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Structures of Norbornane and Norbornadiene as Determined by Gas Electron Diffraction

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The structures of norbornane and norbornadiene in the gas phase have been investigated by electron diffraction. For the most probable models the r_g bond lengths and the bond angles (based on the r_α structure) with estimated limits of error are as follows: For norbornadiene: C_1–$C_2 = 1.535_4 \pm 0.007$ Å, C_2=$C_3 = 1.343_2 \pm 0.003$ Å, C_1–$C_7 = 1.57_3 \pm 0.01_4$ Å, $\angle C_1$–C_7–$C_4 = 94._1 \pm 3._0°$, and θ (the dihedral angle between the C_1–C_2–C_3–C_4 and C_4–C_5–C_6–C_1 planes) $= 115._6 \pm 2._2°$; For norbornane: C–C(average) $= 1.548_8 \pm 0.003$ Å, C_1–$C_2 = 1.53_9 \pm 0.01_2$ Å, C_2–$C_3 = 1.55_7 \pm 0.02_5$ Å, C_1–$C_7 = 1.56_0 \pm 0.02_4$ Å, $\angle C_1$–C_7–$C_4 = 93._1 \pm 1._7°$, and $\theta = 113._1 \pm 1._8°$. The frame structures of these molecules are similar to each other except for the C_2–C_3 bond distances. All the C–C–C valence angles are appreciably smaller than the tetrahedral angle ($\angle C_1$–C_7–C_4 in particular). The C_1–C_7 bridge bonds appear to be longer than the normal C–C single bond. The above structures are compared critically with those reported so far by other investigators. A method for estimation of systematic errors in the structural parameters derived from a least-squares analysis with fixed mean vibrational amplitudes is discussed.

Norbornane (bicyclo[2.2.1]heptane), norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) (Fig. 1), and their derivatives have been investigated in detail by physical and chemical methods with particular attention to the effect of intramolecular strain. Extensive studies by X-ray diffraction[1] have shown that the carbon bond angles in analogous molecules with camphane frameworks are less than the tetrahedral angle. Particularly striking is the value reported for the angle at the methylene bridge ($\angle C_1$–C_7–C_4: 93°—96°), so that the skeleton must be strained considerably. Theoretical calculations of the geometrical parameters and the conformational energy of norbornane also indicate the above trend.[2–6] The total strain energies in norbornane and norbornadiene, as measured by the heats of combustion and hydrogenation, are 18.4 and 29.0 kcal/mol, respectively.[7] Further support for this strain is given by NMR studies,[8] by which an unusual behavior of the rings toward the magnetic shielding and the proton coupling constants was observed and ascribed to the *p*-character of the C–C bonds in the strained rings. Chemical reactivities such as their high rates of solvolysis are also considered to be closely related to the above-mentioned characteristics.[9]

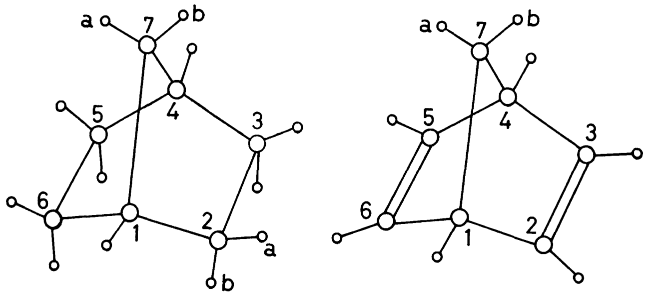

Fig. 1. The numbering of norbornane (left) and norbornadiene (right).

The present study was initiated to obtain as precise information as possible on the gas-phase structures of these molecules by electron diffraction so as to shed light on the strain effect. Several independent studies of electron diffraction,[10–13] including our preliminary report,[14] have recently been published. However, some of the internuclear distances and angles contained significant discrepancies with one another. In order to examine the origin of these discrepancies, a further analysis has here been carried out by making a critical comparison of the experimental data.[15] In addition, care has been taken in the estimation of uncertainties, particularly that of the systematic errors originated in the theoretical mean amplitudes of vibration used in the analysis.

Experimental

Diffraction photographs were taken on Fuji Process Hard plates at 20°C with an apparatus equipped with an r^3-sector.[16]

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[1] For example: D. A. Brueckner, Y. A. Hamor, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, **1962**, 779; G. Ferguson, C. J. Fritcher, J. M. Robertson, and G. A. Sim, *ibid.*, **1961**, 1976; A. C. MacDonald and J. Trotter, *Acta Crystallogr.*, **18**, 243, **19**, 456 (1965); M. C. Baenziger, G. F. Richards, and J. R. Doyle, *ibid.*, **18**, 924 (1965); A. V. Frantini, K. Britts, and I. L. Karle, *J. Phys. Chem.*, **71**, 2482 (1967).

[2] A.I. Kitaygorodsky, *Tetrahedron*, **9**, 183 (1960); **14**, 230 (1961).

[3] C. F. Wilcox, *J. Amer. Chem. Soc.*, **82**, 414 (1960).

[4] N. L. Allinger, J. A. Hirsch, M. A. Miller, I. Tyminski, and F. A. Van-Catledge, *ibid.*, **90**, 1199 (1968).

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[6] N. Bodor and M. J. S. Dewar, *ibid.*, **92**, 4270 (1970).

[7] R. B. Turner, P. Goebel, B. J. Mallon, W. V. E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968).

[8] For example, K. Tori, R. Muneyuki, and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

[9] L. N. Ferguson, *J. Chem. Educ.*, **47**, 46 (1970).

[10] W. C. Hamilton, thesis, California Institute of Technology (1954). V. Schomaker and W. C. Hamilton, unpublished research, cited in W. G. Woods, R. A. Carboni, and J. Roberts, *J. Amer. Chem. Soc.*, **78**, 5653 (1956).

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[12] J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968).

[13] a) G. Dallinga and L. H. Toneman, *Rec. Trav. Chim.*, **87**, 795 (1968). b) *ibid.*, **87**, 805 (1968).

