ACTA CHEMICA SCANDINAVICA 25 (1971) 1271–1276

The Molecular Structure of Tricyclo(3.3.2.0^{4,6})deca-2,7,9-triene (Bullvalene) in the Vapour Phase

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The structure of bullvalene is determined by electron diffraction in the vapour phase. The parameters refined by the least-squares method under the assumption of C_{3v} symmetry are as follows: C_1-C_2 1.523 (0.005) Å, C_2-C_3 1.346 (0.003) Å, C_3-C_4 1.465 (0.004) Å, C_4-C_5 1.542 (0.006) Å, $(C-H)_{av}$ 1.111 (0.007) Å. The angle $C_1C_2C_3$ is 122.6 (0.8)°, and the angle between the threefold axis and the bond C_1-C_2 is 72.5 (0.7)°.

In 1963, Doering and Roth [1,2] predicted that the hypothetical tricyclo(3.3.2.0^{4,6})deca-2,7,9-triene (bullvalene) molecule (Fig. 1) could be expected to undergo rapid Cope-rearrangements. One rearrangement can transform a

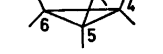

Fig. 1. Tricyclo(3.3.2.0^{4,6})deca-2,7,9-triene (bullvalene).

cyclopropyl carbon atom into a bridgehead atom, and the bridgehead atom and two adjacent atoms into cyclopropyl atoms. Several rapid Cope-rearrangements would make the carbon atoms change positions constantly, thus making these atoms equivalent. Doering and Roth therefore predicted that the NMR spectra of bullvalene would contain only one single sharp band.

The molecule was prepared by Schröder [3,4] in 1963. As predicted, the NMR spectra showed only one sharp peak at high temperature (100°C). At lower temperatures the band broadens, and at about −25°C two separate bands can be observed. No further change occurs in the temperature range to −85°C.[5,6]

The present study was started in order to determine whether the rapid Cope-rearrangements would influence the structure of the molecule in the vapour phase as measured by electron diffraction.

A preliminary note on this work was published in 1967.[7] X-Ray investigations of the structure of bullvalene in the crystal have been published by Johnson *et al.*[8] and Amit *et al.*[9]

EXPERIMENTAL

The sample used in the investigation was obtained from Dr. G. Schröder, Karlsruhe. The diffraction diagrams were recorded at the Oslo apparatus [10] by cand. real. A. Almenningen. The nozzle temperature was 100 ± 6°C. A rotating sector with an angular opening approximately proportional to s^3 was used. The nozzle-to-plate distances were 480.8 and 193.7 mm. The electron wavelength was determined to be 0.06475 Å from gold foil diffraction patterns. As there were some uncertainties as to the purity of the gold at the time the pictures were taken, the wavelength was later corrected by -0.25 %, as found from experiments with CO_2.

Four plates from each distance were selected. The photometer traces of each plate were recorded at intervals $\Delta s = 0.25$ Å^{-1}, and the data were treated according to the procedure described previously.[11] Experimental backgrounds were subtracted from the total scattered intensities, and the overlap regions of the resulting molecular intensity functions for the two nozzle-to-plate distances were averaged. The experimental backgrounds were later adjusted by comparing experimental and theoretical intensity curves. The scattering amplitudes and phases were computed by the partial-wave method described by Peacher and Wills,[12] using Hartree-Fock atomic potentials.[13] The final experimental molecular intensity function covered the range $s = 1.50$ Å^{-1} to 41.75 Å^{-1}.

The numerical parameters were refined on the intensity curve by the least-squares method.[14–17] A diagonal weight matrix was applied.

STRUCTURE ANALYSIS

The experimental molecular intensity curve is shown in Fig. 2. The theoretical curve also shown is calculated, using the final parameters listed in Table 1.

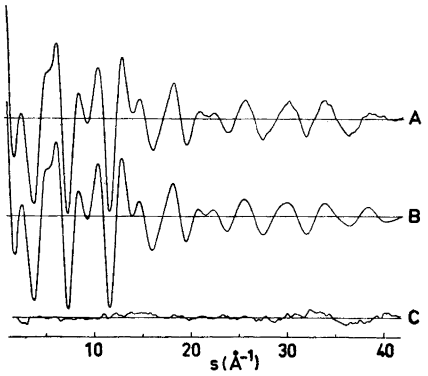

Fig. 2. Tricyclo(3.3.2.0 ^{4,6})deca-2,7,9-triene (bullvalene). Experimental (A) and theoretical (B) molecular intensity functions. C = A − B.

