On the Molecular Structure of Bicyclo(1.1.1)pentane in the Vapour Phase Determined by Electron Diffraction

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The molecular structure of gaseous bicyclo(1.1.1)pentane has been studied by electron diffraction. The parameter values were obtained by least-squares refinement on the intensity data for a molecular model with D_3 symmetry. The carbon-carbon bond distance is determined to be 1.557 (0.002) Å, and the angle $\angle$ CCC at the methylene carbons to be 74.2 (0.2)°. The results are compared to the results obtained in an independent structure investigation by Chiang and Bauer.[1]

The bicyclo(1.1.1)pentane molecule contains highly strained four-membered rings. Wilcox, as early as in 1960, calculated the bond angle strain in the, at that time hypothetical, bicyclo(1.1.1)pentane molecule, and estimated the angle at the methylenic carbons to be 75°.[2] The compound was first prepared by Wiberg and co-workers in 1966, and the authors report that the NMR data are consistent with a short distance between the bridgehead carbons.[3,4] In two derivatives, 2-hydroxy-2-phenylbicyclo(1.1.1)pentane [5] and 1-chlorobicyclo(1.1.1)pentane,[6] the angle at the methylene carbons is reported to be 75° and 73.5°, respectively.

The preliminary results of this investigation were published by Cyvin *et al.*[7] in 1968; recently Chiang and Bauer have reported the results of an independent investigation of the molecule also using electron diffraction.[1]

EXPERIMENTAL

The sample of bicyclo(1.1.1)pentane used in this investigation was kindly supplied by K. B. Wiberg and D. Connor. The electron-diffraction patterns were recorded with the Oslo apparatus at nozzle-to-plate distances of 480.59 mm and 193.59 mm. The wave length of the electron beam was 0.06452 Å, and the temperature at the nozzle about 15°. At each distance, four plates were selected for analysis and treated according to the procedure previously described.[8] The background was subtracted from the average molecular intensity curves derived at each distance, and the modified curves were combined to give a single intensity curve covering the s-range 1.50 Å^{-1} to 42.75 Å^{-1} in intervals of 0.25 Å^{-1}. As the structure determination proceeded, the background curves were reassessed and the composite molecular intensity curves re-calculated.

Preliminary structure parameters obtained from the experimental radial distribution (RD) curve [9] were refined by a least-squares procedure applied to the observed composite molecular intensity curve.[10],[11] In Fig. 1, the theoretical intensity curve, computed using the final parameters (listed in Table 1), is compared to the corresponding experimental curve.
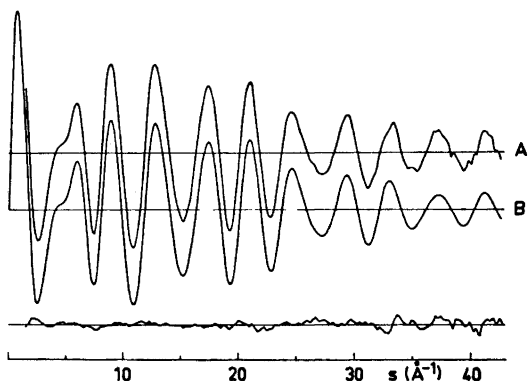

Fig. 1. Bicyclo(1.1.1)pentane. Experimental (A) and theoretical (B) molecular intensity functions.

Table 1. Structure parameters obtained by least-squares refinement on the intensity data. Distances (r_a^{13}-values) and mean amplitudes of vibration (u) in Å, angles in degrees. The standard deviations given in parentheses have been corrected to take into account data correlation [13] and have also been increased to include the uncertainty arising from error in the electron wavelength.[9]