[14] Y. Morino, K. Kuchitsu, and A. Yokozeki, This Bulletin, **40**, 1552 (1967).

[15] Professor S. H. Bauer and Dr. G. Dallinga have kindly supplied the authors with the experimental intensities obtained in their laboratories.

[16] Y. Murata, K. Kuchitsu, and M. Kimura, *Jap. J. Appl. Phys.*, **9**, 591 (1970).

The vapor pressure of norbornane was about 20 Torr, and that of norbornadiene was about 40 Torr. Purified samples of norbornane and norbornadiene were kindly provided by Drs. Hiroshi Tanida and Kazuo Tori of Shionogi Research Laboratory. The vacuum was kept under 5×10^{-5} Torr while the sample gas was introduced into the chamber through a nozzle of 0.2 mm diameter. The beam current was about 0.21 μA. The accelerating voltage (about 40 kV) was stabilized within 0.01% during the experiment, and the electron wavelength was calibrated to within 0.07% with reference to the r_a(C=O) bond length of carbon dioxide, 1.1646 Å.[16] The camera lengths were measured to be 107.77±0.01 and 243.22±0.01 mm. The exposure times were about 210 and 60 sec for the shorter and longer camera lengths, respectively, for norbornane, and about 80 and 40 sec for norbornadiene. The photographs were developed at 20°C for 5 min with FD-131 developer diluted twice.

Four plates for each camera length were used for intensity measurements. The optical densities of the plates were measured at the intervals of integral q values (from 17 to 120 and 15 to 60 for the shorter and longer camera lengths, respectively) using an integrating digital microphotometer.[17] The optical densities thus obtained (0.09 to 0.52), were in the range where the densities were found to be proportional to the electron intensities. Most of the calculations were carried out on a HITAC-5020E computer in the Computer Centre of the University of Tokyo.

Analysis

The molecular intensities, $qM(q)$, were obtained from the observed total intensities by the usual procedure[18]; they are illustrated in Fig. 2.[19] Molecular intensites obtained from different photographic plates deviated from one another randomly by about 0.25.

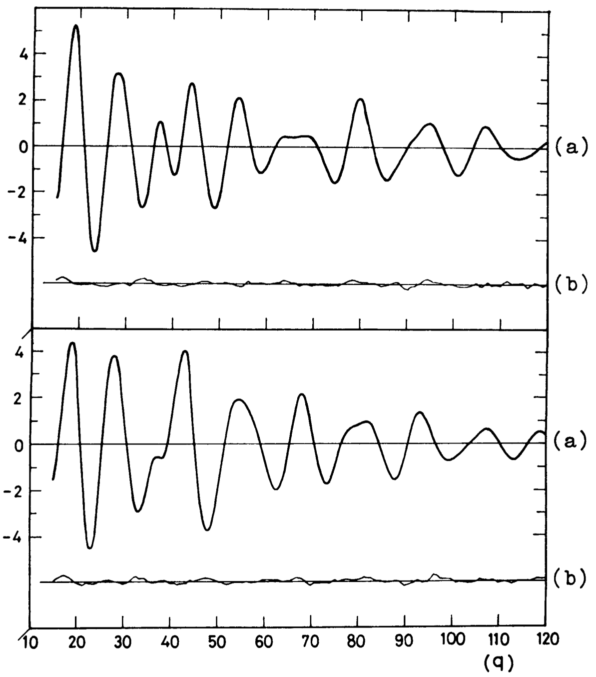

Fig. 2. Molecular intensity curves $qM(q)$ of norbornadiene (upper) and norbornane (lower). (a): best-fit theoretical; (b): experimental minus theoretical.

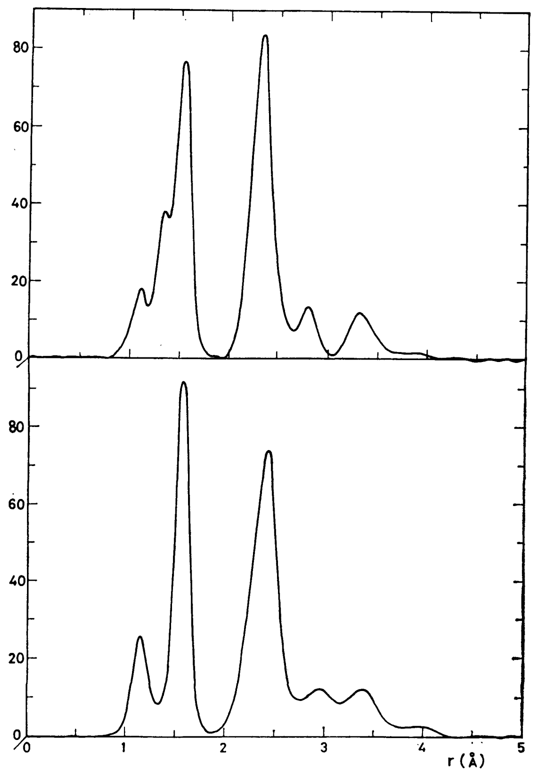

Fig. 3. Experimental radial distribution curves of norbornadiene (upper) and norbornane (lower) with a damping factor of exp($-0.00016q^2$).

Radial Distribution Curves. Modified radial distribution (RD) curves obtained from the molecular intensity curves with a damping factor of exp($-0.00016q^2$) are shown in Fig. 3.

Norbornadiene: Three peaks located in 1—2 Å correspond to the bonded pairs with their maximum positions for C–H at 1.11 Å, C=C at 1.33 Å, and C–C at 1.54 Å. The C–H and C–C peaks are composed of two nonequivalent atom pairs. The peaks in 2—3 Å contain all nonbonded C–C and some of the nonbonded C–H and H–H pairs. In spite of the considerable overlapping of peaks, the RD contour in this region was found to be sufficiently sensitive to determine the carbon skeleton structure. The lower peak at 2.8 Å is almost completely made of the C_2–C_5 and C_3–C_6 pairs, and hence, it affords a good measure of the dihedral angle θ between the C_1–C_2–C_3–C_4 and C_4–C_5–C_6–C_1 planes. A preliminary analysis of this peak showed that θ was about 116°, and from the 2.35 Å peak that $\angle C_1$–C_7–C_4 and $\angle C_1$–C_2–C_3 were about 91° and 107.5°, respectively. The peak in 3—4 Å is made of several nonbonded C···H and H···H pairs. The result of the above analysis was used as a starting model in a least-

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[17] Y. Morino, K. Kuchitsu, and T. Fukuyama, This Bulletin, **40**, 423 (1967).

