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# Molecular Structure of Norbornadiene as Determined by Microwave Fourier Transform Spectroscopy

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**Abstract:** The rotational spectra of six $^{13}$C and D isotopomers of norbornadiene have been measured between 12 and 25 GHz. The Fourier transform technique has been instrumental in observing the weak transitions of the norbornadienes because of the small permanent electric dipole moment. By combining the results from a previous study of norbornadiene, the complete substitution structure has been determined from the rotational constants of the parent and six isotopic species.

Norbornane (bicyclo[2.2.1]heptane) (**1**), norbornene (bicyclo[2.2.1]hept-2-ene) (**2**), and norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) (**3**) are well-studied examples of bridged six-membered ring molecules with considerable intramolecular strain. Norbornadiene **3** served as a test case for the interaction of two nonconjugated double bonds.[1] The interaction of orbitals may occur either through space or through bond. For the rigid parallel arrangement of the double bonds in **3**, the interaction was rationalized from molecular orbital considerations[1,2] to be mostly through space.

The structures of **1**,[3–5] **2**,[6] and **3**,[5,7] which show some common features, were determined first by electron diffraction (ED). Ambiguities remained in the ED structures from different studies despite the special care given to the analyses. For **1** and **2**, rotational constants obtained from microwave spectra[6,8] helped to resolve such problems. For **3**, rotational constants were not available for the analysis. Two different structures were compatible with the measured data.[5] They differed mainly in the value of the angle $C_1C_7C_4$ (cf. Figure 1). Nuclear magnetic resonance (NMR) experiments in nematic solvents[9] provided independent structural data for the hydrogen positions in **3**. The latter data clearly favored the structure with a small angle $C_1C_7C_4$.

It was noticed that electrophilic reactions at the double bonds in **2** and **3** showed pronounced exo stereoselection.[10,11] The two faces of the $\pi$ electron systems are chemically not equivalent. These observations motivated further studies into possible reasons for the stereoselectivity by ab initio calculations.[2,11–14] The electronic effects manifest themselves in a slight deviation from planarity of the double bonds. The hydrogens at the double bonds are tilted by a few degrees of the endo side from the $C_1C_2C_3$ plane.[2,11–13] The first experimental evidence of the tilt was presented in the NMR investigation of **3** in a nematic solvent.[15]

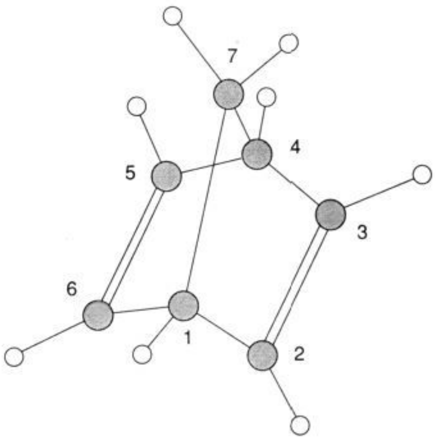

**Figure 1.** Norbornadiene with numbering of nuclei.

Recently, we measured and analyzed the rotational spectrum of **3** between 7 and 17 GHz.[16] The accidentally small permanent electric dipole moment of 0.058 66(9) D makes it difficult to observe the weak transitions with conventional Stark spectroscopy, but pulsed microwave Fourier transform (MWFT) spectroscopy was ideally suited for this study. Even the monosubstituted $^{13}$C species at one of the four equivalent positions of the double bonds was detected in natural abundance.[16]

We report here the measurements of the rotational spectra for the $^{13}$C isotopomers as well as the monodeuterated species of **3** from isotopically enriched samples. The complete substitution structure was determined from the observed moments of inertia of all isotopomers. It was possible to correct further for vibrational effects and to arrive at a near-equilibrium structure which is compared critically to the results of an electron diffraction study and of ab initio calculations.

## Experimental Section

**Chemicals.** Norbornadiene-$^{13}C_1$ isotopomers: 1,4-Dibromobutane was reacted with $K^{13}CN$ (Cambridge Isotope Laboratories, 99% $^{13}$C) to form

