The Molecular Structure of 2-Methyloxacyclobutane, as Studied by Electron Diffraction

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A gas electron diffraction study of 2-methyloxacyclobutane has been carried out at room nozzle temperature. The four membered ring takes a planar conformation. The mean r_a values for the O–C, C–C and C–H bonds are 1.448(5) Å, 1.534(4) Å and 1.118(3) Å, respectively. The endocyclic bond angles are C–C–C = 85.5(18)° and C–C–O = 91.2(15)°, while the angle C–O–C was assumed to be 92°. The position of exocyclic carbon atom was characterized, in addition by $< C_{exocyclic}-C-O = 110.7(7)°$ and torsional angle $C_{exocyclic}-C-O-C = 59.6(40)°$ (0° corresponds to the anti position of $C_{exocyclic}-C$ and O–C bonds).

I. Introduction

Microwave and infrared spectroscopic studies have provided information on the conformation, structure and vibrational properties of trimethylene oxide [1–5], and its derivatives: 3-methylene oxetane [6], 3-oxetanone [7], 2-oxetanone [8, 9], and 4-methyl-2-oxetanone [10, 11]. On the results of these and other microwave, infrared and electron diffraction studies on cyclobutane [12, 13], trimethylene sulfide [14, 15], azetidine [16, 17], silacyclobutane [18, 19], perfluorocyclobutane [20], trimethylene selenide [21], cyclobutanone [22], a considerable amount of knowledge has been accumulated on the structural properties of four-membered cyclic molecules. These studies demonstrated that the ring conformation, e. g. the planarity or non-planarity of the four-membered ring, is governed by a sensitive balance between bond angle strain and torsional strain (the former favours a planar, the latter a non-planar conformation). The resulting conformation depends both on the atoms in the cycle and on the atoms or atomic groups attached to the cycle.

The cyclobutane molecule exhibits a non-planar conformation with puckering angle 35° [12, 13]. Non-planar conformation was verified for trimethylene sulfide with dihedral angle C–S–C, C–C–C = 26° [14, 15], for azetidine with dihedral angle C–N–C, C–C–C = 33° [16, 17], for silacyclobutane with dihedral angle C–Si–C, C–C–C = 36° [18, 19], for perfluorocyclobutane with dihedral angle of 17° [20] and for trimethylene selenide with dihedral angle C–Se–C, C–C–C = 29° [21]. The trimethylene oxide takes a planar conformation in the ground vibrational state with low barrier at 0° dihedral angle, which modifies the excited vibrational levels [1–5].

3-trimethylene oxetane [6], 3-oxetanone [7], 2-oxetanone [8, 9], 4-methyl-2-oxetanone [10, 11] and cyclobutanone [22] in the ground vibrational state take also planar conformation with low barrier at 0° puckering angle.

The oxetane and its substituted derivatives including the title molecule have been extensively studied in liquid phase by nuclear magnetic resonance method [22–28]. From the obtained spectral parameters of the protons in 2-methyloxacyclobutane molecule the distortion of the ring structure, in comparison with that of oxetane ring, was deduced [28]. An extensive survey of literature on stereochemistry of four-membered ring molecules is given by Moriarty [29].

The purpose of the present electron diffraction study is to provide further data on the structure of four-membered ring molecules by the study of the title molecule.

II. Experimental and Structure Refinement

The sample of 2-methyloxacyclobutane was synthetised as described elsewhere [30]. The diffrac-

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tion patterns were recorded with our EG-100 A apparatus in this laboratory. The nozzle was at room temperature, nozzle-to-plate distances of 51 and 19 cm were utilized. The nominal accelerating voltage was 60 kV. The ranges of obtained intensity data were $2.25 \leqq s \leqq 10.875$ Å^{-1} and $6.75 \leqq s \leqq 32.0$ Å^{-1} with data intervals $\Delta s = 0.125$ Å^{-1} and $\Delta s = 0.25$ Å^{-1} for 51 cm and 19 cm camera ranges, respectively. Three diffraction patterns were selected and averaged from each distance. The experimental and data reduction technique was the same as described elsewhere [31, 32].

