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Molecular Structure of Nortricyclene Studied by Gas Electron Diffraction

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The molecular structure of nortricyclene (tricyclo[2.2.1.$0^{2,6}$]heptane) has been studied by gas phase electron diffraction. The average values of the bond distances and their limits of error are: r_g(C–C)$=1.532\pm0.003$ Å and r_g(C–H)$=1.11_4\pm0.01_1$ Å. It is further shown that $r_g(C_3–C_4)=1.55_4\pm0.01_3$ Å, $r_g(C_1–C_2)+r_g(C_2–C_3)=3.04_2\pm0.01_0$ Å, and $\angle C_1–C_7–C_4=96.9\pm0.5°$.

As a part of the structure studies of polycyclic molecules,1) we have recently determined the structures of norbornane (bicyclo[2.2.1]heptane)2) and quadricyclene (tetracyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane)3) by gas electron diffraction. These two compounds have considerably different C_1–C_7–C_4 angles, 93.1±1.7° and 98.5±2°, respectively. Nortricyclene (tricyclo[2.2.1.$0^{2,6}$]heptane), placed between the above molecules, forms a sequence of increasingly strained compounds (Fig. 1); the strain energies are estimated to be about 18, 45, and 100 kcal/mol for norbornane, nortricyclene, and quadricyclene, respectively.4,5) The solvolytic reactivity of 3-bromonortricyclene is about equal to that of *endo*-3-substituted norbornane and very much less than that of *exo*-3-substituted norbornane.6)

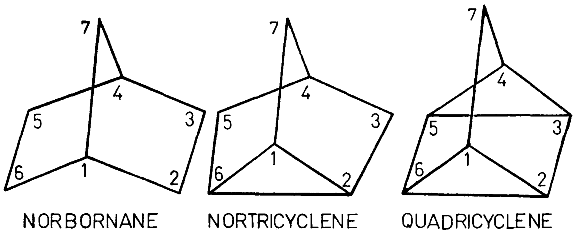

Fig. 1. a) Norbornane, b) Nortricyclene, c) Quadricyclene.

The molecular geometry of nortricyclene was first studied by the visual electron diffraction method by Heilbronner and Schomaker.7) They determined the average C–C bond distance to be 1.527 Å and showed that the C_2–C_3 and C_3–C_4 distances have normal values (about 1.54 Å) if the C_1–C_2 distance is close to that in cyclopropane (about 1.50 Å). They also estimated the C_1–C_7–C_4 angle to be 96.5° with a limit of error of about 2°. One of its derivatives, 4-chloro-

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nortricyclene, has recently been investigated by electron diffraction[8] and by microwave spectroscopy.[9] The present study aims to supply further information on the structure of nortricyclene.

Experimental

A sample of nortricyclene (bp 108—110 °C) with less than 3% impurity, most of which was norbornene, was kindly supplied by Professor I. Tabushi of Kyoto University.[10] Diffraction experiments were carried out at 20 °C with a sample pressure of 30 Torr. Three diffraction photographs taken with 40 kV electrons at a camera length of 107.73± 0.01 mm were analyzed.[11] Diffraction photographs of CO_2 were used for calibration. The molecular intensity curves and the radial distribution curves (Figs. 2, 3) were obtained by standard procedures[12] in the q range from 25 to 120 $Å^{-1}$.

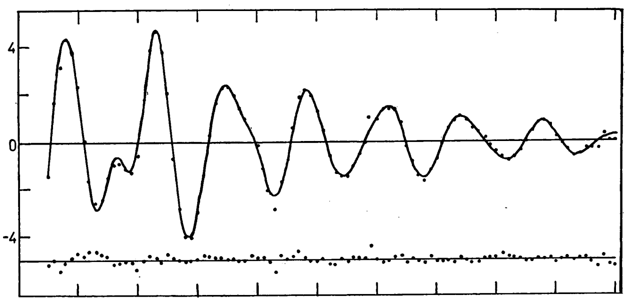

Fig. 2. Experimental molecular intensity for nortricyclene and the residuals (experimental minus best-fit theoretical).

