J. Am. Chem. Soc. 1983, 105, 158-162

Structure Determination of Gaseous Norbornane by Electron Diffraction, Microwave, Raman, and Infrared Spectroscopy. Molecular Mechanics and ab Initio Calculations with Complete Geometry Relaxation

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Abstract: The gas-phase molecular structure of norbornane has been investigated by joint analysis of electron diffraction, infrared, Raman, and microwave spectroscopic data. Constraints were taken from the completely relaxed ab initio (4-21G) geometry of the system in one model and from molecular mechanics calculations in another. The former model was shown to be significantly better. Starting from the ab initio constrained model, the range of models was investigated that fit all available data with respect to the differences between CC bond lengths. This resulted in the following best-fitting model and corresponding uncertainties: (r_g/r_α parameters) $\langle CC \rangle = 1.5479$ (6) Å, $C_1C_2 = 1.536$ (15) Å, $C_2C_3 = 1.573$ (15) Å, $C_1C_7 = 1.546$ (24) Å; $C_7C_1C_2 = 102.0$ (1)°, $C_1C_7C_4 = 93.4$ (1)°, $C_1C_2C_3 = 102.7°$, $C_2C_1C_6 = 109.0°$, $\langle CH \rangle = 1.113$ (3) Å, $\langle CCH \rangle = 112.7$ (3)°. Torsion angles (r_α) are $C_3C_2C_1C_7 = 35.8°$, $C_2C_1C_7C_4 = 56.3°$, $C_3C_2C_1C_6 = 71.6°$. When all uncertainties in determining error ranges were taken into consideration C_1C_2 and C_1C_7 remain essentially unresolved; C_2C_3, however, is longest. The observed sequence of valence angles $C_1C_7C_4 < C_2C_1C_7 < C_1C_2C_3 < C_2C_1C_6$ fits also additional, external information obtained from a statistical analysis of X-ray norbornane fragments.

Norbornane (Figure 1) is a key compound in structural chemistry, and knowledge of its geometry could reveal how structural parameters respond to a substantial strain.

Investigations on the free molecule by gas-phase electron diffraction (GED) have resulted in four structural models[2-5] that differ from one another in important details, particularly in the sequences of the CC bond lengths and of the CCC valence angles (Table I). The problems encountered are inherent to the GED technique. A unique, simultaneous determination of closely spaced distances is often hampered by the occurrence of large correlations between the parameters. Norbornane is a notorious example in this aspect. Assuming C_{2v} symmetry, the carbon skeleton can be described by five parameters, three closely spaced CC bond lengths and two angles. Moreover, if one does not want to introduce extra assumptions, ten additional parameters are needed to position the hydrogen atoms. There are four possibly different CH bond lengths and six valence angles. In order to alleviate some of the difficulties, GED can be augmented by results from theoretical and experimental techniques. From theoretical techniques, one can derive differences between the closely spaced parameters and use them as constraints in the analysis. Obviously, the reliability of the calculated constraints is a critical factor. A number of investigations[6,7] have shown that unconstrained ab initio geometry relaxations, using Pulay's force method[8] with a simple basis set such as 4-21G, produce geometries that are consistently close to experimental. The quality of geometrical constraints derived by ab initio calculations was shown[6] to be better than that calculated by molecular mechanics. Nevertheless, the latter method, with the force field of Ermer and Lifson[9] in particular, has often produced useful results when applied to not severely strained hydrocarbons.[6,10]

Table I. Comparison of Structural Parameters Determined in Norbornane[a]

	Yokozeki[2]	Morino[3]	Dallinga[4]	Chiang[5]	this study
$\langle CC \rangle$	1.549 (3)	1.549 (2)	1.545	1.555	1.5479 (6)
C_1C_2	1.539 (10)	1.542 (10)	1.534 (10)	1.556 (10)	1.536 (15)
C_2C_3	1.557 (20)	1.543 (20)	1.578 (10)	1.551 (10)	1.573 (15)
C_1C_7	1.560 (20)	1.570 (10)	1.535 (30)	1.559 (10)	1.546 (24)
$\langle CH \rangle$	1.126 (5)	1.126 (10)	1.11 (1)	1.11 (1)	1.113 (3)
$C_1C_7C_4$	93.1 (10)	93.2 (10)	95.3 (10)	96 (1)	93.41 (9)
$C_7C_1C_2$	101.6	101.2	100.4	101.6	102.04 (6)
$C_1C_2C_3$	103.4	103.9	104.9	104.1	102.71
$C_1C_2C_6$	108.5	108.1	105.6	103.4	108.97
θ^b	113 (1)	113 (1)	111.3	108 (1)	113.1
$\langle HCH \rangle$	110 (4)	110 (3)	111 (4)	108 (1)	107.2

[a] All values given are r_g values. [b] Dihedral angle between the $C_1C_2C_3C_4$ and $C_1C_6C_5C_4$ planes.

