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A REVISED STRUCTURE OF BICYCLO[2,1,1]HEXENE-2 BY GAS PHASE ELECTRON DIFFRACTION

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An earlier electron diffraction structure of bicyclo[2,1,1]-hexene-2[1] disagrees with the microwave r_s structure.[2] The principal discrepancies are: $\angle C_1C_2C_3$, the dihedral angle between planes $C_1C_5C_4$ and $C_1C_6C_4$ (2ϕ), and a very short non-bonded distance $C_5 \ldots C_6$ in the ED structure. In order to find out possible errors which might be due to the impurity of the sample in the previous ED study, a reinvestigation of the structure of bicyclo[2,1,1]hexene-2 was undertaken. The compound was synthesized according to Meinwald and Uno.[3] Two sets of sectored electron diffraction photographs were taken with the Cornell Electron Diffraction apparatus under the following conditions: high voltage, long sample-plate distance (60 kV, 254.6 mm, $q = 12$–40 Å^{-1}) and short sample-plate distance (60 kV, 121.2 mm, $q = 32$–125 Å^{-1}). $q = (40/\lambda) \cdot \sin(\theta/2)$. For each set, two pictures were taken at the same condition but with different exposure time. The sample was kept at 0° during exposures. MgO diffraction patterns were also recorded concurrently to establish the scale factor. The patterns were traced with a double beam Jarrell-Ash microdensitometer interfaced with a digital recorder. Procedure of data reduction and analysis has been described previously.[4] The following geometrical

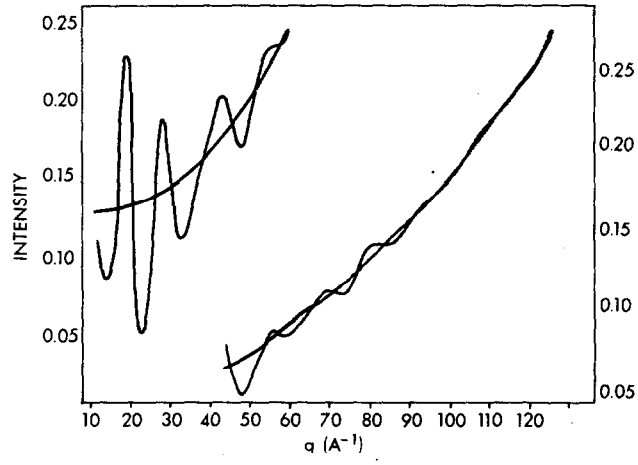

Fig. 1. Total experimental intensity curve and refined background for bicyclo[2,1,1]hexene-2.

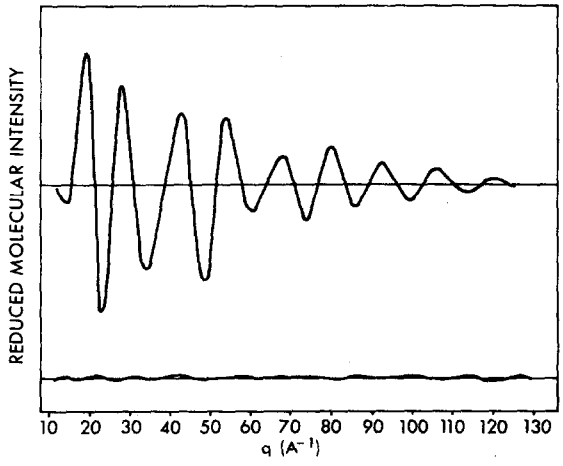

Fig. 2. The reduced experimental molecular intensity for bicyclo [2,1,1]hexene-2; the lower oscillating curve is the difference between experimental intensity and that calculated from the final structure.

parameters were used in calculating the geometry of bicyclo[2,1,1]hexene-2: C–H, C_1–C_2, C_2=C_3, C_5–O (the distance from C_5 to the origin of the cartesian coordinate system, i.e. the middle point of C_2=C_3), $\angle C_1C_2C_3$, $\angle H_2C_2C_3$, $\angle H_1C_1C_2$, $\angle H_5C_5C_1$, θ (the angle between C_5–O and the Z axis which is perpendicular to the plane $C_1C_2C_3C_4$). The structural parameters were refined by applying a least squares analysis to the experimental intensity. The following geometrical parameters and the mean amplitudes of vibrations (l's) were varied in the final least squares analysis: C–H, C_1–C_2, C_2=C_3, C_5–O, $\angle C_1C_2C_3$, θ, $\angle H_5C_5C_1$, $l_{C=C}$, l_{C-C}, and l_{C-H}.

The total experimental intensity curves and the refined background for bicyclo[2,1,1]hexene-2 are plotted in Fig. 1. The experimental intensity was the average values of two pictures taken at same condition with different exposure time as mentioned before. The reduced experimental molecular intensity and the difference between experimental intensity and that calculated from the final structure are shown in Fig. 2. Figure 3 shows the refined experimental radial distribution curve (. . . . .) and that calculated from the best model (——). The lower

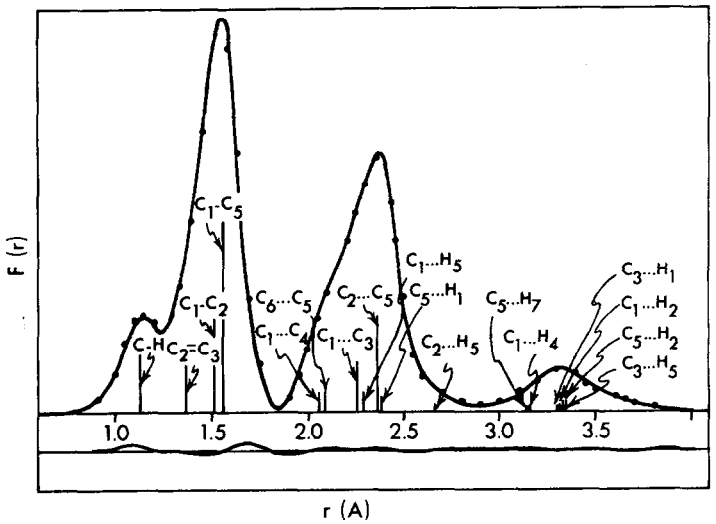

Fig. 3. Experimental radial distribution curve (.....) and the final theoretical curve (——) for bicyclo[2,1,1]hexene-2; the lower oscillating curve is the difference between the theoretical and experimental functions.

