$ and $\angle HCH$, and the two vibrational amplitudes for the bond distances, were simultaneously refined. The rest of the vibrational amplitudes were grouped according to distance type and length; the values for the non-bonded carbon-carbon distances were obtained in separate cycles of the refinements, while the amplitudes for the non-bonded carbon-hydrogen distances partly were obtained this way, partly were fixed at reasonable values.

Theoretical radial distribution functions and autocorrelation power spectra [3,14,15] computed using the parameters obtained in the refinements, were compared with the corresponding experimental curves. While good correspondence was found between theoretical and experimental RD curves, the correspondence between the APS functions calculated for the bond-distance region was not satisfactory (Fig. 4). On an RD curve the position of a peak with contributions from closely spaced distances will be the same as the position of the peak calculated for the average distance. In the power spectrum, however, correlation between contributions from closely spaced distances will cause a shift in the position of a peak calculated for individual distances compared to the position of the peak calculated for their average. The observed discrepancy between the APS functions is therefore to be expected if the

Fig. 4. Bicyclo[2.2.0]hexane. Experimental (dotted) APS curve compared to the theoretical curves calculated for different C − C bond distances (fully drawn) and for identical C − C bond distances (stippled), $\alpha = 0.03$, $\tau_{max} = 30.00$ Å.
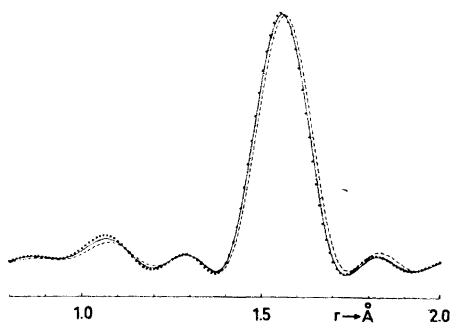
individual C − C bonds are not too close to the average distance. Furthermore it indicates that the data contain enough information to split the carbon-carbon bond distances.

Therefore the analysis was continued. The number of geometrical parameters was increased by introducing an eight parameter model with different carbon-carbon bonds. The refinements fail to converge if the C − C bonded amplitudes are treated independently. Therefore these amplitudes were assumed to be equal and composed one group of u-values. This group, the

* *i.e.* the plane through the bond $C_1 - C_4$ and the two-fold axis of symmetry.

eight geometric parameters, the u-value for the $(C-H)_{av}$ bond and the u-values for the non-bonded carbon-carbon distances were refined simultaneously. The least-squares refinement converges to the results listed in Table 1 independently of the choice of input values for the $C-C$ bond lengths. Now, a very satisfactory agreement between the experimental and theoretial APS curves was obtained, Fig. 4, confirming that the minimum obtained in the least-squares analysis is not a secondary minimum.

Finally the effect of the restrictions on the $C-C$ bonded amplitudes was investigated by introducing the following constraints: $u(C_1-C_4)=u(C_1-C_2)+\Delta$ and $u(C_2-C_3)=u(C_1-C_2)-\Delta$. While negative values for Δ lead to an increase in the error square sum, a slightly better agreement was obtained if Δ was chosen to be positive. For $\Delta=0.002$ Å, the error square sum was lowered by about 2 %, the bond distances were determined to be: C_1-C_2 1.560 Å, C_2-C_3 1.540 Å, and C_1-C_4 1.574 Å. The changes in the distances are small compared to their standard deviations. The same was observed if Δ was negative. Any assumption about differences in the $C-C$ bonded amplitudes is rather uncertain. Other combinations of the u-values were therefore not investigated since it could be concluded from the tests performed that the previous results were not significantly affected by reasonable assumptions concerning the u-values. No additional information could be obtained from the APS-functions as the fit was equally good for the latter calculations as for the former. For these kinds of compounds additional information about the vibrational amplitudes from spectroscopic investigations would be of great interest.