[18] A. Yokozeki, K. Kuchitsu, and Y. Morino, *ibid.*, **43**, 2017 (1970).

[19] Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan (Document No. 7112). A copy may be secured by citing the document number and by remitting, in advance, ¥200 for photoprints. Payment by check or money order payable to: the Chemical Society of Japan, 5, 1-Chome, Kanda-Surugadai, Chiyoda-ku, Tokyo.

squares refinement on molecular intensities.

Norbornane: The first peak of the RD curve corresponds to the bonded C–H distances, the average value of which is 1.11 Å. The second peak at 1.55 Å contains three closely-spaced nonequivalent C–C pairs. Being analogous to norbornadiene, the peaks in 2—3 Å correspond to nonbonded C···C, C···H, and H···H pairs. If the skeleton has C_{2v} symmetry, the longer distance of the C_2–C_5 and C_3–C_6 should correspond to the peak at 2.9 Å. Since all attempts to account for the RD peaks in terms of a C_2 structure were unsuccessful, a C_{2v} structure was favored.

TABLE 1. ESTIMATED FORCE CONSTANTS FOR NORBORNANE AND NORBORNADIENE[a]

K(C–C)	2.3	H(C–C–C)	0.32	F(C–C–C)	0.20
K(=C–C)	3.0	H(C–C=C)	0.25	F(C–C=C)	0.35
K(C=C)	7.4	H(C–C–H)	0.225	F(C–C–H)	0.41
K(C–H)	4.1	H(C=C–H)	0.21	F(C=C–H)	0.36
K(=C–H)	4.3	H(H–C–H)	0.40	F(H–C–H)	0.18
Y(=C–C)	0.16	Y(C=C)	0.50	Y_{cis}(C–C)	0.11
$\underset{gauche}{Y(\mathrm{C–C})}$	0.15	W(C=C–H)	0.35		

a) Estimated force constants taken from those for cyclohexane[23] and several olefins (butene, pentene, *etc.*),[24] The torsional (Y) and wagging (W) force constants are in md·Å, and the others are in md/Å units.

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

Atom pair	l_{ij}	d_{ij}	Atom pair	l_{ij}	d_{ij}
C_1——C_2	508	8	$C_1\cdots\cdots H_7$	1063	31
C_2——C_3	428	27	$C_7\cdots\cdots H_1$	1047	20
C_1——C_7	530	3	$C_1\cdots\cdots H_2$	982	49
$C_1\cdots\cdots C_4$	584	−4	$C_2\cdots\cdots H_{7b}$	1401	−14
$C_1\cdots\cdots C_3$	583	1	$C_3\cdots\cdots H_1$	972	18
$C_2\cdots\cdots C_7$	680	−4	$C_4\cdots\cdots H_1$	943	18
$C_2\cdots\cdots C_6$	714	−5	$C_6\cdots\cdots H_2$	1190	16
$C_2\cdots\cdots C_5$	769	−11	$C_4\cdots\cdots H_2$	955	35
C_2——H_2	784	109	$C_7\cdots\cdots H_2$	996	26
C_1——H_1	785	82	$C_2\cdots\cdots H_{7a}$	996	26
$C_3\cdots\cdots H_2$	984	62	$C_5\cdots\cdots H_2$	1173	12
$C_2\cdots\cdots H_1$	1028	25			

a) For 20°C. The H······H pairs are not listed.

TABLE 3. CALCULATED MEAN AMPLITUDES (l_{ij}) AND SHRINKAGE CORRECTIONS (d_{ij}) FOR NORBORNANE[a] (10^{-4} Å)

Atom pair	l_{ij}	d_{ij}	Atom pair	l_{ij}	d_{ij}
C_1——C_2	530	11	$C_7\cdots\cdots H_1$	1058	21
C_2——C_3	526	23	$C_2\cdots\cdots H_{7b}$	1440	−17
C_1——C_7	530	5	$C_6\cdots\cdots H_{2b}$	1533	−14
$C_1\cdots\cdots C_4$	593	−3	$C_7\cdots\cdots H_{2a}$	1437	−7
$C_2\cdots\cdots C_7$	687	−2	$C_4\cdots\cdots H_{2b}$	1178	19
$C_1\cdots\cdots C_3$	617	0	$C_5\cdots\cdots H_{2b}$	1694	−40
$C_2\cdots\cdots C_6$	371	−1	$C_7\cdots\cdots H_{2b}$	1028	35
$C_2\cdots\cdots C_5$	821	−13	$C_2\cdots\cdots H_{7a}$	1006	28
C_1——H_1	785	84	$C_6\cdots\cdots H_4$	955	19
C_2——H_3	1072	63	$C_2\cdots\cdots H_4$	993	17
$C_1\cdots\cdots H_2$	1072	49	$C_6\cdots\cdots H_{2a}$	1059	34
$C_1\cdots\cdots H_7$	1063	34	$C_5\cdots\cdots H_{2a}$	1089	14
$C_2\cdots\cdots H_1$	1042	28			

a) For 20°C. The H······H pairs are not listed.

