Molecular Structure of 7-Oxanorbornane as Studied by Gas Electron Diffraction

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The structure of 7-oxabicyclo[2.2.1]heptane (7-oxanorbornane) in the gas phase has been investigated by making joint use of the electron diffraction intensities measured in the present study and the rotational constants reported by Creswell. The thermal average bond lengths are: $r_g(C_1-C_2)=1.533\pm0.014$ Å, $r_g(C_2-C_3)=1.571\pm0.015$ Å, $r_g(C-O)=1.442\pm0.010$ Å, and $r_g(C-H)=1.117\pm0.008$ Å. The bond angles in the zero-point average structure (r_{av}) are: $\angle C-O-C=94.5\pm2.2°$, θ (the dihedral angle between the $C_1-C_2-C_3-C_4$ and $C_4-C_5-C_6-C_1$ planes)$=113.5\pm0.8°$ and $\angle H-C-H=105\pm5°$. The uncertainties represent the estimated limits of experimental error. The C_2-C_3 bond is longer than the C_1-C_2 bond, and the latter distance is nearly equal to that of a normal C–C single bond. The C–O bond is about 0.02 Å longer, and the C–O–C bond angle is about 17° smaller than the corresponding parameters in dimethyl ether. These trends are analogous to those observed for norbornane and 7-thianorbornane.

As part of our systematic studies of the structures of polycyclic molecules,[1-7] norbornane (bicyclo[2.2.1]-heptane)[4] and 7-thianorbornane[5] have recently been studied by gas electron diffraction. The effect of intramolecular strain is clearly demonstrated in the valence angles of skeletal atoms. In particular, the $C_1-C_7-C_4$ and C_1-S-C_4 angles are both smaller than the corresponding angles in propane and dimethyl sulfide, respectively, by about 19°. Furthermore, the weighted averages of their C–C bond lengths are significantly longer than a normal C–C single bond. A further analysis of the norbornane structure suggested that the C_1-C_7 and C_2-C_3 bonds were appreciably longer than the C_1-C_2 bond, which seemed to be nearly normal. However, it was difficult to precisely determine the individual C–C bond lengths since the rotational constants were not available. Similar circumstances were also encountered in the analyses of thianorbornane,[5] quadricyclene,[6] and nortricyclene[7] using electron diffraction data only. On the other hand, a set of rotational constants for 7-oxanorbornane (Fig. 1) for the normal isotopic species in the ground vibrational state has now become available, and hence, a joint analysis[9-12] of electron diffraction intensities and the rotational constants should be sufficient to uniquely determine the skeletal structure. There is no previous structure work on this molecule except in two theses.[8,13] Thus it is the purpose of the present study to apply this method to a cyclic system for the first time to examine whether there is any significant difference between the C_1-C_2 and C_2-C_3 bond lengths and whether the oxygen valence angle follows the same trend as that observed in the carbon and sulfur valence angles in norbornane and thianorbornane.

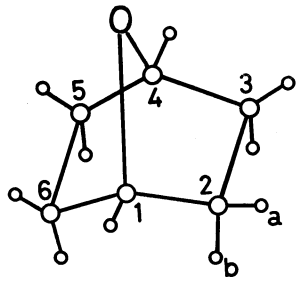


Fig. 1. 7-Oxanorbornane.

Experimental

A commercial sample (Aldrich), kindly supplied by Professor Dewitt Coffey, Jr. of California State University, San Diego, was used after distillation (bp 115 °C). A gas chromatographic analysis indicated that the sample was at least 99.9% pure.