The experimental and final theoretical molecular intensities and radial distribution functions are presented in Figs. 1 and 2, respectively. The assignment of more important features of radial distribution, based on the final model, is also given in Figure 2. The peak at 1.11 Å comes from contribution of C – H bonded distances, the peak at 1.50 Å comes from contribution of bonded C – C and O – C distances. The peaks at 2.10 Å and 2.50 Å contain the contribution of distances separated by one bond angle (the first one comes mainly from O1 . . . C3 * and C2 . . . C4 endocyclic, the second one from O1 . . . C5 and C3 . . . C5 exocyclic distances). The contribution of C4 . . . C5 distance appears at the outer part of the radial distribution, at about 3.25 Å.

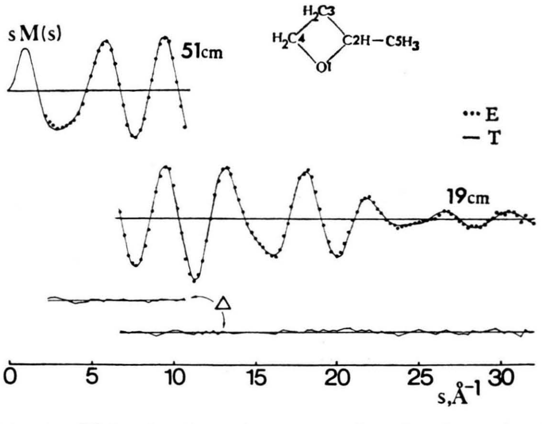

Fig. 1. Molecular intensity curves for the 51 and 19 cm camera ranges (E experimental; T theoretical), △ represents the differences between experimental and theoretical molecular intensities. The numbering of atoms is also presented.

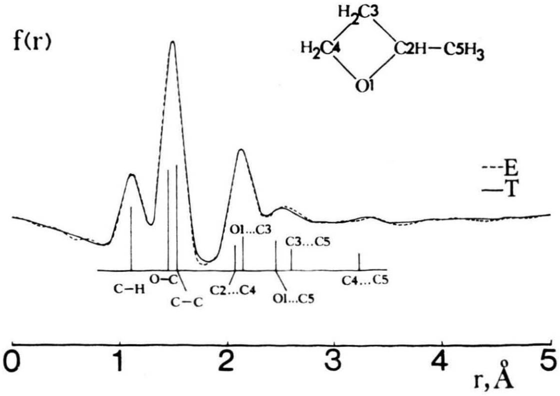

Fig. 2. Experimental E and theoretical T radial distributions and the difference curve. The more important individual interatomic distances and their relative weights are also indicated.

The inspection of the radial distribution function shows that the electron diffraction data alone do not allow the determination of all geometrical parameters and mean amplitudes of vibration. To facilitate the analysis the following assumptions were made concerning the geometry:

(i) The two O – C bond lengths are equal;
(ii) All three C – C bond lengths are equal;
(iii) All C – H bond lengths are equal;
(iv) The bond configuration around C3 and C4 atoms have a C_{2v} symmetry;
(v) All H – C – H angles are 109.5°;
(vi) The bond configuration around C5 atom has a C_{3v} symmetry;
(vii) One of the C5 – H bonds takes a syn position with respect to the O1 – C2 bond.

The calculated molecular intensities and radial distributions have a limited sensitivity on the assumptions (iii) – (vii) due to the relative low scattering power of the hydrogen atoms.

Taking into account the above assumptions, the geometry of the ring skeleton was characterized by the following four independent parameters: the O – C and C – C bond lengths, the C2 – O1 – C4 bond angle and the dihedral angle (β) between the planes C2 – O1 – C4 and C2 – C3 – C4. The position of C5 atom was specified by two further angles: the O1 – C2 – C5 bond and C4 – O1 – C2 – C5 torsional angles. The zero value of C4 – O1 – C2 – C5 torsional angle corresponds to anti position of C4 – O1 and C2 – C5 bonds. If β and the C4 – O1 – C2 – C5 angle have equal signs and the absolute value of C4 – O1 – C2 – C5 is smaller than 180°, the C5 and C3 atoms are on the same side of C4 – O1 – C2 plane (axial position of C2 – C5 bond). The position of hydrogen atoms attached to

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* The numbering of atoms corresponds to Figure 3.