Least-Squares Refinements on Intensity Curves. The intensity curve was fitted to the corresponding theoretical expression by a least-squares method with a preset weight function.[20] The mean amplitudes and shrinkage corrections of vibration[21] for all the internuclear distances were calculated on the basis of an estimated force model using the Urey-Bradley force field,[22] to which force constants for simple molecules with analogous geometrical arrangements (cyclohexane,[23] pentene, butene, *etc.*)[24] were transferred (listed in Table 1). A detailed procedure for the calculations is given elsewhere.[21] Numerical results are listed in Tables 2 and 3; they were used as fixed constants in the analysis. Systematic errors due to this constraint are examined in later sections. The asymmetry parameters κ for the bonded C–H were estimated to be 1.0×10^{-5} Å^3 and used as constants.[25]

Choice of Independent Parameters. *Norbornadiene*: This molecule is expected to have a C_{2v} structure. The RD analysis and a preliminary least-squares analysis on the intensity curves showed that the equilibrium structure of this molecule belongs to this symmetry. Thus the total number of independent parameters is twelve. In order to make the analysis easier, the following additional assumptions were taken into account.

1) The C–C–H angles are equal at the bridgehead, *i.e.*, $\angle$H–C_1–C_2=$\angle$H–C_1–C_6=$\angle$H–C_1–C_7.

2) All the C(sp^3)–H bond distances are equal.

3) The C(sp^2)–H bond distances are equal to that in ethylene, $r_\alpha=1.0896$ Å.[26]

4) The vinylene group (C_1–CH=CH–C_4) is planar.

These assumptions reduced the number of independent parameters to eight. Regarding the skeleton structure, three distances (C_1–C_2, C_2=C_3, and C_1–C_7) and two angles ($\angle C_1$–C_7–C_4 and θ defined above) were chosen. The parameters for hydrogen positions were $\angle$H–C_7–H, $\angle$C=C–H and the (weighted-average) C(sp^3)–H distance.

Norbornane: As mentioned in the preceding subsection, a C_{2v} structure was favored for this molecule, in which the structure are defined by fifteen independent parameters. Additional assumptions on the r_α structure[21,27] were as follows.

1) The H–C_2–H plane is perpendicular to the C_1–C_2–C_3 plane and bisects the C_1–C_2–C_3 angle, and *vice*

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[20] Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Crystallogr.*, **18**, 549 (1965).

[21] K. Kuchitsu and S. Konaka, *J. Chem. Phys.*, **45**, 4342 (1966).

[22] The authors are grateful to Drs. Ichiro Nakagawa and Toyotoshi Ueda for allowing them to use programs "BGLZ" and "MV" and for their helpful advice on the force constants.

[23] H. Takahashi and T. Shimanouchi, *J. Mol. Spectrosc.*, **13**, 43 (1964).

[24] T. Shimanouchi, Y. Abe, and Y. Alaki, *Polymer J.* **2**, 199 (1971). The authors thank Professor Takehiko Shimanouchi and the other authors for giving their experimental results before publication.

[25] K. Kuchitsu, This Bulletin, **40**, 498 (1967).

[26] K. Kuchitsu, *J. Chem. Phys.*, **44**, 906 (1966).

[27] G. Dallinga and L. H. Toneman, *J. Mol. Structure*, **1**, 11 (1967); K. Kuchitsu, T. Fukuyama, and Y. Morino, *ibid.*, **1**, 463 (1968).

versa.

2) The C–C–H angles are equal at the bridgehead, *i.e.*, $\angle$H–C_1–C_2=$\angle$H–C_1–C_6=$\angle$H–C_1–C_7.

3) All the C–H bond distances are equal.

4) All the H–C–H bond angles are equal.

Thus the number of independent parameters was reduced to seven. For the skeleton structure, three non-equivalent carbon-carbon distances, C_1–C_2, C_2–C_3, and C_1–C_7, and two angles, $\angle C_1$–C_7–C_4 and θ, were chosen as parameters. For hydrogen positions, a weighted-average C–H bond distance and the H–C–H angle were varied. In our earlier report,[14] the C_1–C_2 and C_2–C_3 distances were assumed to be equal, but this constraint has been released in the present analysis.

Results of the Analysis. The above analysis led to the most probable parameters with random standard

TABLE 4. LEAST-SQUARES RESULTS FOR NORBORNADIENE AND NORBORNANE[a)]

Independent parameters	Norbornadiene		Norbornane
	I	II	
C_1——C_2	$1.533_2 \pm 0.001_4$	$1.532_9 \pm 0.001_3$	$1.536_2 \pm 0.002_9$
C_2——C_3	$1.338_7 \pm 0.001_2$	$1.338_3 \pm 0.001_1$	$1.552_7 \pm 0.008_7$
C_1——C_7	$1.571_1 \pm 0.003_1$	$1.571_2 \pm 0.003_0$	$1.557_9 \pm 0.008_6$
$\angle C_1$–C_7–C_4	$92.2 \pm 0.4°$	$96.0 \pm 0.2°$	$93.1 \pm 0.6°$
θ	$114.7 \pm 0.3°$	$116.4 \pm 0.4°$	$113.1 \pm 0.6°$
$\angle$C=C–H	$125._2 \pm 1._4°$	$122._3 \pm 1._3°$	——
$\angle$H–C–H	$114._7 \pm 3._0°$	$112._6 \pm 2._9°$	$109._9 \pm 1._5°$
C(sp^3)–H	$1.109_4 \pm 0.004_7$	$1.110_8 \pm 0.004_6$	$1.111_7 \pm 0.002_0$
k	$0.97_9 \pm 0.01_1$	$0.98_5 \pm 0.01_0$	0.986 ± 0.009

a) The r_a structures (in Å units for distances) with the random standard errors derived from least-squares analyses. The index of resolution k is dimensionless. For norbornadiene, two structures I and II significantly different from each other (particularly in the C_1–C_7–C_4 angle) have been obtained (see text).