Diffraction photographs were taken at camera lengths of 107.8 and 243.2 mm with an apparatus equipped with an r^3-sector.[14] The accelerating voltage was about 40 kV. During the exposure the sample was maintained in thermal equilibrium with its liquid phase at room temperature. The vapor pressure was about 10 Torr. The scale factors of the diffraction patterns were calibrated to within 0.10% with reference to the r_a(C=O) distance of carbon dioxide (1.1646 Å) measured under nearly the same experimental conditions. Other experimental details are described elsewhere.[14,15]

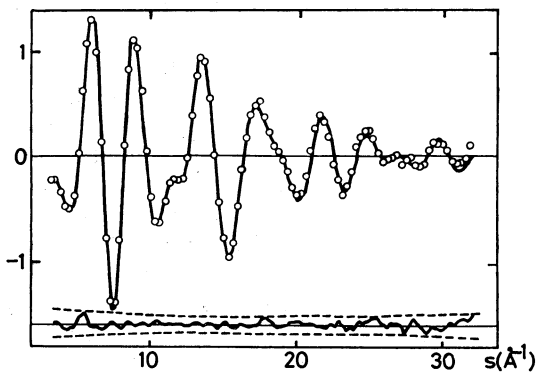


Fig. 2. Molecular intensities for 7-oxanorbornane. Observed values are shown as open circles, and the solid curve represents the best-fit theoretical intensity. The lower solid and broken curves represent the residuals and the error limits, respectively, in the $sM(s)$ to a fractional error of 1×10^{-3} in the original photocurrent.

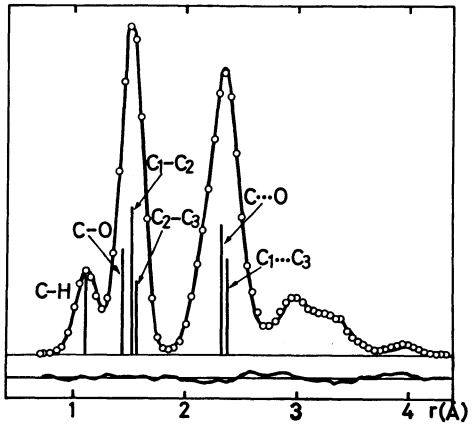


Fig. 3. Experimental (open circles) and the theoretical radial distribution curves for 7-oxanorbornane. Vertical bars represent principal atom pairs. A damping factor, $\exp(-0.0022s^2)$, was used. The residuals are shown below in the same scale.

Two photographic plates taken at the long camera length and three at the short camera length were selected for intensity measurements. Molecular intensities in the ranges $s=3.1$—18.8 and 7.9—32.0 Å^{-1} were obtained from the long and short distance data, respectively, by use of hand-drawn backgrounds. Since they agreed with each other in the overlapping region within experimental error, they were joined at $s=12.6$ Å^{-1}. The elastic and inelastic scattering factors and the phase shifts were taken from the tables prepared by Schäfer *et al.*[16] A typical molecular intensity curve is shown in Fig. 2,** and the corresponding radial distribution curve is shown in Fig. 3. Most of the calculations were carried out on a HITAC 8800/8700 in the Computer Center of the University of Tokyo.

Analysis

Preliminary Analysis of Electron Diffraction Data. The molecular intensities were analyzed by a least-squares method with the following initial assumptions:

1) The molecule had C_{2v} symmetry.
2) The H–C_2–H plane was perpendicular to the C_1–C_2–C_3 plane and bisected the C_1–C_2–C_3 angle, and *vice versa*.
3) The C–C–H angles and the O–C–H angle at the bridgehead were equal to one another, *i.e.*, $\angle C_2$–C_1–H$=\angle C_6$–C_1–H$=\angle$O–C_1–H.
4) All the C–H bond lengths were equal.
5) The C_1–C_2 and C_2–C_3 bond lengths were equal.
6) The H–C–H bond angles were equal to 110°.

With these approximations, the structure was defined by five parameters: the weighted average C–C bond length, the C–O bond length, the weighted average C–H bond length, the C_1–O–C_4 angle and the dihedral angle between the C_1–C_2–C_3–C_4 and C_4–C_5–C_6–C_1 planes (denoted as θ). Assumptions 1—4 were maintained throughout, but constraints 5 and 6 were released in a later stage of the joint analysis of diffraction and spectroscopic data.

** Numerical experimental data of the leveled total intensity and the background have been deposited with the Chemical Society of Japan (Document No. 7503).