Table 1. Results of the least-squares refinement of molecular parameters for 2-methyloxacyclobutane (estimated total errors in parantheses)[a].

Independent distances and angles	Geometrical parameters	Amplitudes of vibration
O–C	1.448 (5)	0.050 (6)[b]
C–C	1.534 (4)	0.054
C–H	1.118 (3)	0.073 (2)
$<$ C2–O1–C4	92 (assumed value)	
$< \beta$	2.5 (55)	
$<$ O1–C2–C5	110.7 (7)	
$<$ C4–O1–C2–C5	59.6 (40)	
$<$ H–C2–O1	104.2 (100)	
$<$ H–C2–O1–C4	−134.3 (70)	
Dependent distances and angles	**Geometrical parameters**	**Amplitudes of vibration**
O1 ... C3	2.132 (30)	0.058 (30)[b]
C2 ... C4	2.084 (30)	0.059
O1 ... C5	2.455 (11)	0.064 (15)[b]
C3 ... C5	2.604 (16)	0.066
C4 ... C5	3.229 (16)	0.143 (34)
$<$ C3–C2–C5	116.2 (9)	
$<$ C2–C3–C4	85.5 (18)	
$<$ O1–C2–C3	91.2 (15)	

[a] Distances (r_a values) in Å, angles in °.
[b] With fixed differences between l_{ij} values.

C4, C3 and C5 were specified by C – H bond length. The position of hydrogen atom attached to C2 carbon atom was characterized by bond angle H – C2 – O1 and by torsional angle H – C2 – O1 – C4 (zero value of the latter corresponds to the anti position of C2 – H and O1 – C4 bonds).

The least-squares refinement procedure was applied to the molecular intensities [33]. The initial values of geometrical parameters and mean amplitudes were compiled from other molecules. The amplitudes of near lying distances were refined with fixed differences. In the course of the refinement unreasonably low values were obtained for amplitudes of O1 ... C3 and C2 ... C4 distances. A high correlation was revealed between these amplitudes and C2 – O1 – C4 angle as indicated by the correlation matrix corresponding to the final structure and presented in Table 2 (the correlation matrix includes also the C2 – O1 – C4 angle though this parameter was not refined, see later). It was decided to carry out the least-squares refinement at the fixed values of C2 – O1 – C4 angle in the range around 92°. This value was determined for C – O – C angle in trimethylene oxide molecule by microwave spectroscopy [4]. It turned out that the bond lengths,

Table 2. The correlation matrix for 2-methyloxacyclobutane[a].

	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9
x_1	1000								
x_2	−902	1000							
x_3	135	−83	1000						
x_4	181	−15	17	1000					
x_5	143	−25	−49	520	1000				
x_6	319	302	50	75	404	1000			
x_7	−103	−38	82	−605	−958	−308	1000		
x_8	−176	60	−40	−28	−515	−116	568	1000	
x_9	28	17	34	−8	336	291	−399	−849	1000
l_1	930	−916	153	80	65	−358	−23	−157	−1
l_2	128	−97	115	−51	−42	−150	34	−91	−4
l_3	369	−28	18	917	396	−11	−457	90	−73
l_4	−37	−9	−34	−201	−304	−272	253	211	−314
l_5	−47	−34	6	−203	−630	−340	595	516	−452
k_1	498	−466	238	−10	−28	−344	32	−175	−28
k_2	368	−293	−93	91	159	−238	−166	−225	−62

	l_1	l_2	l_3	l_4	l_5	k_1	k_2
l_1	1000						
l_2	234	1000					
l_3	322	−8	1000				
l_4	47	134	−146	1000			
l_5	1	39	−106	189	1000		
k_1	699	446	142	179	39	1000	
k_2	427	101	123	27	−66	416	1000