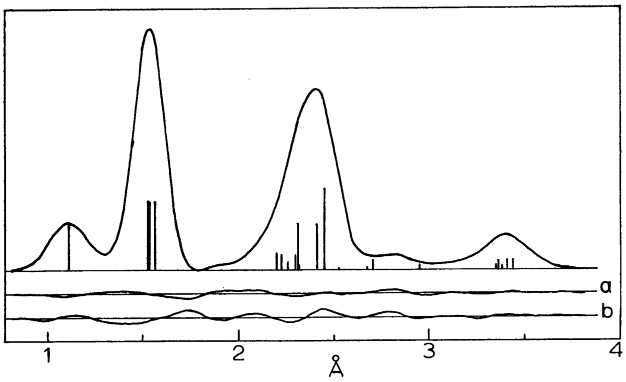

Fig. 3. Experimental radial distribution curve for nortricyclene with an artificial damping factor of $\exp(-0.00160s^2)$ and the residuals [(a) experimental minus best-fit theoretical and (b) experimental minus best-fit theoretical with all the C–C bond lengths assumed to be equal].

Analysis

The data were analyzed under the following assumptions:

1) The molecule has C_{3v} symmetry.
2) All C–H bond lengths are equal.
3) Angle H–C–H equals 110°, the angle in norbornane.[2]
4) The H–C_i–H and C–C_i–C angle bisectors (i= 3, 5, 7) are colinear.
5) The methine C–H bonds make equal angles with the adjacent C–C bonds.
6) Vibrational mean square amplitudes and shrinkage corrections (r_a-r_α)[2,13] were calculated from a reasonable set of Urey-Bradley force field parameters (Table 1) and held constant. The calculated values are listed in Table 2.

TABLE 1. UREY-BRADLEY FORCE FIELD PARAMETERS ASSUMED FOR NORTRICYCLENE[a]

K_{CC}	2.2	H_{CCC}	0.3	$F_{C\cdots C}$	0.2
K_{CH}	4.0	H_{CCH}	0.2	$F_{C\cdots H}$	0.5
		H_{HCH}	0.43	$F_{H\cdots H}$	0.05

a) The units of K and F are md/Å and of H are md. The estimated force constants are taken from Table 1 of Ref. 2 and modified slightly.

TABLE 2. CALCULATED MEAN AMPLITUDES (l_{ij}) AND SHRINKAGE CORRECTIONS (d_{ij}) FOR NORTRICYCLENE[a] (10^{-4}Å)

Atom pair	l_{ij}	d_{ij}	Atom pair	l_{ij}	d_{ij}
C_1–C_2	534	14	$C_7\cdots H_2$	1095	23
C_2–C_3	530	16	$C_1\cdots H_{7a}$	1059	59
C_3–C_4	525	16	$C_4\cdots H_{7a}$	1059	59
C–H	771	131	$C_7\cdots H_4$	1033	27
$C_1\cdots C_4$	586	−1	$C_1\cdots H_4$	947	20
$C_3\cdots C_5$	721	−5	$C_5\cdots H_{7a}$	1016	34
$C_1\cdots C_3$	665	−4	$C_5\cdots H_{7b}$	1537	−23
$H_{7a}\cdots H_{7b}$	1302	120	$C_6\cdots H_{7a}$	1019	30
$C_1\cdots H_2$	1025	56	$C_6\cdots H_{7b}$	1441	−11
$C_3\cdots H_2$	988	60	$C_4\cdots H_2$	929	37

a) The amplitudes and shrinkage corrections[2] (r_a-r_α) calculated for 20 °C.