Table 1. Estimated force constants for 7-oxanorbornane[a]

K(C–C)	2.3	H(C–C–O)	0.28	F(C–C–O)	0.6
K(C–O)	2.8	H(C–C–C)	0.32	F(C–C–C)	0.2
K(C–H)	4.3	H(C–O–C)	0.53	F(C–O–C)	0.47
Y(C–C)$_g$	0.17[b]	H(H–C–O)	0.26	F(H–C–O)	0.74
Y(C–C)$_c$	0.11[b]	H(H–C–C)	0.2	F(H–C–C)	0.48
Y(C–O)	0.15	H(H–C–H)	0.42	F(H–C–H)	0.07

a) Estimated force constants taken from cyclohexane[18] and ethyl ether.[19] The torsional force constants (Y) are in md·Å, and the others are in md/Å units. b) Symbols g and c represent the C–C axes which have *gauche* and *cis* C···C atom pairs, respectively.

Table 2. Mean amplitudes (l_{ij}) and shrinkage corrections (r_a-r_α) for 7-oxanorbornane[a]

	l_{ij}	r_a-r_α		l_{ij}	r_a-r_α
C_1–C_2	523	10	$C_1\cdots H_{3a}$	1131	22
C_2–C_3	522	23	$C_1\cdots H_{3b}$	1131	22
C_1–O	501	4	$C_2\cdots H_4$	978	15
C_1–H_1	771	78	$C_2\cdots H_{6a}$	1062	31
$C_1\cdots C_3$	609	0	$C_2\cdots H_{6b}$	1501	−11
$C_2\cdots C_6$	727	−1	$C_1\cdots H_4$	916	20
$C_1\cdots C_4$	565	−2	$C_2\cdots H_{5a}$	1054	17
$C_2\cdots C_5$	832	−15	$C_2\cdots H_{5b}$	1659	−38
$C_2\cdots$O	608	1	O$\cdots H_1$	977	24
$C_1\cdots H_2$	1055	47	O$\cdots H_{2a}$	1331	2
$C_2\cdots H_1$	1037	23	O$\cdots H_{2b}$	988	36
$C_2\cdots H_3$	1055	61	$H_{2a}\cdots H_{2b}$	1267	116

a) Calculated at 20°C (in 10^{-4}Å).

The mean amplitudes and the vibrational corrections for shrinkage effects (r_a-r_α)[17,18] for all the internuclear distances were calculated on the basis of an estimated force model using the Urey-Bradley force field listed in Table 1: the force constants were transferred from cyclohexane[19] and ethyl ether.[20] The numerical results listed in Table 2 were used as fixed constants in the analysis. The asymmetry parameter κ for the C–H bond was estimated to be 1×10^{-5} Å^3 by a diatomic approximation.[21] The κ parameters for other atom pairs were ignored.

The r_α structure[18] was determined with a conventional diagonal matrix[22] by a least-squares analysis of molecular intensities. The r_α and r_g structures with estimated limits of error are listed in Table 3.

The estimated error limits contain contributions from several sources:[9,23] 1) random errors estimated from the standard deviations of the least-squares analysis

Table 3. Preliminary analysis of the electron diffraction data for 7-oxanorbornane (in Å and degree)

	r_α	r_g	ε[a]
$(C–C)_{av}$	1.543_1	1.546_3	0.007
C–O	1.440	1.444	0.014
C–H	1.103	1.116	0.012
$\angle$COC	96.2	—	2.6
θ	112.2	—	1.4
$\angle$HCH	(110.0)	—	assumed

a) Estimated limits of error.

and the discrepancies observed in each refined parameter among different plates, 2) experimental systematic errors originating mainly from the uncertainties in the scale factors (0.07%) and sector imperfections (0.05%), 3) the uncertainty in the C–H bond length caused by the assumed value for κ(C–H) (0.002 Å), (The uncertainties in the other κ parameters ignored cause negligible errors.) 4) the effect of the uncertainties in the fixed mean amplitudes, 5) uncertainties originating from assumption 5 on the C–C bond lengths, and 6) those from assumption 6 on the H–C–H bond angle.