TABLE 5. ERROR MATRIX FOR NORBORNADIENE[a)]

	C_1–C_2	C_2–C_3	C_1–C_7	C–H	$\angle C_1$–C_7–C_4	θ	$\angle$H–C–H	$\angle$C=C–H	k
C_1——C_2	14 13	7	−20	11	25	−22	38	42	−31
C_2——C_3	7	12 11	−12	10	13	−10	9	30	−17
C_1——C_7	−18	−11	31 30	−19	−39	35	−64	−50	47
C——H	8	9	−16	47 46	15	−19	77	54	−35
$\angle C_1$–C_7–C_4	12	6	−19	15	62 34	−38	103	43	−67
θ	−25	−13	39	−14	−21	53 63	−78	−72	55
$\angle$H–C–H	46	21	−72	65	−66	−120	461 501	197	−147
$\angle$C=C–H	40	28	−49	46	30	−76	201	258 226	−119
k	−30	−18	44	−29	6	69	−167	−120	107 105

a) Error matrix for the independent parameters. Units (10^{-4}) for the distances are Å, those for the angles are rad., and the index of resolution k is dimensionless. The upper and lower triangles represent the elements for the solutions I and II in Table 4, respectively (see text).

TABLE 6. ERROR MATRIX FOR NORBORNANE[a)]

	C_1–C_2	C_2–C_3	C_1–C_7	C–H	$\angle C_1$–C_7–C_4	θ	$\angle$H–C–H	k
C_1——C_2	29	−86	−21	−4	39	−57	−86	−22
C_2——C_3		87	−48	7	32	50	128	−48
C_1——C_7			86	−6	−65	66	−44	60
C——H				20	2	−5	46	6
$\angle C_1$–C_7–C_4					97	−84	105	−68
θ						99	−30	74
$\angle$H–C–H							313	38
k								92

a) Error matrix for the independent parameters. Units (10^{-4}) for the distances are Å, those for the angles are rad., and the index of resolution k is dimensionless.

errors shown in Table 4. The corresponding error matrices[28] are listed in Tables 5 and 6. Two alternative sets of solutions were obtained for norbornadiene. In particular, the C_1–C_7–C_4 angle converged to I 92.2°±0.4° and II 96.0°±0.2°, depending on the initial values of the analysis; any initial value smaller than 94° led to solution I, while any of those larger than that led to solution II. Changes in the other parameters due to correlation with the C_1–C_7–C_4 parameter were within about three times the corresponding random standard errors (see Table 4). These alternative solutions (I and II) were equally probable, since the variances ($[V^*PV/(n-m)]^{1/2}$) for the solutions were 0.106 and 0.105, respectively. In this connection, the differences in the observed and the most probable theoretical intensities were similar to those among the observed intensities derived from different photographic plates. Accordingly, the variances derived from the above analysis did not provide a clearcut criterion on the resolution of this ambiguity. This problem is further investigated in the following section.

Estimation of Systematic Errors. For some of the parameters, systematic errors due to the uncertainties in the mean amplitudes fixed in the analysis are more important than the random standard errors. In other words, a unique determination of the structure depends critically on the correctness of the estimated amplitudes.[18] In order to investigate this problem, the following method has been considered.

Suppose a probability of finding a set of correct estimates of the mean amplitudes between l_1, l_2,$\cdots$and l_1+dl_1, l_2+dl_2,$\cdots$ is represented by $w(l)dl \equiv w(l_1, l_2,\cdots)\cdot dl_1 dl_2\cdots$. This function is not necessarily a Gaussian, nor may be symmetric about the most probable set. In principle, this function can be estimated if a probability of finding correct estimates of the force constants K, $w(K)dK$, is known. In reality, an order-of-magnitude estimation of $w(l)$ is barely practicable, but it seems to be sufficient for the present purpose.

When a least-squares technique is applied to the molecular intensity with mean amplitudes fixed at l_1, l_2,$\cdots$, the most probable estimates of the variable parameters, x_1, x_2,$\cdots$ and their standard errors depend on l parametrically and constitute a probability distribution of the estimate, $W(x;l)dx$; this function should conform, at least approximately, to a multidimensional Gaussian. The uncertainties in the mean amplitudes fixed in the analysis smear this error distribution in such a way that the total distribution, $P(x)dx$, is a folding of the $W(x;l)$ and $w(l)$ functions,

$$P(x)dx = \int W(x;\, l)w(l)dldx, \tag{1}$$

from which the systematic uncertainties from this origin in the x parameters may be estimated. The above equation can be integrated if analytical functions are assumed for $W(x;l)$ and $w(l)$; otherwise a numerical method may be used. Since a non-random problem is dealt with, the present analysis cannot have a full statistical significance. However, one may still apply the criterion of least squares to an automatic searching for a *plausible* set of parameters and their *possible uncertainties.*

In the present problem, the $w(l)$ function was estimated from our past experience: For simple molecules, errors in the experimental mean amplitudes are less than 10%, and those in the values calculated from assumed force fields are of a similar order. Usually, experimental and theoretical mean amplitudes for bonded atom pairs have smaller uncertainties than those for nonbonded atom pairs. Therefore, the uncertainties in the calculated mean amplitudes (Tables 2 and 3) were assumed to be 10 and 20% for bonded and nonbonded atom pairs, respectively.[29] The $w(l)$ function was assumed to be a product of individual probabilities, $w(l) = \prod_i w_i(l_i)$, where $w_i(l_i)$ were assumed to be independent of each other, constant in the ranges mentioned above and vanishing outside. Equation (1) was calculated by an approximate Monte-Carlo method. A set of the mean amplitudes l_i were prepared randomly by use of a function

$$l_i = l_{i0}\{1+2c_i(r-0.5)\}, \tag{2}$$

where c_i is the estimated uncertainty in the theoretical amplitude l_i (10 or 20%), l_{i0} is given in Tables 2 and 3, and r is a set of uniform random numbers (0.0—1.0) generated by a program G5/TC/RUN1[30] in the program library of the Computer Centre of the University of Tokyo. Least-squares analyses were carried out with more than 20 sets of the fixed mean amplitudes sampled by Eq. (2) for either molecule. The resulting ranges Δ for the most-probable parameter values are listed in Table 7 together with their random standard errors σ_r, which characterize the widths of the $W(x;l)$ function; it turns out that the choice of the l sets does not influence σ_r significantly. In the total limits of error estimated from the table, the widths of $P(x)$ as represented by σ_r and Δ as well as other experimental systematic errors[27] (uncertainties in the scale factor (0.07%), sector imperfection (0.05%), *etc.*) were taken into ac-