7) The asymmetry parameter κ for the C–H bond was assumed to be 1.0×10^{-5} $Å^3$, and the rest of the κ parameters were ignored.[14]

Under the above assumptions the structure is defined by five parameters: the C_1–C_2 (r_1), C_2–C_3 (r_2), C_3–C_4 (r_3) and C–H (average) distances (r_g) and angle C_1–C_7–C_4 (θ defined in the r_α structure[13]). The constraint that all the C–C bond distances were equal was added initially and the average bond distances were determined by a least squares analysis.[15] The best estimates and limits of error were: $r_g(\text{C–C})_{av}=1.531_8\pm0.002$ Å and $r_g(\text{C–H})_{av}=1.114\pm0.011$ Å, and the effective C–C

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[12] Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan (Document No. 7311).

[13] K. Kuchitsu and S. J. Cyvin, "Molecular Structures and Vibrations" (S. J. Cyvin, Ed.), Elsevier, Amsterdam (1972), Chapter 12.

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TABLE 3. ERROR MATRIX[a)]

	C_2–C_3	C_3–C_4	C–H_{av}	∠C_1–C_7–C_4	k
C_2–C_3	39	−37	−8	17	−52
C_3–C_4		39	2	−16	54
C–H_{av}			34	−14	22
∠C_1–C_7–C_4				23	−32
k					124

a) Defined in Ref. 16. Units of distances, angle and index of resolution (k) are 10^{-4} Å, 10^{-4} rad. and 10^{-4}, respectively.

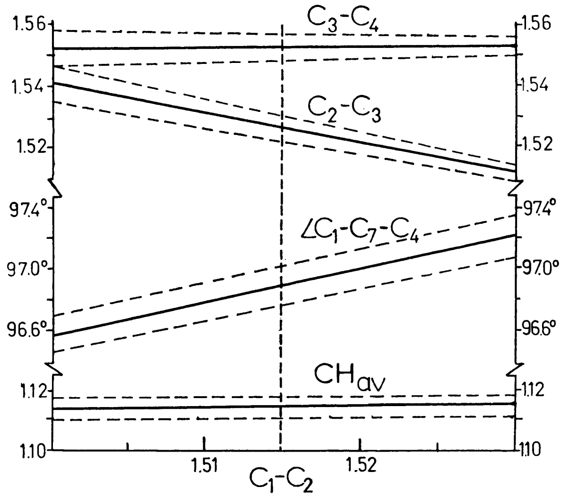

Fig. 4. Correlation of refined parameters with C_1–C_2 in nortricyclene. The vertical dashed line indicates the most probable structure. See text.

mean amplitude was 0.0549±0.003 Å.

Then the constraint of equal C–C distances was released. A series of least squares analyses showed that our experimental data contained information to determine four structural parameters. Thus the r_1 parameter was fixed to several different values, and the rest of the parameters were refined. A typical error matrix[16)] is given in Table 3. The most probable estimates of the varied parameters do not depend on the choice of their initial values, but they are not necessarily independent of the choice of r_1. The dependence of the refined parameters on r_1 is shown in Fig. 4 where the value of each parameter bracketed by one standard deviation is plotted against r_1. The r_3 and the C–H_{av} distances are nearly independent of r_1, but the r_2 distance and θ vary linearly with r_1, so that the following equations are found to exist:

$$r_1 + r_2 = 3.04_2 \pm 0.01_0 \text{ Å} \tag{1}$$

$$\theta = 96.8_6 \pm 0.4 + 20(r_1 - 1.515)^\circ \tag{2}$$

The above relations were also confirmed by examination of the weighted sum of squared residuals, ***V′PV***, determined for each model. The sum forms a deep valley in the parameter hyperspace along the path defined by Eq. (1). ***V′PV*** varies very slowly along that path and forms a shallow minimum at $r_1 \sim 1.51_5$ Å. The parameter values corresponding to this r_1 value are listed in Table 4. The observed intensity and

TABLE 4. THE STRUCTURE OF NORTRICYCLENE[a)]