In order to estimate the errors due to source 4, the following method[24] was employed. The uncertainties in the calculated mean amplitudes are essentially caused by those in the assumed force constants; they were tentatively assumed to be 10% for bonded atom pairs and 20% for nonbonded atom pairs.[3] Least-squares refinements were carried out by separately varying each of the fixed mean amplitudes systematically to the limit of the estimated uncertainty. This procedure was applied to all the fixed mean amplitudes except for the H···H pairs, which had only a negligible effect. The uncertainties due to sources 5 and 6 were similarly estimated: the maximum difference between the C_1–C_2 and C_2–C_3 bond lengths was estimated to be $\pm$0.03 Å, and the H–C–H bond angle was assumed to be $110\pm5°$. Uncertainties arising from the fixed mean amplitudes are appreciable for all parameters, those from equal C–C bond lengths are appreciable only for the angles, and uncertainties from the assumed H–C–H bond angle are almost negligible.

Joint Analysis of Electron Diffraction Intensities and Rotational Constants. The rotational constants for the ground vibrational state, A_0, B_0, and C_0, determined by Creswell[8] from microwave spectroscopy, were transformed into A_z, B_z, and C_z by making vibrational corrections.[17,24] The uncertainties in A_z, B_z, and C_z (listed in Table 4) mainly originating from the uncertainties in these corrections[12] were tentatively estimated to be 20% of the total vibrational corrections.

The r_α structure determined in the foregoing analysis was extrapolated to zero Kelvin[17,18] by use of a diatomic approximation for bond stretching anharmonicity and the quadratic force constants for the perpendicular amplitudes, and the corresponding rotational constants, A_α^0, B_α^0, and C_α^0, were calculated from the r_α^0 structure. They agree with the corresponding rotational constants derived from microwave spectroscopy within their uncertainties, as shown in Table 4. Therefore, the latter constants were merged into a joint least-squares analysis.[9–12]

Table 4. Observed and calculated rotational constants for 7-oxanorbornane[a] (in cm^{-1})

	0[b]	z[c]	α^0[d]	av[e]
A	0.1309502(2)	0.130916(8)	0.1309(7)	0.130916(5)
B	0.1102560(1)	0.110232(4)	0.1102(2)	0.110232(4)
C	0.0949851(9)	0.094954(6)	0.096 (2)	0.094953(5)

a) Uncertainties attached to the last significant digits are given in parentheses. b) Observed rotational constants for the ground vibrational state. Ref. 8. c) Average rotational constants calculated from A_0, B_0 and C_0 with corrections for vibrational effects. The limits of error are estimated from the uncertainties in the quadratic force constants used for calculating the corrections. d) Rotational constants calculated from the r_α^0 structure given in Table 3. e) Best-fit rotational constants corresponding to the r_{av} structure, listed in Table 5, derived from the combined analysis of diffraction and microwave data. Uncertainties represent 2.5 times the estimated standard deviations.

The weights for the rotational constants were adjusted so that the 2.5 times the standard deviations for the rotational constants were approximately equal to their uncertainties. They were 5×10^9, 7×10^9, and 5×10^9 for A_z, B_z, and C_z, respectively, in comparison with unit weights assigned to the molecular intensities from s=6.3 to 26.7 $Å^{-1}$ taken at $\pi/10$ intervals.

It was now possible to release the constraint on the C–C bond lengths, since the rotational constants A_z and B_z were sensitive to the C_2–C_3 and C_1–C_2 bond lengths, respectively. Furthermore, three mean amplitudes, l(C–C), l(C_2···O), and l(C–H) were also varied: the two C–C amplitudes, l(C_1–C_2) and l(C_2–C_3), were

Table 5. Error matrix for 7-oxanorbornane[a]