|	r_a angles	u	
$C-C$	1.557 (0.002)	0.048	
$C_1 \cdots C_3$	1.874 (0.004)	0.050	(0.001)
$C_2 \cdots C_4$	2.151 (0.003)	0.051	(0.002)
$(C-H)_{av}$	1.109 (0.004)	0.081	
$C_1 \cdots H_2$	2.222 (0.008)	0.083	(0.003)
$C_1 \cdots H_2'$	2.338 (0.007)		
$C_1 \cdots H_3$	2.987 (0.005)	0.107	(0.022)
$C_2 \cdots H_1$	2.395 (0.004)		
$C_2 \cdots H_4$	3.182 (0.006)	0.108	(0.016)
$C_2 \cdots H_4'$	2.495 (0.012)		
$H_2 \cdots H_2'$	1.835 (0.020)	0.129	
$H_2 \cdots H_1$	2.817 (0.007)	0.144	
$H_2 \cdots H_3$	3.015 (0.006)		
$H_2 \cdots H_4$	3.591 (0.010)	0.132	
$H_2 \cdots H_4'$	2.340 (0.028)	0.170	
$H_2 \cdots H_5'$	4.146 (0.009)	0.132	
$H_1 \cdots H_3$	4.096 (0.007)	0.115	
$\angle C_1C_2C_3$	74.2 (0.2)		
$\angle HCH$	111.7 (1.8)		
δ	8.8 (0.3)		
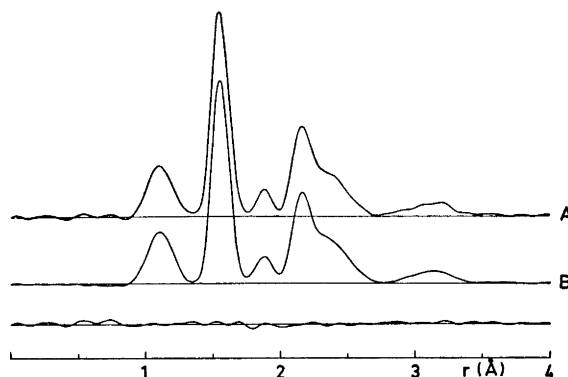
Fig. 2. Bicyclo(1.1.1)pentane. Experimental (A) and theoretical (B) radial distribution functions, $k = 0.0009$ Å².

STRUCTURE ANALYSIS AND RESULTS

The experimental radial distribution function is shown in Fig. 2. The peaks at about 1.1 Å and 1.55 Å represent the bond distances. The next well resolved peak just below 1.9 Å can only be caused by the distances between the bridge-head carbons. Distances between carbon atoms in the equatorial plane and also some non-bonded carbon-hydrogen distances contribute to the peak complex between 2.1 Å and 2.6 Å. A closer inspection of the shape of the curve at about 2.4 Å suggests that the distances from the bridgehead carbons to the hydrogens in the methylene groups are not identical. Therefore the least-squares refinements were performed for a model with D_3-symmetry only, characterized by the following independent parameters: $C-C$, $(C-H)_{av}$, $\angle C_1 C_2 C_3$, $\angle HCH$, and δ, where δ is the angle between the equatorial plane and the plane through the HCH atoms. The numbering of the atoms in the molecule is given in Fig. 3. A diagonal weight matrix was applied, and all the independent parameters were refined simultaneously. However, it was not possible to refine all the u-values for the non-bonded distances independently;
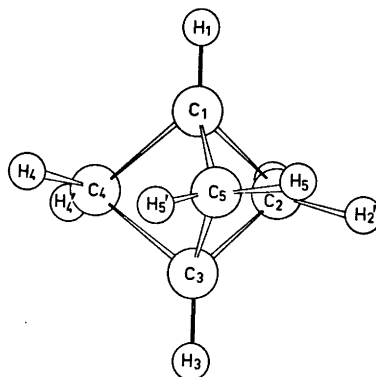

Fig. 3. Numbering of the atoms in bicyclo(1.1.1)pentane.

therefore, these were refined in blocks. Within each block, the u-values were assumed to be equal or to have a constant difference. The results obtained in the preliminary refinements were used by Cyvin and co-workers to estimate theoretical u-values.[7] In the last cycles of the least-squares refinements, the u-values were re-grouped according to the similarities suggested by these estimates. It was shown that changing the refinement scheme for the u-values lead to no significant changes in the other structure parameters. However, better agreement between experimental and corresponding theoretical intensities was obtained. Both curves are shown in Fig. 1; the fit is very satisfactory.