From experimental techniques one can add complementary experimental data to the GED analysis. For example, rotational constants determined by microwave spectroscopy (MW) can provide structural details difficult to obtain in any other way, provided the appropriate corrections for harmonic vibration-rotation interactions are made.[11] This is possible in this case since the microwave spectrum of norbornane has recently been recorded and interpreted by Choplin.[12]

Kuchitsu et al.[2] have pointed out that particularly in norbornane the correctness of the vibrational amplitudes used in the GED analysis is a critical factor in the determination of the differences between the CC bond distances. Since the fundamental vibrational frequencies of norbornane have been determined,[13] it is now

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[1] Research Associate Belgian National Science Foundation (NFWO).

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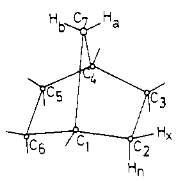

Figure 1. Structural formula and numbering of atoms. Subscripts n and x are used on H atoms to denote endo and exo positions, respectively.

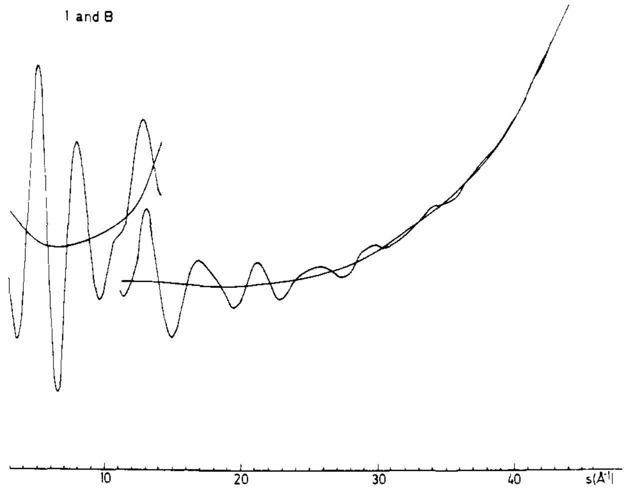

Figure 2. Experimental intensities and final backgrounds.

possible to use a reliable harmonic force field to predict the vibrational amplitudes.

Previous analyses of norbornane used GED more or less as a "stand-alone" technique. We report here a study in which GED is augmented by all presently available spectroscopic data (microwave, Raman, and IR). The data were combined with geometrical constraints obtained from ab initio calculations after complete geometry relaxation (MOCED model). For comparison, a second model was used with constraints calculated by molecular mechanics (MM model). Furthermore, the range of solutions that is in agreement with all experimental data is investigated. This will show how well the theoretical models correspond to the best-fitting model and to what extent the differences between models are significant. It will also reveal the uncertainty one can expect for small differences between similar bond lengths.

Experimental Section

A commercial sample of norbornane (Aldrich) with a purity better than 98% was used. During the experiments the sample was kept at 24 °C. Diffraction patterns were recorded on the Antwerp electron diffraction apparatus manufactured by Technisch Physische Dienst, TPD–TNO, Delft, by employing an accelerating voltage of 60 kV, stabilized to within 0.01% during measurements. The wavelength, calibrated against the known CC bond length of benzene,[14] was determined as $\lambda = 0.049088\ (5)$ Å. Four plates (Kodak Electron Image) were selected from recordings taken at a nozzle-to-plate distance of 600.05 (2) mm and three plates from a nozzle-to-plate distance of 200.09 (2) mm. The plates were measured on the oscillating double beam Joyce–Loebl densitometer of the University of Leiden. Optical density values were converted to intensities by using the one-hit model of Forster.[15]