	X_1	X_2	X_3	X_4	X_5	X_6	X_7	l_1	l_2	l_3	k_1	k_2
X_1	20	−23	8	−11	33	−20	30	14	10	−19	−20	37
X_2		35	−10	15	−40	28	44	−18	−7	21	36	−19
X_3			19	−7	10	15	47	8	−11	−19	−14	−45
X_4				28	−12	17	55	−7	2	10	17	27
X_5					57	−35	45	24	18	−31	−37	65
X_6						30	58	−14	−13	8	27	−47
X_7							230	24	11	−59	65	62
l_1								14	10	−13	−11	39
l_2									30	11	10	67
l_3										32	27	45
k_1											101	66
k_2												257

a) X_1=C_1–C_2, X_2=C_2–C_3, X_3=C–O, X_4=C–H, X_5=∠C–O–C, X_6=θ, X_7=∠H–C–H, l_1=(C–C), l_2=(C–H), l_3=(C_2···O), k_1, k_2=indices of resolution for the long and short distance data (0.92 ± 0.03 and 1.02 ± 0.07), respectively. Units ($\times10^{-4}$) for the distances and mean amplitudes are Å, those for the angles are rad, and those for the indices are dimensionless.

assumed to be equal to each other. The mean amplitudes l(C–O) and $l(C_1\cdots C_3)$ were not varied, however, since they were correlated strongly with the other refined parameters. Therefore, ten independent parameters were now refined. The corresponding error matrix is given in Table 5.

Chiang *et al.*[25] suggested that the methylene group in norbornane could have a structure distorted from local C_{2v} symmetry. However, it was not necessary to release assumption 2) and introduce an additional parameter representing the distortion in any of our analyses of norbornane,[4] thianorbornane[5] and oxanorbornane (the present study) to fit the experimental electron diffraction intensities to within the estimated experimental error.

The error limits were estimated by the method described in the preceding section. Since it was possible to release the constraints 5) and 6) and to vary a part of the mean amplitudes, the systematic uncertainties due to these constraints were eliminated in the present joint analysis. The final structure and mean amplitudes with estimated error limits are listed in Tables 6 and 7.

Table 6. Structure of 7-oxanorbornane from diffraction and microwave data[a]
(in Å and degree)

	r_{av}	r_g	ε[b]		r_{av}[c]	ε[b]
C_1–C_2	1.528_8	1.533	0.014	$\angle C_1C_2C_3$	100.3	0.6
C_2–C_3	1.567_2	1.571	0.015	$\angle C_6C_1C_2$	110.7	0.4
C–O	1.437_5	1.442	0.010	$\angle C_2C_1O$	103.6	1.3
C–H	1.103_7	1.117	0.008	$\angle H_1C_1C_2$	112.7	0.6
$\angle$COC	94.5	—	2.2	$\angle H_2C_2C_1$	113.0	1.5
θ	113.5	—	0.8			
$\angle$HCH	105	—	5			

a) Final result of the present study. b) Estimated limits of error. c) Calculated from the independent parameters.

Table 7. Observed mean amplitudes for 7-oxanorbornane (in Å)

	l_{obsd}[a]	l_{calcd}[a,b]
C–C[c]	0.048 (10)	0.052_3 (5)
C–H	0.071 (19)	0.077_1 (8)
$C_2\cdots O$	0.076 (18)	0.060_8 (12)

a) Estimated limits of error in 10^{-3}Å are given in parentheses. b) Taken from Table 2. Uncertainties are tentatively estimated to be about 10% for C–C and C–H and about 20% for $C_2\cdots O$. c) $l(C_1$–$C_2)$ and $l(C_2$–$C_3)$ are assumed to be equal to each other.

Discussion

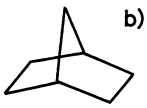
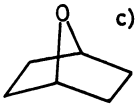
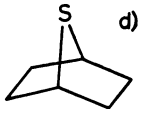
The r_g-r_{av} structure of 7-oxanorbornane determined in the present study is consistent with the rotational constants determined by Creswell.[8] This structure is compared in Table 8 with those of norbornane[4] and 7-thianorbornane.[5] The following points may be noted:

1) Weighted averages of the C_1–C_2 and C_2–C_3 bond lengths in these molecules are essentially equal to one another and about 0.01 Å longer than the normal single C–C bond length.