To test the significance of the value obtained for the parameter δ, the Hamilton test was applied. Including the u-value for the distances $C_1 \cdots H_2$ and $C_1 \cdots H_2'$ as an independent parameter, the refinements were repeated for fixed values of δ between $0°$ and $11°$. It was shown that the changes in the other geometric structure parameters were very small in this interval, while the above-mentioned u-value increased with a decrease in the angle. Fig. 4
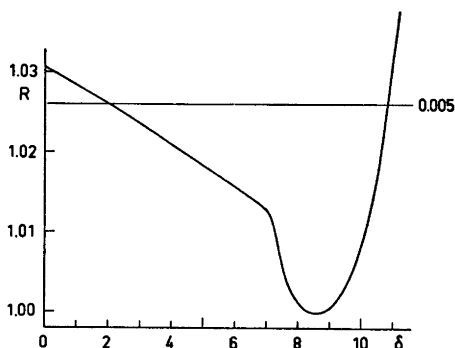

Fig. 4. The curve is the R-factor for bicyclo(1.1.1)pentane as a function of δ. The horizontal line is the R-factor at the 0.005 significance level.

shows Hamilton's R-factor [14] as a function of δ and the 0.005 significance level. According to the Hamilton test, the possibility that $\delta = 0°$ can be rejected at this level. However, the correct use of the Hamilton test presupposes that there are no systematic errors present in the data and the use of a proper weight matrix in the least-squares refinement. Our data may not fulfill these assumptions and our experience with the test applied on electron-diffraction data is limited. Therefore, the fact that the test strongly favours D_3 molecular symmetry may be misleading.

Two approaches were tried in order to extract information about the $C-H$ bonds. In the first, the u-values were kept at the values predicted by Cyvin et al.[7] and the two $C-H$ bond distances were refined separately. In the second, both the $C-H$ distances and their u-values were included in the refinements. The results for the $C-H$ distances are given in Table 2. The other independent structural parameters did not change significantly from the values already given in Table 1.

The agreement is slightly improved in the second refinement, but the u-value obtained for the C_1-H_1 distance is extremely small. If a larger, and

Table 2. C−H bond distances (r_a^{12}-values) determined by least-squares refinement on the intensity data: 1) the u-values were kept at values assigned by Cyvin *et al.*;[7] 2) the u-values were refined. The standard deviations given in parentheses have been corrected to take into account data correlation [13] and have also been increased to include the uncertainty arising from error in the electron wavelength.[9]

Distances	Refinement No. 1		Refinement No. 2	
	r_a (Å)	u (Å)	r_a (Å)	u (Å)
$C_1 - H_1$	1.108 (0.026)	0.076	1.097 (0.016)	0.056 (0.015)
$C_2 - H_2$	1.109 (0.010)	0.083	1.116 (0.009)	0.092 (0.010)

more reasonable u-value is adopted, both the bond length and the corresponding standard deviation increase. The result can therefore only give information about the lower limit of the $C_1 - H_1$ bond length which is seen to be nearly independent of the choice of refinement scheme due to the increase in the standard deviation with increase in the corresponding $C_1 - H_1$ distance.

DISCUSSION

The results obtained in this investigation are listed in Table 1. Chiang and Bauer [1] have reported the following parameters as the result of an independent investigation of the molecule: $C_1 - C_2$ 1.545 ± 0.006 Å, $C_1 \cdots C_3$ 1.845 Å, $C_2 \cdots C_4$ 2.147 Å and the angle $C_1C_2C_3$ 73.3 ± 1.0°, the angle being in agreement with the value found in the present investigation. By adopting a value larger than 73.3°, but within the given error limit, the discrepancies in the carbon skeleton may be explained by a scaling error in one of the investigations.