Coherent scattering factors were taken from Bonham and Schäfer;[16] incoherent scattering factors are from Tavard et al.[17] The data were further processed by standard procedures.[18] Leveled intensities were obtained in the following regions: 60 cm, $3.75\ \text{Å}^{-1} \le s \le 15.00\ \text{Å}^{-1}$; 20 cm, $11.50\ \text{Å}^{-1} \le s \le 44.50\ \text{Å}^{-1}$; $\Delta s = 0.25\ \text{Å}^{-1}$. Figure 2 shows the experimental intensities with the final backgrounds. The quality of the intensities was checked by comparing our experimental $sM(s)$ curve with previous experimental data taken at Tokyo University, Japan, kindly put at our disposal by Prof. Dr. K. Kuchitsu. The agreement (Figure 3C) is very satisfactory.

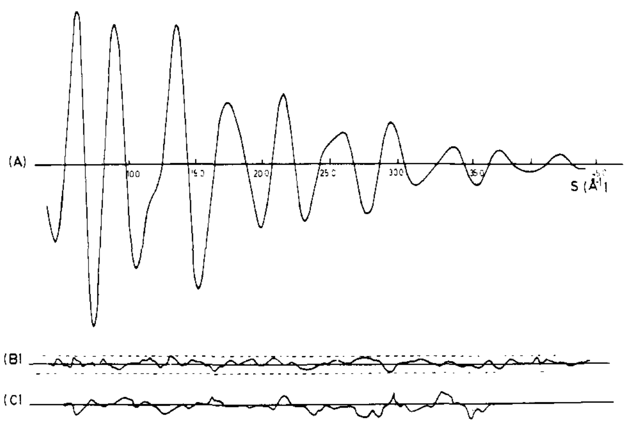

Figure 3. (A) Experimental combined $sM(s)$ curve with (B) difference experiment–theoretical model Ib and (C) difference experiment (Antwerp) − experiment (Tokyo).

Table II. Force Constants of Norbornane[a]

description	L & H	this study	unit
C_1C_2 stretch	3.49	3.34	mdyn/Å
C_2C_3 stretch	3.67	3.46	mdyn/Å
C_1C_7 stretch	3.91	4.33	mdyn/Å
C_1H_1 stretch	4.73	4.73	mdyn/Å
C_2H_2 stretch	4.70	4.70	mdyn/Å
C_7H_7 stretch	4.73	4.73	mdyn/Å
$H_7C_7H_7$ bend	0.53	0.46	mdyn Å
$H_2C_2H_2$ bend	0.52	0.45	mdyn Å
$H_7C_7C_1$ bend	0.54	0.59	mdyn Å
$H_1C_1C_2$ bend	0.66	0.59	mdyn Å
$H_1C_1C_7$ bend	0.70	0.59	mdyn Å
$H_2C_2C_3$ bend	0.54	0.49	mdyn Å
$H_2C_2C_1$ bend	0.54	0.52	mdyn Å
$C_1C_7C_4$ bend	1.61	1.14	mdyn Å
$C_2C_1C_6$ bend	1.84	1.86	mdyn Å
$C_2C_1C_7$ bend	0.92	0.71	mdyn Å
$C_1C_2C_3$ bend	0.91	0.84	mdyn Å
$C_4C_3C_2C_1$ torsion	2.00[b]	0.38	mdyn Å
$C_4C_3C_2H_2$ torsion		0.03	mdyn Å
$H_2C_2C_3H_3$ torsion		0.03	mdyn Å
C_1C_2 stretch/C_2C_3 stretch	1.08	1.08	mdyn/Å
C_1C_2 stretch/C_1C_7 stretch	0.53	0.53	mdyn/Å
C_1C_7 stretch/$H_1C_1C_2$ bend	−0.23	−0.23	mdyn
C_1C_2 stretch/$C_2C_1C_7$ bend	0.17	0.18	mdyn
C_1C_7 stretch/$C_7C_1H_1$ bend	0.51	0.51	mdyn
C_1C_2 stretch/$C_1C_2C_3$ bend	1.03	1.03	mdyn
C_2C_3 stretch/$C_1C_2C_3$ bend	0.16	0.16	mdyn
$C_2C_1C_6$ bend/$C_2C_1C_7$ bend	0.17	0.14	mdyn Å
$C_4C_3C_2C_1$ torsion/$C_4C_5C_6C_1$ torsion[c]	0.56	0.30	mdyn Å
(skeletal twist/HC_2H bend)[d]	0.32	0.00	mdyn Å

[a] A comparison of the force field of Levin and Harris (L & H) with the force field refined in this study. [b] Levin and Harris assign a force constant of 2.00 mdyn Å to a "skeletal twist" mode, but it is not clear what internal coordinate this mode corresponds to. [c] Described as "skeletal twist/skeletal twist". [d] In our force field we have no cross term between a skeletal torsion and a HC_2H bend.