DISCUSSION

In the preliminary refinements the average $C-C$ bond distance was determined to be 1.556 (0.002) Å. It was also shown that the individual bond distances in bicyclo[2.2.0]hexane are not of the same length. However, it was not possible to make a precise determination of these bonds by means of electron diffraction. The correlation matrix, Table 2, shows a large correlation between the bond distances C_1-C_2 and C_2-C_3. This is reflected in their large standard deviations 0.011 Å and 0.020 Å, respectively. The C_1-C_4 bond is less correlated to other parameters. However, the standard deviation is large since the distance only appears once in the molecule. The least-squares refinement converges to the results listed in Table 1 even if the values for the C_1-C_4 and C_2-C_3 bond distances are exchanged in the input. The observations that the bond between the bridgehead atoms is elongated compared to the external bonds and that the shortest bonds are the ones opposite the elongated bond are therefore believed to be real, even though there is some uncertainty as to the precise lengths of the $C-C$ bonds.

A comparison of the puckering of the four-membered rings in the various bicyclic compounds studied confirms the view that the angle β decreases with the strain invoked by the fusing ring.[16] Bohn and Tai[17] have found that the four-membered ring in bicyclo[2.1.0]pentane is planar within experimental limits. In the present investigation of bicyclo[2.2.0]hexane β is determined to be 11.5°, while Barnett and Davis[16] have determined the crystal structure

Table 2. Correlation matrix. (The coefficients whose absolute values are less than .20 are not given).

Parameter	C_1-C_2	C_1-C_4	C_2-C_3	ϕ	$\angle CCC$	$(C-H)_{av}$	$\angle CCH$	$\angle HCH$	$u(C-C)$	$u(C-H)$	$u(C_1\cdots C_3)$	$u(C_2\cdots C_6)$	$u(C_2\cdots C_5)$	Scale
C_1-C_2	1.00													
C_1-C_4	-0.39	1.00												
C_2-C_3	-0.91		1.00											
ϕ	-0.48	0.36	0.37	1.00										
$\angle CCC$	-0.86	0.42	0.74	0.38	1.00									
$(C-H)_{av}$						1.00								
$\angle CCH$	0.58		-0.59	-0.51	-0.35		1.00							
$\angle HCH$	0.23					0.22	-0.36	1.00						
$u(C-C)$	-0.60	-0.42	0.80		-0.44		-0.43		1.00					
$u(C-H)$										1.00				
$u(C_1\cdots C_3)$	0.22		-0.28	-0.22			0.20				1.00			
$u(C_2\cdots C_6)$							-0.46		-0.24			1.00		
$u(C_2\cdots C_5)$	-0.31		0.28	0.20	0.33		-0.20						1.00	
Scale									0.24	0.21			0.31	1.00

of a derivative of *trans*-bicyclo[4.2.0]octane and report that the puckering of the four-membered ring is about the same as in cyclobutane itself.

In two fused ring compounds consisting of four-membered rings only, *anti*- and *syn*-tricyclo[4.2.0.0²,⁵]octane, the puckering (β) of the rings within each molecule was determined to be the same.[3] The β-angles [8.0 (2.5) Å and 9.0 (2.6) Å, respectively] are not significantly different from the corresponding angle in bicyclo[2.2.0]hexane. It is in fact interesting to note that the geometric parameters determining the carbon skeletons of bicyclo[2.2.0]hexane and of *anti*-tricyclo[4.2.0.0²,⁵]octane are about equal, in the latter compound the $(C-C)_{av}$ and the angle $C_1C_2C_3$ are reported to be 1.557 (0.002) Å and 111.9 (0.5)°, respectively. It is therefore reasonable to assume that the strain of each four-membered ring is the same in the two compounds. In *syn*-tricyclo[4.2.0.0²,⁵]-octane, however, the $(C-C)_{av}$ bond seems to be slightly longer, 1.566 (0.003) Å. The angle $C_1C_2C_3$ is definitely larger, 119.0 (0.3)° in this molecule. Compared to *anti*-tricyclo[4.2.0.0²,⁵]octane the larger angle was ascribed to the larger repulsion in the former compound where the shortest H···H distance is only about 2.13 Å. There was some doubt as to the significance of the discrepancy in the $(C-C)_{av}$ bond lengths in the tricyclooctanes. However, it is evident that in these fused cyclobutane rings the average $C-C$ bond lengths is longer than 1.548 Å, the value given for the parent compound.

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