2) The C_2–C_3 bond in oxanorbornane is longer than the C_1–C_2 bond, which is similar to a normal single bond. The C_2–C_3 bonds of norbornane and bicyclo[2.2.2]octane[1] are also longer than the C_1–C_2 bonds, but in oxanorbornane, the difference appears to be larger (*ca.* 0.04 Å). The C_2–C_3 bond length of 1,4-diazabicyclo[2.2.2]octane[2] is also about 0.02 Å longer than that of cyclohexane.[26]

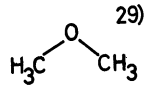
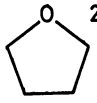
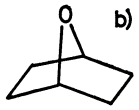
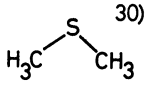
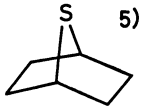
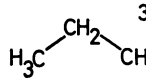
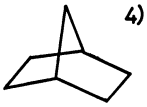
3) The dihedral angle θ in oxanorbornane is nearly equal to that in norbornane and about 2° less than that in thianorbornane.

Table 8. Comparison of skeletal structures[a]
(in Å and degree)

	b) 	c) 	d) 
$(C–C)_{av}$[e]	1.545 (10)[f]	1.546 (8)	1.549 (3)
C_1–C_2	1.539 (12)	1.533 (14)	—
C_2–C_3	1.557 (25)	1.571 (15)	—
θ	113.1 (18)	113.5 (8)	115.3 (2)
$\angle C_1C_2C_3$[g]	103.3 (7)	100.3 (6)	105.8 (8)

a) Distances in r_g and angles in r_α (r_{av} for c). Uncertainties represent estimated limits of error attached to the last significant digits. b) Bicyclo[2.2.1]heptane, Ref. 4. c) 7-oxanorbornane, the present study. d) 7-thianorbornane, Ref. 5. e) The weighted average value of the C_1–C_2 and C_2–C_3 bond lengths. f) Calculated from the C_1–C_2 and C_2–C_3 bond lengths reported in Ref. 4. g) Calculated from the independent parameters.

Table 9. Comparison of the skeletal structures of related molecules[a]

	29) 	28) 	b) 
C–O	1.418 (3)[c]	1.428 (2)	1.442 (10)
$\angle$COC	111.5 (15)a	106—111[d]	94.5 (22)av
	30) 	31) 	5) 
C–S	1.805 (3)	1.841 (2)	1.837 (6)
$\angle$CSC	99.0 (3)av	93.4 (5)a	80.1 (8)α
	32) 	33) 	4) 
C–C	1.532 (3)	1.546 (1)	1.56_0 (2_4)
$\angle$CCC	112.4 (12)α	102—106[d]	93.1 (17)α

a) r_g distances in Å and r_a (a), r_α (α), and r_{av} (av) angles in degree with the uncertainties quoted in the literature attached to the last significant digits. b) The present study. c) Estimated from the r_a distances reported in the literature by addition of l^2/r_a. d) Pseudorotation.

4) Oxanorbornane has the smallest C_1–C_2–C_3 angle among the three, this angle being about 9° less than the tetrahedral angle.

The structure of oxanorbornane is compared in Table 9 with those of tetrahydrofuran[27,28] (a monocyclic ether), and dimethyl ether[29] (an acyclic ether). The C–O–C bond angle in oxanorbornane is about 17° smaller than that in dimethyl ether and in tetrahydrofuran (nearly free pseudorotation). Also the C–O bond in oxanorbornane is longer than those in tetrahydrofuran and dimethyl ether by about 0.01 and 0.02 Å, respectively.

These trends conform to those observed in the corresponding hydrocarbons and sulfides[30–33] (except that the C–S bond in tetrahydrothiophene seems to be slightly longer than or nearly equal to that in thianorbornane), and present a quantitative basis for semiempirical or empirical calculations[34] of the effect of intramolecular strain in bicyclic compounds.

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