The radial distribution (RD) function obtained by Fourier inversion of the modified experimental intensity curve is shown in Fig. 3. The first peak at about 1.1 Å represents the C−H bond distances, and the second peak the C−C bond distances. Since the shoulder on the left side of this peak can only be due to the C−C double bond distances, it is evident that there are two types of carbon-carbon bonded distances, that is single bond and double bond. The rest of the RD curve represents nonbonded distances; the shortest are the C···H distances over one angle which contribute to the peak at about

2.15 Å. The two peaks at about 2.55 Å and 3.15 Å represent C···C distances over one and two angles, respectively. Outside 3.4 Å the contribution comes from longer C···H distances.

Table 1. Bullvalene. Experimentally determined distances (r_a), angles and root-mean-squares amplitudes of vibration (u). Standard deviations for the distances, given in brackets, are corrected as suggested by Seip *et al.*[24] and have also been increased to include the uncertainty arising from error in the electron wavelength.[25]

	r_a (in Å)	u (in Å)
C_2-C_3	1.346 (0.003)	0.045 (0.002)
C_1-C_2	1.523 (0.005)	
C_3-C_4	1.465 (0.004)	0.048 (0.002)
C_4-C_5	1.542 (0.006)	
$C_2\cdots C_9$	2.515 (0.011)	
$C_1\cdots C_3$	2.518 (0.012)	0.066 (0.002)
$C_2\cdots C_4$	2.509 (0.012)	
$C_3\cdots C_5$	2.639 (0.005)	
$C_1\cdots C_4$	3.037 (0.019)	
$C_2\cdots C_{10}$	3.110 (0.009)	0.089 (0.002)
$C_3\cdots C_{10}$	3.124 (0.013)	
$C_2\cdots C_5$	3.190 (0.011)	
$(C-H)_{av}$	1.111 (0.007)	0.076 (0.004)
$C_2\cdots H_3$	2.118 (0.006)	
$C_3\cdots H_2$	2.118 (0.006)	
$C_2\cdots H_1$	2.138 (0.010)	
$C_3\cdots H_4$	2.101 (0.010)	0.084 (0.008)
$C_4\cdots H_3$	2.181 (0.012)	
$C_4\cdots H_5$	2.287 (0.006)	
$C_1\cdots H_2$	2.276 (0.007)	
$C_2\cdots H_8$	3.325 (0.010)	
$C_3\cdots H_1$	3.388 (0.014)	
$C_2\cdots H_4$	3.378 (0.014)	
$C_4\cdots H_2$	3.492 (0.011)	0.102 (0.011)
$C_3\cdots H_5$	3.536 (0.006)	
$C_1\cdots H_8$	3.520 (0.007)	
$C_4\cdots H_7$	3.530 (0.010)	
$C_4\cdots H_1$	4.112 (0.020)	
$C_3\cdots H_8$	4.084 (0.008)	
$C_1\cdots H_4$	4.117 (0.019)	
$C_3\cdots H_7$	4.103 (0.014)	0.123 (0.010)
$C_2\cdots H_7$	4.129 (0.010)	
$C_2\cdots H_5$	4.234 (0.012)	
$C_4\cdots H_8$	4.268 (0.011)	
	Angles (in degrees)	
$\angle\alpha$ [a]	72.5 (0.7)	
$\angle C_1C_2C_3$	122.6 (0.8)	
$\angle C_2C_3C_4$	126.3	
$\angle C_3C_4C_5$	122.7	
$\angle C_2C_1C_8$	111.4	
$\angle C_3C_4H_4$	115 [b]	

[a] α is the angle between the bond C_1-C_2 and the threefold axis.
[b] Assumed.

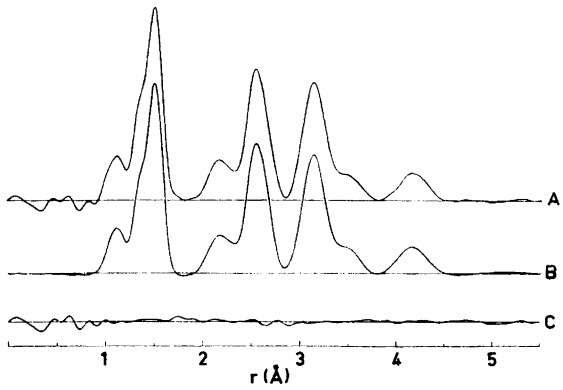

Fig. 3. Tricyclo(3.3.2.0^{4,6})deca-2,7,9-triene (bullvalene). Experimental (A) and theoretical (B) radial distribution functions. C = A − B. $k = 0.0009$ Å^2.

The molecule was refined under the assumption of C_{3v} symmetry. The parameters used in the refinement of the carbon skeleton were the bond distances C_1-C_2, C_2-C_3, C_3-C_4, C_4-C_5, the angle between the C_1-C_2 bond and the three-fold axis (α) and the angle $C_1C_2C_3$. The numbering of the atoms in the molecule is shown in Fig. 1.