Vibrational Analysis

From the observed infrared and Raman spectra in the solid phase, Levin and Harris[13] extracted a force field for norbornane that reproduced the fundamental vibrational frequencies with a root-mean-square deviation of 20.5 cm^{-1} and a maximum deviation of 61.2 cm^{-1}. Starting from their values, we further refined the force field until the experimental frequencies were reproduced with

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Table III. Calculated Vibrational Amplitudes (U_{lj}) and Vibrational Corrections ($r_a - r_\alpha{}^0$) for Norbornane (10^{-4} Å)

	U_{lj}	$r_a - r_\alpha{}^0$		U_{lj}	$r_a - r_\alpha{}^0$
C(1)-C(7)	523	9	C(2)---H(7,b)	1045	33
C(1)-C(2)	592	2	C(7)---H(1)	1045	33
C(2)-C(3)	551	15	H(2,x)	1459	−10
C(1)-C(3)	621	−1	H(2,n)	1107	27
C(1)---C(4)	612	−6	H(7,a)	785	119
C(2)---C(5)	816	−10	H(1)---H(2,x)	1750	1
C(2)---C(6)	783	−6	H(2,n)	1674	14
C(2)---C(7)	741	−6	H(3,x)	1860	−10
C(1)---C(1)	785	92	H(3,n)	1430	−10
C(1)---H(2,x)	1157	33	H(4)	1274	33
H(2,n)	1157	33	H(7,a)	1609	23
H(3,x)	1210	14	H(2,x)---H(2,n)	1274	119
H(3,n)	1157	14	H(3,x)	1860	−10
H(4)	973	15	H(3,n)	1490	65
H(7,a)	1107	43	H(5,x)	1430	33
C(2)---H(1)	1107	23	H(5,n)	1705	65
H(2,x)	785	119	H(6,x)	1490	33
H(2,n)	785	119	H(6,n)	1750	6
H(3,x)	1157	33	H(7,a)	2240	−71
H(3,n)	1157	33	H(7,b)	1674	18
H(4)	1014	−23	H(2,n)---H(3,n)	1860	−5
H(5,x)	1609	15	H(5,n)	2240	−71
H(5,n)	1550	−23	H(6,n)	2187	23
H(6,x)	1157	23	H(7,a)	1674	17
H(6,n)	1539	−23	H(7,b)	1430	38
H(7,a)	1550	−23	H(7,a)---H(7,b)	1274	119

Table IV. Experimental Microwave B_0 Values, Corrections Required for Harmonic Vibration–Rotation Interactions, and Resulting B_z Values and $B_\alpha{}^{0a}$

	B_0, cm^{-1}	$B_0 - B_z$, 10^{-6} cm^{-1}	B_z, cm^{-1}	$B_\alpha{}^0$, cm^{-1}
A	0.123 227 8 (2)	26 (50)	0.123 202	0.123 201 (30)
B	0.107 160 5 (1)	39 (50)	0.107 121	0.107 122 (30)
C	0.092 558 6 (1)	37 (50)	0.092 522	0.092 521 (30)

[a] Parameters derived from joint microwave–electron diffraction analysis, best-fitting model. Estimated errors are in parentheses. The four MOCED and MM models eventually gave the same values.

an rms deviation of 14.7 cm^{-1} and a maximum deviation of 32.9 cm^{-1}. The results are collected in Table II.

From this force field, which we believe is the best presently available, vibrational amplitudes and vibrational corrections (Table III) were calculated, as well as $B_0 - B_z$ corrections (Table IV) on the rotational constants. The B_0 constants, determined by microwave spectroscopy in the 26–40-GHz region, were taken from Choplin.[12]

To allow the incorporation of microwave data into GED the r_a distances were converted to $r_\alpha{}^0$ (at 0 K) by using standard relations.[11a] Anharmonicity and centrifugal stretching effects were neglected. In the conversion of B_0 to B_z centrifugal distortions and corrections arising from electron contributions were discarded. The estimated error (ϵ_z) on B_z was calculated on the assumption that the errors in the infrared frequencies are about 5 cm^{-1}.