In 1-chlorobicyclo(1.1.1)pentane studied by Cox and Harmony,[6] using microwave spectroscopy, the determination of the carbon-carbon bond distances is based on an assumption concerning the shortening of the bond adjacent to the chlorine atom due to the effect of the electronegativity of this atom. The value reported for the $C_2 - C_3$ bond distance, 1.556 Å, is in very good agreement with the result obtained in the current investigation. However, the mean CC bond distance, 1.545 Å, is in better agreement with the results obtained by Chiang and Bauer.

In cyclobutane itself, different C−C bond lengths are reported, 1.568 Å and 1.548 Å from electron diffraction investigations,[15,16] and 1.558 Å from a Raman spectroscopic investigation.[17] The value of 1.548 Å, which is reproduced in dicyclobutyl,[18] is usually accepted as the correct value for cyclobutane. However, increased bond lengths have been found both in derivatives of cyclobutane [19,20] and in cyclobutane rings in fused systems.[21,22] A comparison with cyclobutane itself is therefore dubious.

However, a comparison of the results obtained in the present investigation with the results reported by Chiang and Bauer also shows that there are other

serious discrepancies in the experimental data. A study of the two experimental RD curves reveals that the distance between the bridgehead carbons is well resolved in the current investigation (Fig. 2), while the corresponding region on the RD curve, published by Chiang and Bauer, contains no peak. To obtain correspondence between the experimental and theoretical RD curve in this region, the latter authors have assigned a u-value of 0.16 Å to the $C_1 \cdots C_3$ distance, a value much higher than any of the u-values assigned to the non-bonded carbon-hydrogen distances. The u-value assigned to the distance between one bridgehead carbon and the hydrogen atom bonded to the other bridgehead carbon is 0.10 Å. It is therefore reasonable to expect a lower u-value for the $C_1 \cdots C_3$ distance, in agreement with the results of the present investigation. However, this will lead to larger discrepancies between experimental and theoretical data than shown by Chiang and Bauer. The latter authors have also found a higher u-value for the CC bond distance (0.060 ± 0.006 Å) than for the distance between the methylene carbons (0.053 ± 0.004 Å). The value determined for the CC bond distance in this investigation (0.048 Å) seems more reasonable.

The experimental RD curve shown in Fig. 2 has a distinct shoulder at about 2.4 Å, which is not reproduced in the curves published by Chiang and Bauer. The discrepancies between the experimental curves in this region are larger than the differences expected due to application of different artificial damping factors. The determination of the molecular symmetry is very dependent on this part of the curve, since the contribution to this region mainly is due to distances between the bridgehead carbons and hydrogens in the methylene groups. Chiang and Bauer conclude that the molecule has D_{3h} symmetry and that the possibility of D_3 symmetry can be excluded. In the present investigation it has been shown that the experimental evidence favours a twisting of the CH_2-groups from the equatorial plane. In the undistorted model, the distance $H_2 \cdots H_4'$ was found to be about 2.32 Å, and the angle HCH was determined to be 111.2°. Distorting the CH_2-groups allows an opening of the angle to 111.7°. Chiang and Bauer determined the shortest $H \cdots H$ distance to be 2.45 Å, approximately twice the van der Waals radius of hydrogen, and conclude that no significant stabilization would be achieved by an out-of-plane distortion. However, their calculation of the distance is based on a very low value determined for the angle HCH, namely 104°. Randic et al.[23] have found that the exocyclic orbitals at the methylene carbons are $sp^{2.46}$ hybridized, and that the angle between the orbitals is 114°. Therefore, even the value of 111.7° seems too small compared to the expected, but it may plausibly be explained by the repulsion between the methylene groups. A distortion of the CH_2-groups in agreement with the experimental evidence is therefore reasonable.

Both D_{3h} and D_3 symmetry are equally consistent with the indication given by the IR spectrum, that the molecule is a symmetrical top.[4] The differences are very small in the moments of inertia for the two symmetry species.

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