Except for the $(C-H)_{av}$ bond distances, the positions of the hydrogen atoms are not refined. The hydrogen atoms bonded to carbon atoms C_2, C_3, and C_4 are assumed to be in the same plane as atoms C_1, C_2, C_3, and C_4, and the C−H bonds at C_2 and C_3 are assumed to bisect their respective angles CCC. The angle $C_3C_4H_4$ is assumed to be 115°, the same as the angle HCH in cyclopropane.[18] The structure of the carbon skeleton is insensitive to asumptions concerning hydrogen atom positions.

The contribution from the nonbonded H···H distances was treated as constant during each refinement.

It was not possible to refine the u-values for all the distances independently. Therefore, only the u-value for the C−C double bond was refined separately. The rest of the u-values were refined by grouping distances of the same type and of nearly the same length, and giving each distance in the group the same u-value. The u-values for each group were then refined.

The correlation matrix shows great correlation (−0.72) between the C_1-C_2 and C_4-C_5 distances. The uncertainty in the determination of these two distances is shown in their relatively large standard deviations. It was shown, however, that the least-squares refinements converged to the same final values for the parameters, independent of the choice of input values for the C−C single bonds.

The two angular parameters are closely correlated with a correlation coefficient of −0.95. The correlation matrix shows also strong correlation (absolute values from 0.72 to 0.81) between these angles and the u-values for the dependent C···C distances.

Table 1 lists the final structure parameters in bullvalene.

DISCUSSION

Investigations of the NMR-spectra of bullvalene show that the molecule undergoes rapid Cope-rearrangements at about 100°C. In this investigation of the structure of the compound at the same temperature, no evidence of rearrangement was found. The bond distances and angles (Table 1) are in accordance with those expected for a single structure and not with an average of several rapidly isomerizing structures as shown by NMR. This has its explanation in the rate of isomerization [6] being slow, compared to the time required for the electron wave to pass the molecule.

A comparison of the parameters found in the present investigation with the mean distances found in two X-ray investigations [8,9] is given in Table 2.

Table 2. Structural parameters of bullvalene from the present investigation, compared to the results (mean values) of two X-ray investigations.[8,9]

	E.D.	X-Ray [9]	X-Ray [8]
C_1-C_2	1.523	1.508	1.51
C_2-C_3	1.346	1.319	1.33
C_3-C_4	1.465	1.452	1.45
C_4-C_5	1.542	1.539	1.54
$\angle C_1C_2C_3$	122.6	124.1	126.
$\angle C_2C_3C_4$	126.3	126.7	

In the latter studies, the error limits are given as ± 0.02 Å [8] and ± 0.007 Å,[9] respectively. The distances found in the vapour phase are all longer, but except for the double bond, the differences may not be significant. The double bond was found to be quite normal (1.346 (0.003) Å) in the present study, while one of the X-ray investigators determined the distance to be significantly shorter.

The CCC bond angles at C_1 and C_2 are 111.4° and 122.6°, respectively. The C_1-C_2 distance, however, was found to be 1.523 (0.005) Å, which is longer than expected for a $C(sp^3)-C(sp^2)$ bond. The distances found in the crystal are closer to the expected value.

The C_3-C_4 distance is found to be very close to the single bond in 1,3-butadiene [19] of 1.467 (0.001) Å. The corresponding bonds in vinylcyclopropane [20] and in bicyclopropyl [21] are 1.475 (0.003) Å and 1.487 (0.004) Å, respectively. It has therefore been suggested that the cyclopropyl residue chemically may act as a double bond. This has been verified by theoretical calculations [22,23] which show that the exocyclic orbitals in cyclopropane are almost sp^2-hybridized. Our experimental value is in good agreement with the length of a $C(sp^2)-C(sp^2)$ bond, even though the bond angles at C_3 and C_4 may suggest different hybridization at these atoms. The CCC bond angle at the atom C_3 is 126.3°, and the angle between the bond C_3-C_4 and the cyclopropyl plane is 128.6°, much larger than the corresponding angle in cyclopropane itself (122.5°).

The correspondence is very good between the values determined for the C–C distance in the cyclopropyl ring in the vapour phase and in the crystal. The distance is considerably longer than in cyclopropane itself (1.510 ± 0.002 Å). In vinylcyclopropane, the corresponding distance (1.522 (0.001) Å) is also found to be longer than in cyclopropane.

Acknowledgements. We are very much indebted to Dr. G. Schröder, who has kindly placed at our disposal the sample used in this investigation. We also want to thank cand. real. A. Almenningen for taking the electron diffraction diagrams, and we thank Professor O. Bastiansen for his interest in this work and for many helpful discussions. We also wish to thank the *Norwegian Research Council for Science and Humanities* for financial support.

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Received August 14, 1970.