A comparison of our calculated amplitudes and shrinkages (Table III) with those previously estimated by Kuchitsu et al.[2] from an approximate force field shows a reasonable agreement except for $U(C_2C_6)$ and $U(C_2H_{5x})$, and the correction for C_2H_4.

Model Consideration and Refinements

Two theoretical models of norbornane were calculated. One resulted from ab initio calculations, using a 4-21G basis set and allowing all geometrical parameters to relax completely. C_{2v} symmetry was imposed during the relaxation.[19] The other model was obtained by molecular mechanics calculations using Ermer and Lifsons force field.[9] No symmetry restrictions were imposed. The relaxed structure, however, has C_{2v} symmetry.

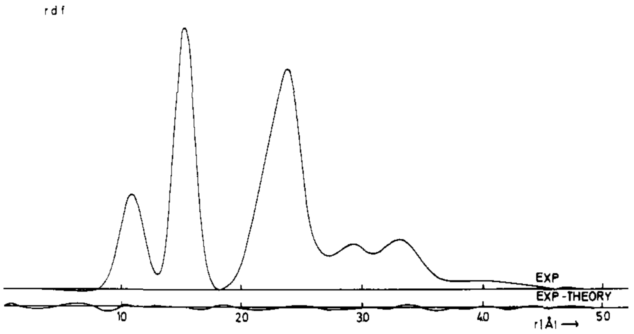

Figure 4. Experimental radial distribution curve and difference with the theoretical one for model Ib. A damping factor of $\exp(-0.0020s^2)$ was used.

The results, collected in Table V, columns A and D, are split into parameters to be used as refinables in the GED analysis and constraints to be kept fixed during the refinements. It is clear that the two models are contradictory in several aspects. First, according to the ab initio results, the sequence of bond lengths is $C_1C_7 \approx C_1C_2 < C_2C_3$, whereas molecular mechanics gives $C_1C_7 < C_2C_3 \approx C_1C_2$. Second, molecular mechanics predicts C_1C_7 = 1.527 Å, shorther than a normal CC bond (1.535 Å in the force field used), and the two other CC bonds only slightly longer than the unstrained CC-length. In contrast, ab initio predicts all CC bonds to be longer than the r_e (4-21G) value of an unstrained CC bond (1.529 Å in ethane[7e]). Third, there are substantial differences in the valence angles, particularly $C_1C_7C_4$, as well as in the valence angles involving hydrogen. In fact, the differences between the two models are so large that experiment may well reveal a preference. The best model can then be taken as the starting point to find the true best-fitting model with respect to the order of the CC bonds. Therefore, the two theoretical models were used in independent refinements: (I) MOCED approach,[6] combining MW and GED data with fixed constraints taken from the ab initio calculations, and (II) MM approach combining MW and GED data with fixed constraints taken from the molecular mechanics calculations. A further subdivision was made in each approach: (a) refinement of the five geometrical parameters only—vibrational amplitudes were kept fixed at the values (Table III) calculated from our force field; (b) refinement of the five geometrical parameters as well as four vibrational parameters belonging to C_1C_7, C_1C_4, C_2C_5, and CH, respectively—the differences $U(C_2C_3) - U(C_1C_7)$, $U(C_1C_2) - U(C_1C_7)$, $U(C_1C_3) - U(C_1C_4)$, $U(C_2C_6) - U(C_1C_4)$, and $U(C_2C_7) - U(C_1C_4)$ were constrained to the calculated values; all other amplitudes were held fixed at their calculated values. Results[20] of the four series of refinements are given in Table V, columns B, C, E, and F as models Ia, Ib, IIa, and IIb. Correlations between the parameters are shown in Table VI; $B_\alpha{}^0$ values resulting from the joint analysis (MW + GED) are given in Table IV.