[a] The elements of correlation matrix are multiplied by 1000. $x_1 = r(\mathrm{O-C})$, $x_2 = r(\mathrm{C-C})$, $x_3 = r(\mathrm{C-H})$, $x_4 = < \mathrm{C_2O_1C_4}$, $x_5 = < \mathrm{C_2O_1C_4}$, $\mathrm{C_1C_3C_2}$, $x_6 = < \mathrm{O_1C_2C_5}$, $x_7 = < \mathrm{C_2C_5}$, $\mathrm{C_2O_1C_4}$, $x_8 = < \mathrm{HC_2O_1}$, $x_9 = < \mathrm{HC_2}$, $\mathrm{C_2O_1C_4}$, $l_1 = l(\mathrm{O-C})$, $l_2 = l(\mathrm{C-H})$, $l_3 = l(\mathrm{O_1 \ldots C_3})$, $l_4 = l(\mathrm{O_1 \ldots C_5})$, $l_5 = l(\mathrm{C_4 \ldots C_5})$, k_1, k_2 scale factors for short and long camera distances, respectively.

the more important non-bonded distances and corresponding amplitudes, except the C2 ... C4 and O1 ... C3 distances and its amplitudes have a limited sensitivity on the particular choice of C2 – O1 – C4 angle in the range 90.5 – 93.5°. On the other hand it is expected that the O1 ... C3 and C2 ... C4 endocyclic amplitudes have higher values than the C – O and C – C bonded distances, but lower than the C3 ... C5 and O1 ... C5 exocyclic amplitudes. This condition is satisfied if $91.5 \lesssim \mathrm{C2-O1-C4} \lesssim 92.5°$. In the final stage of the refinement $<$C2 – O1 – C4 was fixed at the value 92°. The final results of the least-squares refinement are presented in Table 1 together with estimated total errors. The total errors include the standard deviations from the least-squares refinement multiplied by $\sqrt{2}$ for data correlation and an estimated 0.2 and 2% experimental error for the distances and amplitudes, respectively. In addition, the errors were increased by adding the changes in the parameters that occured when the assumed values of C2 – O1 – C4 angle were changed to cover the interval 90.5, 93.5°. As regards the bond configuration around C2 atom, the results of the refinement show, the bond angle O1 – C2 – C5 is 110.7° very close to the tetrahedral value, on the other hand the value of C3 – C2 – C5 angle is 116°. To give confidence to this result the refinement was repeated from an initial structure corresponding to $<$O1 – C2 – C5 = 116° and $<$C3 – C2 – C5 = 109°, the selection of this initial structure had no effect on the results of the refinement.

III. Discussion

The results indicate that the ring takes a planar conformation within experimental error. The slight deviation of the dihedral angle from zero value probably is a consequence of puckering vibration. The change of the sign of dihedral angle leads to increase of the R-factor, this may indicate the asymmetric character of the potential governing the puckering vibration. In Table 3 the structure of ring skeleton is given for 2-methyloxacyclobutane and for some other molecules with identical ring composition. The corresponding structural parameters of 2-methyloxetane, 3-methylene oxetane, 3-oxetanone and trimethylene oxide are very close to each other.

The present results give additional support to the observations of Mastryukov et al. [34] according to which the C – O bond is longer in four-membered rings than in other environments. Some relevant data on C – O bond lengths are presented in Tables 3 and 4.

Table 3. Comparison of structural parameters of the ring skeleton in derivatives of trimethylene oxide [a].

	2-methyl-oxacyclo-butane [b]	3-methy-lene oxetane [c]	3-oxeta-none [d]	trimethy-lene oxide [e]
O_1-C_2	1.448	1.449	1.441	1.449
C_2-C_3	1.534	1.523	1.524	1.549
$< C_2-O_1-C_4$	92.0 [f]		94.82	91.98
$< C_2-C_3-C_4$	85.5	87.05	88.23	84.55

[a] Bond lengths in (Å), angles in (°).
[b] Present study, r_a values.
[c] Reference [6], r_0 structure.
[d] Reference [7], *a* partial substitution structure.
[e] Reference [4], r_0 structure.
[f] Assumed value, see the text.

Table 4. The C—O bond length in some molecules as determined by electron diffraction and microwave spectroscopy (distances in Å) [a].

Mole-cule	dimethyl ether [b]	ethylene oxide [c]	tetra-hydro-furan [d]	1,4-thioxan [e]
r(C—O)	1.410	1.431	1.428	1.418

[a] For C—O bond lengths in four membered ring see Table 3.
[b] Reference [35], r_s value.
[c] Reference [36], r_s value.
[d] Reference [37], r_g value.
[e] Reference [38], r_a value.

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