	Present study[b)]	H.S.[c)]
C–C_{av}	$1.531_8 \pm 0.003$ Å	1.527
C_1–C_2	1.515(ass.)$\pm a$[d)]	1.50
C_2–C_3	$1.52_7 \pm 0.01_3 \mp 1.1a$	1.54
C_3–C_4	$1.55_4 \pm 0.01_3$	1.54
∠C_1–C_7–C_4	$96.9 \pm 0.4 \pm 20a^\circ$	97±2°
C–H_{av}	$1.11_4 \pm 0.01_1$	1.10
k	$0.95_7 \pm 0.04$	

Dependent parameters[d)]

∠H–C–H	110°(ass.)	∠C_1–C_2–C_3	107.0°
∠C_3–C_4–C_7	101.5°	∠H–C_1–C_2	122.6°
∠C_3–C_2–(C_1–C_2–C_6)	109.7°		

a) The distances are r_g and the angles are derived from the thermal average (r_α) structure.

b) The errors are 2.5 times a standard deviation derived from a combination of constraint, least squares and scaling errors (See text and Table 5). The values proportional to a indicate the correlation of each parameter with the value of C_1–C_2. The estimated upper limit of a is 0.015 Å.

c) r_a structure. Ref. 7.

d) Dependent parameter values calculated from the structure determined in the present study.

radial distribution curves and those calculated from the best model agree with each other within experimental error (Figs. 2 and 3).

The error limits given in Table 4 contain contributions from several sources: (a) Most of the errors due to constraints 2) through 7) listed above are small compared to the least squares standard errors, as listed in Table 5. They are assumed to be the changes in the refined parameter values caused separately by: (1) allowing the methine C–H distance to be 0.01 Å less than the methylene distance, (2) changing angle H–C–H by 3°, (3) displacing the H–C_i–H angle bisectors by 2° from their respective C–C_i–C angle bisectors toward C_4, (4) bending the methine C–H bond 3° away from the three-fold axis, (5) increasing each vibrational amplitude uniformly by 5%, (6)

TABLE 5. ERRORS DUE TO CONSTRAINTS IN THE STRUCTURE ANALYSIS

Test[a)]	C–C_{av}[b)]	C–H_{av}[b)]	∠C_1–C_7–C_4[c)]	k[d)]
1	1	1	3	0
2	1	21	2	3
3	0	1	1	0
4	0	4	6	1
5	0	10	6	12
6	2	9	1	0
7	0	5	0	0
σ[e)]	7	34	13	10
Scale[f)]	6	4	0	0
Total[g)]	30	108	40	40

a) Change in the parameters assumed in the least squares analysis. Tests 1 through 7 correspond to those described in text.

b) c) The units are 10^{-4} Å and 10^{-2} degrees, respectively.

d) Index of resolution (10^{-3}).

e) Standard deviation of the least squares analysis.

f) Standard systematic uncertainty in the scale factor.

g) Total estimate of the limit of error.

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Table 6. Comparison of related structures

	Norbornane[a] ED[b]	Nortricyclene[a] ED[c]	Quadricyclene ED[d]	4-Chloronortricyclene	
				ED[e]	MW[f]
$C-C_{av}$	1.549 (3)	1.532 (3)	1.529 (3)	1.527 (3)	1.530
C_1-C_2	1.539 (12)	1.51_5 (1_5)	1.51 (2)	1.510 (16)	1.527
C_2-C_3	1.55_7 (25)	1.52_7 (2_1)	1.56 (2)	1.535 (10)	1.525
C_1-C_7	1.56_0 (24)		1.54 (3)		
C_3-C_4	1.539 (12)	1.55_4 (1_3)	1.51 (2)	1.537 (5)	1.538
$\angle C_1-C_7-C_4$	93.1 (17)	96.9 (5)	98.5 (20)	95.6	96.2
$\angle C_1-C_2-C_3$	103.3	107.0	104.6	107.0	106.6
$\angle (C_1-C_2-C_6)-(C_2-C_3-C_5-C_6)$	106.7	100.9	107.0	102.5	101.8

a) The distances are r_g, and the angles are θ_a defined in Ref. 13. The error limits in parentheses refer to the least significant figure.