Estimated standard deviations are tabulated after multiplication by an arbitrary factor, 3, to take systematic effects into account. Even then the values are too small because of some large correlations between certain parameters. The weighting scheme used for the GED data was proportional to s and scaled down at both ends of each s interval. The rotational constants were given a relative weight $w = k/\epsilon_z{}^2$, where ϵ_z is the estimated error on $B_\alpha{}^0$. The constant k was chosen such that the mean weighted differences between experimental and calculated data points (be it GED or MW) are approximately equal. This resulted in $k = 10^{-6}$, giving the B's a weight of 40 000. Other weighting schemes were tried, reducing the relative weight of the B's down to 400. No significant change in the values of the parameters was noted. Only the

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(20) It is necessary to impose fixed constraints in the way outlined above. Attempts to refine the three CC bond distances independently were unsuccessful. For example, a starting model with $C_1C_7 > C_1C_2 > C_2C_3$ converged to a final model with $C_1C_7 > C_1C_2$ if the vibrational amplitudes were not refined, but the same starting model converged to a model with $C_1C_2 > C_1C_7$ if the amplitudes were refined.

Table V. Calculated and Refined Structural Models[a]

	A[b]	B[c]	C[d]	D[e]	E[f]	F[g]	G[h]
Refinable Parameters							
C_1C_2	1.5507	1.5423 (6)	1.5425 (6)	1.538	1.5508 (6)	1.5509 (6)	1.5361 (6)
$C_7C_1C_2$	101.59	101.45 (6)	101.44 (6)	102.6	100.8 (1)	100.8 (1)	102.04 (6)
$C_1C_7C_4$	94.56	94.62 (9)	94.64 (9)	91.6	95.9 (1)	96.0 (1)	93.41 (9)
C_1H_1	1.079	1.093 (3)	1.093 (3)	1.107	1.094 (3)	1.094 (3)	1.094 (3)
$C_1C_2H_{2x}$	110.8	111.4 (3)	111.3 (5)	110.3	111.3 (3)	111.2 (3)	111.2 (3)
Constraints							
C_2C_3-C_1C_2	0.0215			−0.001			0.035
C_1C_7-C_1C_2	−0.0014			−0.011			0.008
C_2H_{2x}-C_1H_1	0.003			0.0			0.003
C_2H_{2n}-C_1H_1	0.002			0.0			0.002
C_7H_7-C_1H_1	0.003			0.001			0.003
$C_1C_2H_{2n}$-$C_1C_2H_{2x}$	1.06			1.4			1.06
$C_3C_2H_{2n}$-$C_1C_2H_{2x}$	1.55			1.5			1.55
$C_1C_7H_7$-$C_1C_2H_{2x}$	2.24			1.3			2.24
$C_7C_1H_1$-$C_1C_2H_{2x}$	5.39			2.5			5.39
$C_3C_2H_{2x}$-$C_1C_2H_{2x}$	0.04			0.0			0.0
Vibrational Parameters							
$U(C_1C_7)$	0.052		0.052 (1)			0.052 (1)	0.052
$U(C_1C_4)$	0.061		0.058 (2)			0.058 (8)	0.061
$U(C_2C_5)$	0.081		0.085 (9)			0.089 (12)	0.081
U(CH)	0.079		0.078 (4)			0.077 (4)	0.079
Indices of Resolution							
k (60 cm)		0.77 (1)	0.76 (1)		0.75 (1)	0.75 (1)	0.77 (1)
k (20 cm)		1.06 (3)	1.05 (3)		1.04 (4)	1.04 (4)	1.07 (3)
R Values[i]							
R (GED)		1.858	1.805		2.048	1.977	1.792
R (MW)		0.036	0.024		0.059	0.056	0.010
R (GED + MW)		0.843	0.819		0.931	0.898	0.813

[a] Distances in Å, angles in deg, vibrational parameters in Å. [b] Column A: calculated (r_e) structure by ab initio.[19] [c] Column B: refined MOCED model Ia, $r_\alpha{}^0$ structure. [d] Column C: refined MOCED model Ib, $r_\alpha{}^0$ structure. [e] Column D: calculated structure by molecular mechanics. [f] Column E: refined MM model IIa, $r_\alpha{}^0$ structure. [g] Column F: refined MM model IIb, $r_\alpha{}^0$ structure. [h] Column G: best-fitting model (see text), $r_\alpha{}^0$ structure. [i] Defined as $R = [\Sigma w(I_{\text{obsd}}-I_{\text{calc}})^2/\Sigma w I_{\text{obsd}}{}^2]^{1/2}$.