TABLE 7. ESTIMATION OF ERRORS

Independent parameters	Norbornadiene		Norbornane	
	σ_r[a]	$\Delta/2$[b]	σ_r	$\Delta/2$
$(C$——$C)_{av}$	$\cdots$	$\cdots$	0.001_0	0.001
C_1——C_2	0.001_4	0.004	0.002_9	0.010
C_2——C_3	0.001_1	0.001	0.008_7	0.021
C_1——C_7	0.003_0	0.009	0.008_6	0.021
∠C_1–C_7–C_4	0.2_1°	$2._8^\circ$	0.6_5°	$1._5^\circ$
θ	0.3_5°	$2._0^\circ$	0.6_4°	$1._7^\circ$
C(sp^3)–H	0.004_6	0.003	0.002_0	0.003
∠C=C–H	$1._3^\circ$	$3._0^\circ$	$\cdots$	$\cdots$
∠H–C–H	$3._0^\circ$	$7._5^\circ$	$1._5^\circ$	$4._0^\circ$

a) Random standard errors derived from least-squares analyses. Units for the distance parameters are Å.

b) One half the range Δ (difference between the upper and lower bounds of the most probable values) derived from the analyses with fixed mean amplitudes (see text).

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TABLE 8. COMPARISON OF THE STRUCTURAL PARAMETERS IN NORBORNADIENE

Parameters	Present[a]	Ref. 14[b]	Ref. 13b[c]	Ref. 11[c]	Ref. 10[c]	Calcd[d]
C_1——C_2	$1.535_4\pm0.007$	1.535 ± 0.005	1.554 ± 0.002	1.549 ± 0.008	$1.522\pm0.01_1$	
C_2══C_3	$1.343_2\pm0.003$	1.343 ± 0.005	1.341 ± 0.002	1.357 ± 0.005	1.333 ± 0.008	
C_1——C_7	$1.57_3\pm0.01_4$	$1.57_5\pm0.01_0$	1.514 ± 0.004	$1.56_8\pm0.01_5$	$1.55_8\pm0.01_6$	
$\angle C_1$-C_7-C_4	$94._1\pm3._0^\circ$	$92.0\pm0.8^\circ$	$99.5\pm0.6^\circ$	96.5° ……	$96._7\pm2._3^\circ$	92°
θ	$115._6\pm2._2^\circ$	$115.0\pm0.8^\circ$	111.4° ……	115.4° ……	110.8° ……	113°
C(sp^3)-H	$1.12_3\pm0.01_4$	$1.11_4\pm0.02_0$				
$\angle$C=C-H	$124\pm3^\circ$	$123\pm4^\circ$				
$\angle$H-C-H	$113\pm8^\circ$	(112°)				

a) The r_g distances (Å) and the r_α angles determined in the present study with estimated limits of error (see text).
b) The r_g distances converted from the r_α distances given in Ref. 14.
c) Distances (r_g) are estimated by adding about 0.0015 Å to those reported in the references (probably r_a).
d) Calculated by a strain-relief scheme (see text).

TABLE 9. COMPARISON OF THE STRUCTURAL PARAMETERS IN NORBORNANE

Parameters	Present[a]	Ref. 14[b]	Ref. 13a[c]	Ref. 12[c]
$(C$——$C)_{av}$	$1.548_8\pm0.003$	1.549 ± 0.002	1.545 ……	1.555 ……
C_1——C_2	$1.53_9\pm0.01_2$	$1.54_2\pm0.01_5$	$1.53_4\pm0.01_4$	$1.55_6\pm0.01_2$
C_2——C_3	$1.55_7\pm0.02_5$	$1.54_3\pm0.02_5$	$1.57_8\pm0.01_8$	$1.55_1\pm0.01_5$
C_1——C_7	$1.56_0\pm0.02_4$	$1.57_0\pm0.01_6$	$1.53_5\pm0.03_5$	$1.55_9\pm0.01_5$
$\angle C_1$-C_7-C_4	$93._1\pm1._7^\circ$	$93._2\pm1._5^\circ$	$95._3\pm1._6^\circ$	$96._0\pm1._0^\circ$
θ	$113._1\pm1._8^\circ$	$113._0\pm1._5^\circ$	$111._3^\circ$ ……	$108._0\pm1._5^\circ$
$(C$——$H)_{av}$	$1.125_6\pm0.005$	$1.12_6\pm0.01_2$	1.11 ± 0.01	$1.11_5\pm0.01_5$
$\angle H$-C-H_{av}	$110\pm4^\circ$	$110\pm3^\circ$	$111\pm4^\circ$	$108\pm1^\circ$

a) The r_g distances (Å) and the r_α angles determined in the present study with limits of error (See text).
b) The r_g distances converted from the r_α distances given in Ref. 14.
c) Distances (r_g) are estimated by adding 0.0018 Å to the C–C distance and also 0.0055 Å to the C–H distances reported in the references (probably r_a).

count. They are listed in the first columns of Tables 8 and 9 accompanying the most probable parameters. For some of the parameters (*e.g.*, the C=C distance in norbornadiene), the P distributions seem to be essentially equal to the W distributions, whereas for other parameters (*e.g.*, the C_1–C_7–C_4 and θ angles) the W functions are broadened into the P functions so that the uncertainties in the parameter values originate entirely from the choice of the mean amplitudes.

For norbornadiene, the most-probable estimates of the C_1–C_7–C_4 parameter obtained in the above analyses scattered from 92° to 96°, whereas the values did not always depend on the starting parameters as mentioned in the preceding subsection. Since the error surface seems to have a broad minimum around 94° with respect to this parameter, a simple average over the estimated P distribution was taken as the final estimate of this parameter.

Despite the large uncertainties in the individual C–C bond distances mentioned above, their weighted-average values have been determined with much better accuracy. The C–C distance in norbornadiene has also been obtained uniquely without serious correlation with the mean amplitudes.