b) Ref. 2.

c) The present study.

d) Ref. 3.

e) Ref. 8. The distances are r_a and angles are calculated from those with neglect of shrinkage effects.

f) Ref. 9. The distances and angles are derived from Kraitchman's equation.

diminishing each shrinkage correction by 10% and (7) changing the C–H asymmetry parameter by 30%. (b) The reproducibility of each of the refined parameters among the three plates was less than or equal to the least squares standard deviation. (c) As for the effects of the above assumptions on the separate analysis of the r_2 and r_3 distances, the mean amplitudes of the C–C bonds (5) are the only important source of error. When the three C–C amplitudes were increased uniformly by 5%, the least squares values for the r_2 and r_3 distances were changed by 0.006 Å and −0.007 Å, respectively. (d) An estimated standard error[17] of 0.04% in the scale factor was counted. (e) The square root of the sums of squares of the above errors was multiplied by 2.5 to give the error limit listed after each parameter in Table 4.

With reference to the r_a(C–C) distances in cyclopropane,[18] 1.510 ± 0.002 Å and in 4-chloronortricyclene,[8] 1.510 ± 0.016 Å, r_1 is assumed to be $1.515 \pm a$ Å, where the upper limit of a is estimated to be 0.015. The second error limit proportional to a, listed separately in Table 4, accounts for the uncertainty in r_1 and the effects of the correlation among the parameters shown in Fig. 4. Thus the final estimates of the r_2 and θ parameters are 1.53 ± 0.02 Å and $96.9 \pm 0.5°$, respectively.

It should be mentioned that the above assignment of the radial distribution peak at 2.4 Å is not unique. This peak is mainly composed of the three nonbonded C–C distances: C_1-C_3, C_1-C_4, and C_3-C_5, and an alternative assignment corresponding to θ equal to 105.3°, instead of 96.9°, is also consistent with the electron diffraction data, as Heilbronner and Schomaker pointed out.[7] They noted, however, that the force field consistent with such an equilibrium structure does not compare reasonably with force fields of related molecules. Further evidence that this assingment is hardly acceptable is given by a comparison of this angle with the corresponding angle in 4-chloronortricyclene (Table 6). In the chloro compound the microwave rotational constants[9] allow no ambiguity of this sort, and the C–C assignment in the electron diffraction study[8] is also less ambiguous than in nortricyclene.

Discussion

The nortricyclene structure reported by Heilbronner and Schomaker[7] has been confirmed to be accurate to within their reported limits of error (Table 4). The present study has considerably increased the accuracy of the molecular intensity and of the structural parameters. The average C–C bond length, 1.532 ± 0.003 Å, is nearly equal to the corresponding average value for 4-chloronortricyclene, 1.527 ± 0.003 Å (r_a)[8] or 1.530 Å (r_0).[9] It is considerably shorter than the average bond length in norbornane,[2] 1.549 ± 0.003 Å, but not significantly different from the value in quadricyclene,[3] 1.529 ± 0.003 Å. This reflects the effect of formation of a cyclopropane ring, with its relatively short bonds, in the transformation from norbornane to nortricyclene. In the transformation from nortricyclene to quadricyclene, however, there seem to be balancing effects of formation of a cyclobutane ring, with its relatively long bonds, and that of another cyclopropane ring. The C_3-C_4 bond, 1.55_4 Å, is longer than C_2-C_3, 1.52_7 Å, and appears to be only slightly longer than the value in cyclopentane, 1.546 ± 0.001 Å.[19] The C_2-C_3 bond seems to be similar to the r_s value, 1.522 Å, found in methylcyclopropane.[20] Bond angles determined in the present study agree reasonably well with the corresponding angles in the chloro compound. Angle $C_1-C_7-C_4$ increases regularly among norbornane, nortricyclene and quadricyclene. A more precise deter-

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mination of the C–C bond distances must await the availability of rotational constants so that a combined electron diffraction-spectroscopy analysis[1,21] may be carried out.

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