Table VI. Correlation Coefficients (×100) among Parameters[a]

	g_1	g_2	g_3	g_4	g_5	U_1	U_2	U_3	U_4	k_1	k_2
g_1	100	−39	42	−5	−68	12	9	−9	3	15	7
g_2	−42	100	−98	−55	67	2	6	18	1	1	5
g_3	45	−98	100	51	−66	−2	−5	−17	−1	0	−5
g_4	−4	−54	49	100	−67	−11	−14	−14	−4	−7	−12
g_5	−69	69	−62	−67	100	0	3	18	0	−6	3
U_1						100	37	88	1	30	43
U_2							100	42	1	45	70
U_3								100	−5	39	45
U_4									100	1	3
k_1	15	−5	5	1					−12	100	37
k_2	1	−2	2	0	−1					0	100

[a] Geometrical parameters g_1-g_5, vibrational amplitudes U_1-U_4, and indices k_1 and k_2 have the meaning and sequence defined in Table V. The upper triangle of the matrix gives the values for model Ib; the lower triangle those of the best-fitting model. Values of the other models do not significantly deviate from the tabulated ones.

least-squares standard deviations of the angles $C_1C_7C_4$ and $C_7C_1C_2$ as well as the correlation coefficients are mildly affected by the choice of the weighting scheme. This, however, has no bearing on the further conclusions.

Figures 3 and 4 give for model Ib respectively the experimental $sM(s)$ curve and the radial distribution curve together with their differences with respect to theory.

Discussion of Refined Structures: Best-Fitting Model

A comparison of models a and b shows that with the use of constraints the refinement of vibrational parameters has hardly any effect on the value of the geometrical parameters. The amplitudes themselves shift only very little, and the shifts are nearly equal in both the MOCED and MM models. Therefore, it seems unlikely that our choice of vibrational parameters would influence the comparison between MOCED and MM models.

The R factors of the MM models are always larger than those of the MOCED models, irrespective of whether microwave data are included or excluded or of whether vibrational amplitudes are refined or kept fixed. Using Hamilton's test[21] on the R-factor ratios we reject the MM models at a significance level of $\alpha = 0.05$. The values of the refined parameters for both sets of models are close to those calculated by the ab initio model. Since the starting values calculated by molecular mechanics seem to be wrong, we do not trust the MM constraints either.

In order to find out if the MOCED model, Ib, really gives the best fit to the experimental data, particularly with respect to the sequence of the CC bond lengths, we refined a number of models changing the differences $\Delta_1 = C_1C_7 - C_1C_2$ and $\Delta_2 = C_2C_3 - C_1C_2$ in steps of 0.005 Å. Other constraints concerning the hydrogen atoms were kept at the MOCED values and vibrational amplitudes were fixed at the calculated values. Refinements of the five geometrical parameters on the MW + GED data resulted in the R values as function of Δ_1 and Δ_2 given in Figure 5. The minimum value, $R = 0.817$, is found at $\Delta_1 = 0.008$ Å and $\Delta_2 = 0.035$ Å. Applying Hamilton's test[21] at the significance levels $\alpha = 0.05$ and $\alpha = 0.005$, the critical R values are 0.832 and 0.842, respectively. The inner dotted line in Figure 5 represents the $R = 0.832$ contour; thus models outside the region can be rejected at a significance level $\alpha = 0.05$. The next dotted line is the $R = 0.842$ contour, and models outside the region can be rejected at $\alpha = 0.005$. It follows that only the ab initio calculated model and the experimental model of Dallinga and Toneman[4] are at the very edge of the latter region; all others can be rejected.

Discussion of Molecular Structure and Conclusions

The geometry and the refined parameters of the best-fitting model are collected in Table I, last column, and Table V, column G, respectively. The average CC bond length (1.5479 (6) Å) is

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(21) W. C. Hamilton in "Statistics in Physical Science", Ronald Press, New York, 1964, p 157.