Comparison with Previous Results. The experimental values reported in the literature[10–14] are compared with the present results in Tables 8 and 9, where our preliminary results in the earlier communication[14] (r_α structures[21,27]) have been revised within their limits of error by taking into account the multiminimum solutions discussed above and the systematic errors due to the fixed mean amplitudes in the least-squares refinements.

Some of the parameters reported by other authors contradict one another beyond the quoted uncertainties. Possible sources of the discrepancies are considered to be (A) differences in the experimental intensity curves and (B) those in how the mean amplitudes are treated in the analysis.

Norbornadiene: The results obtained here are similar to those in Ref. 11 except for the scale. The double bond distance affords a good measure of the scale, since this distance can be determined with little ambiguity. The C=C distance determined here is in good agreement with that reported in Ref. 13b, whereas a scaling error of about 1% is involved in those of Refs. 10 and 11. On the other hand, the principal origin of the difference between the present structure and that of Ref. 13b is to be sought in source (B), since the experimental molecular intensity of Dallinga and Toneman[13b] agrees with ours to within the reproducibility of the observed intensity ($\Delta qM(q) \lesssim 0.25$), and yet their results differ significantly from any of the others: (1) Their C_1–C_2 bond distance is longer than the C_1–C_7 distance, contrary to the results of all the other authors, and (2) their C_1–C_7–C_4 angle is much larger than those determined by the others.

The choice of the mean amplitudes seems to be responsible for the difference between Dallinga's results and ours. They adopted the mean amplitudes in cyclohexadiene, butadiene, *etc.* with no discrimination among the nonequivalent pairs and used them as fixed constants: all the C–C amplitudes equal to 0.052 Å, all the nonbonded $C\cdots C$ amplitudes equal to 0.066 Å, all the nonbonded $C\cdots H$ amplitudes equal to 0.084 Å, and so forth. According to our estimates given in Table 2, however, significant differences exist among the amplitudes for nonequivalent pairs: For example, nonbonded $C\cdots C$ and $C\cdots H$ amplitudes range from 0.058 Å to 0.077 Å and from 0.094 Å to 0.140 Å, respectively. Judging from our finding discussed in the preceding subsection, their assumptions probably give rise to considerable systematic errors in their structural parameters. In fact, a theoretical molecular intensity curve based on their structural parameters and our theoretical mean amplitudes (Table 2), instead of their estimated amplitudes, deviates from our experimental curve beyond the uncertainties in the measurement. Furthermore, when some of the mean amplitudes were varied indiscriminately in the analysis of our intensity, a result similar to Dallinga's was obtained: C_1–C_2=1.558 Å, C_1–C_7= 1.528 Å, $\angle C_1$–C_7–C_4=97° and θ=112°; however, the amplitudes obtained in this analysis seemed physically unrealistic: The C_1–C_2 (0.0600±0.0035 Å) and C_1–C_7 (0.0450±0.0028 Å) amplitudes are much too large and too small, respectively, and the $C_1\cdots C_3$ nonbonded amplitude (0.052±0.0022 Å) was similar to that of a bonded pair. After all, Dallinga's parameters seem to be one of the multisolutions resulting from a questionable choice of the mean amplitudes.

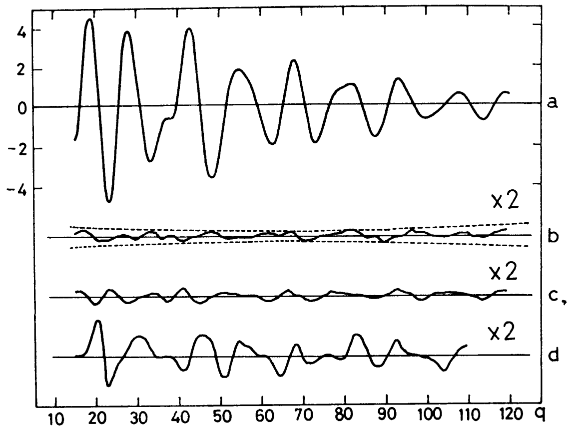

Fig. 4. Comparison of the experimental molecular intensity curves $qM(q)$ for norbornane. a: Present study; b: $[qM(q)_{\text{exp}} - qM(q)_{\text{calc}}]\times 2$ for the present measurement, where broken lines indicate the uncertainty level; c: [Curve a$-qM(q)$ measured by Dallinga and Toneman (Ref. 13a)]×2; d: [Curve a$-qM(q)$ measured by Chiang *et al.* (Ref. 12)]×2.

Norbornane: Our results are in good agreement with Dallinga's,[13a] except that the order of the C_2–C_3 and C_1–C_7 bond lengths is reversed, whereas Chiang's results[12] deviate from the others in the C–C weighted-average and θ; the C–C average is about 0.01 Å (see footnote c of Table 9) longer than the others, and the θ is about 4° smaller. The discrepancy in the C–C average seems to be a scaling error of about 0.5%. In this connection, experimental molecular intensity curves[12,13a,15] are compared in Fig. 4. Dallinga's curve agrees with ours to within the experimental uncertainties illustrated in Fig. 4 as broken lines, whereas Chiang's curve deviates significantly.[31] Therefore, the difference between Chiang's results and the others appears to be due to source (A), while that between Dallinga's results and ours is due to source (B). The differences between the individual C–C bond distances (C_1–C_2, C_2–C_3, and C_1–C_7) are within the estimated systematic errors due to the uncertainties in the mean amplitudes used in the analysis (see preceding section), so that it seems to be a hard problem at the present stage to discriminate the individual C–C bond distances unambiguously by electron diffraction alone. Additional information such as the rotational constants determinable from microwave spectroscopy may provide an effective solution of this problem.[27]

Discussion

Molecular Structure. The final results are listed in the first columns of Tables 8 and 9 with estimated limits of error including random and systematic errors.