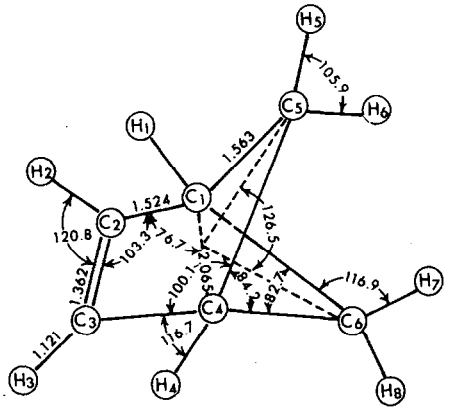

Fig. 4. The geometry of bicyclo[2,1,1]hexene-2.

oscillating curve is the difference between the experimental and calculated radial distribution functions. The geometry of bicyclo[2,1,1]hexene-2 is shown in Fig. 4. The structural parameters as derived from the least squares analysis are listed in Table 1. The error limits cited are thrree times the standard deviations which are the diagonal elements of the error matrix. The error matrix is reproduced in Table 2. A comparison of the geometrical parameters from electron diffraction and microwave spectroscopic studies is shown in Table 3. The geometrical parameters agree with the microwave structure except C_2=C_3 bond length which is 0.02 Å longer than that in the microwave structure. The calculated moments of inertia from ED structure are also in agreement with the microwave results (Table 4). From this reinvestigation, we realize that the purity of a

Table 1. Structural parameters of bicyclo[2,1,1]hexene-2

Type	r_{ij}	l_{ij} (Å)
C_1-C_2	1.524(0.007)Å	0.063(0.005)
C_2=C_3	1.362(0.003)Å	0.061(0.004)
$(C-H)_{ave}$	1.121(0.004)Å	0.096(0.008)
C_5-O[a]	2.268(0.005)Å	
$\angle C_1C_2C_3$	103.3(0.4°)	
$\angle H_2C_2C_3$	120.8°[b]	
$\angle H_1C_1C_2$	116.7°[b]	
$\angle H_5C_5C_1$	116.9 (0.8°)	
θ[c]	62.5(0.3°)	

(a) C_5-O is the distance from C_5 to the origin of the cartesian coordinate system, i.e., the middle point of C_2=C_3.

(b) Refined from radial distribution function; the value was obtained by manual adjustments of the parameter to agree with the experimental radial distribution curve.

(c) θ is the angle between C_5-O and the Z-axis.

Table 2. Error matrix

$C_2=C_3$	C_1-C_2	$\angle C_1C_2C_3$	C_5-O	θ	C-H	$\angle H_5C_5C_1$	$\ell_{C=C}$	ℓ_{C-C}	ℓ_{C-H}
0.0008									
-0.0003	0.0023								
-0.0006	-0.0112	0.1312							
-0.0002	0.0005	-0.0121	0.0017						
0.0042	0.0038	0.0976	-0.0074	0.0955					
-0.0004	-0.0006	-0.0002	-0.0007	-0.0048	0.0012				
-0.0061	-0.0104	0.0754	-0.0102	-0.0269	-0.0068	0.2548			
-0.0003	0.0011	-0.0049	0.0004	0.0030	-0.0005	-0.0033	0.0013		
-0.0005	0.0028	-0.0088	0.0004	0.0049	-0.0006	-0.0065	0.0011	0.0017	
-0.0003	-0.0005	-0.0047	0.0005	-0.0047	-0.0005	-0.0008	-0.0010	-0.0004	0.0025

Table 3. Comparison of structural parameters of bicyclo[2,1,1]hexene-2[a]

Parameter	This work	Previous ED[b]	MW[c]
C-H	1.121	1.120	——[d]
C_1-C_2	1.524	1.537	1.528
$C_2=C_3$	1.362	1.332	1.341
C_1-C_5	1.563	1.548	1.568
$\angle C_1C_2C_3$	103.3	108.4	103.3
2ϕ	126.5	123.5	126.7
$\angle C_5C_1C_2$	100.1	93.8	100.4
$\angle C_5C_1C_6$	84.2	72.2	85.33
$\angle C_1C_5C_4$	82.7	96.0	81.40

a. Distances in Angstrom, angles in degrees

b. See reference 1.

c. See Reference 2.

d. Not reported

Table 4. The moments of inertia of bicyclo[2,1,1]hexene-2

	Calculated from ED(amuA^2)	Experimental Value[a] (amuA^2)
I_a	87.03	86.625
I_b	107.95	107.765
I_c	118.92	117.915

compound might be a very important factor for electron diffraction structure study. This may eliminate some of the discrepancies in various electron diffraction and microwave spectroscopic structures. Once the purity of a sample is established, a combined analysis of electron diffraction and microwave spectroscopic rotational constants will give a unique solution to structures with nearly equal interatomic distances,[5] because electron diffraction alone cannot resolve these distances unambiguously.

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