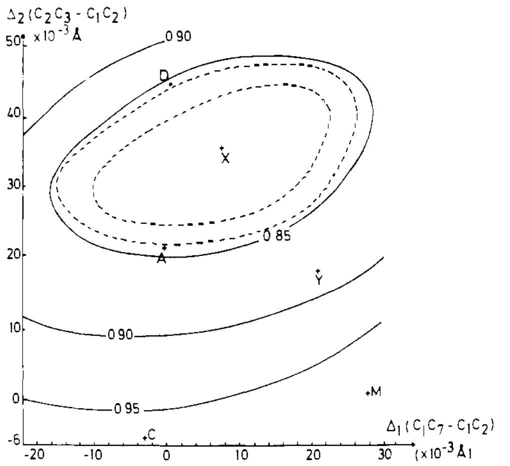

Figure 5. Contour plot of R values as function of Δ_1 and Δ_2. The inner dotted line represents the $R = 0.832$ contour, the next the $R = 0.842$ contour (see text). Solid lines are R contour lines starting at $R = 0.85$, with a spacing $\Delta R = 0.05$. The best-fitting model is indicated by X, other models: (A) ab initio model,[19] (D) taken from Dallinga et al.,[4] (C) taken from Chiang et al.,[5] (Y) taken from Yokozeki et al.,[2] (M) taken from Morino et al.[3]

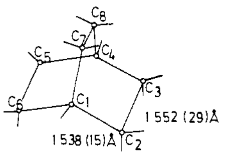

Figure 6. Geometry of bicyclo[2.2.2]octane.

determined with great precision and confirms in this aspect three[2-4] out of four[5] previous determinations. Interestingly, the mean CC bond length in norbornane is also very close to the mean CC bond length (1.546 (2) Å) in cyclopentane,[22] both being about 0.01 Å longer than a normal CC bond. This underlines the fact that norbornane can be considered a fusion of two cyclopentane rings in the envelope or C_s form.

Unfortunately, the precision of the individual CC bond lengths is much less. Considering all models that can be accepted at the 5% level of significance, the following upper and lower limits are to be observed: C_1C_2 from 1.530 to 1.545 Å, C_2C_3 from 1.563 to 1.578 Å, and C_1C_7 from 1.532 to 1.556 Å, showing that previous error estimates have been overoptimistic.

From Figure 5 we conclude that, notwithstanding the most powerful experimental and theoretical techniques (GED, microwave, IR, Raman, and ab initio) are combined, it is still not possible to say whether C_1C_2 is longer or shorter than C_1C_7. Additional external information is required to resolve the question. However, C_2C_3 is almost certainly the longest CC bond. The elongation could be due to the fact that it is the only bond about which all substituent atoms are eclipsed. An analoguous phenomenon is observed[23] in bicyclo[2.2.2]octane, where C_2C_3 is also much larger than C_1C_2 (see Figure 6). Alternatively, the small top angle ($C_1C_7C_4 = 93.4°$) could also contribute to the lengthening of C_2C_3. With regard to the valence angles, we are confident that the sequence $C_1C_7C_4 < C_2C_1C_7 < C_1C_2C_3 < C_2C_1C_6$ is correct, even though the difference between $C_2C_1C_7$ and $C_1C_2C_3$ seems hardly significant. In this case we were able to find the wanted additional external information in a statistical analysis of norbornane X-ray fragments. The latter analysis showed[24] convincingly that the presently available averaged norbornane X-ray skeleton gives useful information about the valence angles in free norbornane. Unfortunately, the same analysis showed that no useful information about bond lengths can be obtained in this way. Finally, the puckering of the five-membered rings in norbornane is expected to be larger than those in cyclopentane. The mean CCC valence angle in each of the rings has therefore to be smaller in norbornane than in cyclopentane. This is indeed the case (100.4° vs. 104.4°), but the effect is mainly located in the top angle $C_1C_7C_4$.

Acknowledgment. We express our gratitude to Prof. Dr. K. Kuchitsu (Tokyo, Japan) for supplying to us the electron diffraction intensities of a previous determination. The help of Dr. F. C. Mijlhoff and Ing. G. Renes (University of Leiden, The Netherlands) with the Joyce Loebl photometer is gratefully acknowledged. L. D. thanks the Belgian Organisation IWONL for a predoctoral grant.

Registry No. Norbornane, 279-23-2.

Supplementary Material Available: Data containing structure specifications, rotational constants, vibrational parameters, and refinements and histograms (49 pages). Ordering information is given on any current masthead page.

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(22) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Am. Chem. Soc.*, **92**, 5013 (1970).

(23) A. Yokozeki, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jpn.*, **43**, 2017 (1970).

(24) D. Van Hemelrijk, W. Van de Mieroop, A. T. H. Lenstra, and H. J. Geise, unpublished results.