The frame structure of norbornadiene is similar to that of norbornane, except that the C=C double bond distance seems to be slightly longer than that in ethylene (r_g=1.337 Å).[26] The C_1–C_2 bond distance is found to be about 0.03 Å longer than the C–C single bond adjacent to a C=C double bond (*e.g.*, 1.501 Å (r_s) in propylene[32]), and the C_1–C_7 bridge bond distance is about 0.03 Å longer than that in cyclohexane, 1.540 Å (r_g).[33] These lengthenings seem to indicate the effect of strong intramolecular strain, which also makes the C_1–C_7–C_4 angle decrease from the tetrahedral angle by more than 15°. Analogously, the C_1–C_2=C_3 angle is about 18° smaller than the C–C=C angle in *cis*-2-butene (*ca.* 125°),[34] whereas the C=C–H angle, 124°, seems to be normal.

For norbornane, the average value of the C–C bond distance, 1.548_8±0.003 Å, is about 0.01 Å longer than the normal single bond distance. Probably, this lengthening is due to the C_1–C_7 and C_2–C_3 bonds; they appear to be about 0.02 Å longer than the C_1–C_2 distance, though the differences are within their limits of error. The $C_1\cdots C_4$ distance, 2.26Å, is nearly equal to or a few hundredths of an angstrom shorter than that in norbornadience; the corresponding distances in the bicyclo[2.2.2]-compounds (octane, octene, and octadiene) are about 0.3 Å longer.[29] All the C–C–C angles (the C_1–C_7–C_4 in particular), except for the C_2–C_1–C_6 angle (108.6°), are appreciably smaller than the tetra-

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[31] It is likely that the difference in the diffraction intensities obtained by Chiang *et al.*[12] from those obtained by Dallinga[13a] and in the present study (shown in Fig. 4) is due to the samples rather than to the apparatuses, since Chiang *et al.* found no essential difference between the intensity patterns taken at Cornell University and at the University of Oslo (by Bohn) by the use of portions of the same sample. (S. H. Bauer, private communication, April, 1971).

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TABLE 10. COMPARISON OF THE EXPERIMENTAL AND THEORETICAL STRUCTURES FOR NORBORNANE

Parameters	Obsd[a]	Calcd[b]					
		A	B	C	D	E	F
$(C—C)_{av}$	1.549	1.538	1.541	1.521			
$C_1—C_2$	1.53_9	1.534	1.543	1.520			
$C_2—C_3$	1.55_7	1.534	1.547	1.526			
$C_1—C_7$	1.56_0	1.551	1.531	1.513			
$\angle C_1–C_7–C_4$	$93._1°$	92.8°	93.9°	93.7°	92.0°	94—96°	93.0°
$\angle C_1–C_2–C_3$	$103._3°$	103.4°	102.9°	103.0°	103.0°	104°	103.0°
θ	$113._1°$	114.3°	110.1°	114.8°	113.9°	109°	113.0°

a) Observed structure determined in the present study (see Table 9). The $C_1–C_2–C_3$ angle was calculated from the independent parameters.

b) Theoretical structures calculated by a conformational analysis of the SCF-MINDO (A) or the strain-relief scheme (B—F). A: Ref. 6; B: Ref. 5; C: Ref. 4; D: Ref.2; E: Ref. 3; F: Present study (see text).

hedral angle. As discussed below, those anomalous values are consistent with the predictions based on the calculation of strain on bond angles and the interaction of the nonbonded C···C, C···H, and H···H atoms. X-ray observations[1)] on similar angles in certain derivative molecules in the crystal phase are also in line with the above findings. Therefore, the angular distortions found in crystals should primarily be of intramolecular origin rather than of intermolecular origin.[18)]

Intramolecular Strain. A calculation was made to account for the striking features in the skeletons of these molecules discussed above by means of a minimization of empirical strain energy.[29)] A modified Urey-Bradley field similar to that developed by Jacob *et al.*[35)] was employed with a "softer" set of nonbonded potential functions taken from Hendrickson's papers.[36)] The force constants for the C–C–C and C–C=C angles were assumed to be equal to each other, 0.687 md·Å, and the equilibrium values for the former and the latter angles were chosen to be the tetrahedral and trigonal angles, respectively, while the torsional constant was taken from the height of the rotational barrier for ethane, 2.93 kcal/mol[37)] for the carbon-carbon single bond. The analyses were made with bond lengths fixed to the values observed in the present work, and angular parameters for the skeleton were varied simultaneously in order to minimize the potential energy. The results, listed in the last column of Tables 8 and 10, account for the experimental values. Similar predictions made by other researchers[2–6)] for norbornane, compared in Table 10, agree essentially with the present results in spite of the difference in the force fields and in the schemes, except that the dihedral angles θ in Refs. 3 and 5 are too small.

In order to account for the observed lengthening in the C–C bonds, bond lengths for the norbornane skeleton were varied in the above conformational analysis, where the stretching force constant and the equilibrium distance of the C–C bond were taken as 2.2 md/Å and 1.533 Å, respectively. The analysis resulted in all the C–C bond distances ($C_1–C_2$, $C_2–C_3$, and $C_1–C_7$) longer than 1.6 Å. This absurdity is no doubt due to the strong nonbonded repulsion assumed among the carbon atoms, since the mean next-to-bonded C···C distance of 2.412 Å is substantially shorter than the average value of 2.545Å in normal alkanes.[38)] Gleicher and Schleyer[5)] ignored those interactions of the 1–3 type in summing up all the nonbonded interactions, because they used a modified valence force field. The calculation made by Allinger *et al.*[4)] is based on a similar scheme. However, neither prediction of the bond lengths, compared in Table 10, is in agreement with the observation. On the other hand, a conformational analysis made by Boder and Dewar[6)] for norbornane by a semiempirical SCF-MO (MINDO/2) method predicted the $C_1–C_7$ distance to be longer than $C_1–C_2$ and $C_2–C_3$ distances, although their C–C weighted average was about 0.01 Å shorter than the observed value. According to another prediction of Dallinga and Ros[39)] on the basis of an iterative extended Hückel method, the $C_1–C_7$ and $C_1–C_2$ distances for norbornane are practically equal and about 0.03 Å shorter than $C_2–C_3$. Therefore, a fully quantitative prediction of bond lengths in such bicyclic compounds seems to be beyond the reach of our control at the present stage.

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