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**Table I.** Rotational Constants (MHz) and Quartic Centrifugal Distortion Constants (kHz) of the Isotopomers of Norbornadiene

| | parent[a] | 1-$^{13}C$ | 2-$^{13}C$ | 7-$^{13}C$ | 1-$d_1$ | 2-$d_1$ | 7-$d_1$ |
|---|---|---|---|---|---|---|---|
| $A$ | 4273.6281(2) | 4226.1374(4) | 4249.8528(8) | 4207.9201(5) | 4099.8060(5) | 4187.9717(6) | 4140.5928(4) |
| $B$ | 3610.3002(2) | 3608.5196(4) | 3564.4932(8) | 3563.2224(5) | 3602.3548(5) | 3488.0254(6) | 3492.7456(4) |
| $C$ | 3186.4370(2) | 3161.5206(5) | 3147.2145(8) | 3186.5242(6) | 3094.6623(7) | 3077.5369(7) | 3168.4107(4) |
| $\Delta_J$ | 0.311(18) | 0.304(27) | 0.487(48) | 0.188(32) | 0.364(35) | 0.204(43) | 0.291(28) |
| $\Delta_{JK}$ | −0.07256(62) | −0.051(13) | −0.0644(62) | −0.065(18) | −0.090(28) | −0.0834(82) | −0.0548(33) |
| $\Delta_K$ | 0.26841(73) | 0.240(10) | 0.2580(55) | 0.260(14) | 0.243(22) | 0.2929(67) | 0.2492(34) |
| $\delta_J$ | 0.00478(7) | 0.0087(15) | 0.00549(69) | 0.0023(21) | 0.0112(34) | 0.00525(89) | −0.00159(31) |
| $\delta_K$ | 0.09221(66) | 0.076(14) | 0.0834(81) | 0.079(23) | 0.098(23) | 0.0680(95) | 0.0696(39) |
| $\sigma$[b] | 0.9 | 1.6 | 2.8 | 1.8 | 2.0 | 2.4 | 1.8 |
| $n$[c] | 25 | 24 | 33 | 23 | 25 | 25 | 33 |

[a] Reference 16. [b] Residual error of a measured transition frequency (kHz). [c] Number of measured transition frequencies in the least-squares fit.

**Table II.** Nuclear Coordinates (Å) of Norbornadiene in the Principal Axis System

| | substitution coordinates[a] | | | pseudoequilibrium coordinates[b] | | |
|---|---|---|---|---|---|---|
| nucleus | $a$ | $b$ | $c$ | $a$ | $b$ | $c$ |
| 1-C | 0.0 | 1.1222 | 0.2821 | 0.0 | 1.1189 | 0.2794 |
| 2-C | 1.2366 | 0.6688 | −0.5088 | 1.2348 | 0.6681 | −0.5042 |
| 7-C | 0.0 | 0.0 | 1.3653 | 0.0 | 0.0 | 1.3618 |
| 1-H | 0.0 | 2.1558 | 0.6241 | 0.0 | 2.1541 | 0.6216 |
| 2-H | 1.9226 | 1.3326 | −1.0132 | 1.9214 | 1.3312 | −1.0115 |
| 7-H | 0.9085 | 0.0 | 1.9768 | 0.9081 | 0.0 | 1.9744 |

[a] Using the formulas of Kraitchman for carbon and hydrogen substituted in position 2, the formulas of Rudolph for the remaining positions. [b] Calculated from the pseudoequilibrium structure of Table IV.

adipic acid nitrile-1,6-$^{13}C_2$.[17] The product was hydrolyzed with concentrated HCl to adipic acid-1,6-$^{13}C_2$. The dried acid was mixed with $Ba(OH)_2$ and pyrolyzed at 290 °C.[18] The two-phase distillate of the pyrolysis was extracted with ether. The solution was separated from water and dried with $CaCl_2$, and the solvent was distilled off to yield cyclopentanone-1-$^{13}C_1$.[18,19] After reduction of the latter with $LiAlH_4$ in ether, cyclopentanol-1-$^{13}C_1$ was obtained.[19] It was heated to 140 °C with a mixture of $K_4P_2O_7$ and $H_3PO_4$.[20] Cyclopentene-1-$^{13}C_1$ was collected, dried, and brominated in $CCl_4$ to form 1,2-dibromocyclopentane-1-$^{13}C_1$.[20] A solution of the latter in $CCl_4$ was added dropwise to CaO in a reactor heated to 230 °C.[21] A gentle flow of $N_2$ transported cyclopentadiene-2-$^{13}C_1$ in gaseous form out of the reactor. A mixture of cyclopentadiene-1-$^{13}C_1$, -2-$^{13}C_1$, and -5-$^{13}C_1$ was obtained after storing the primarily synthesized isomer for 18 h at 60 °C and 50 mbar.[22] The [4 + 2]-cycloadducts[23] of the isomerized cyclopentadiene with *cis*-1,2-bis(4-toluenesulfonyl)ethylene[19] were reduced to the corresponding mixture of norbornadiene-1-$^{13}C_1$, -2-$^{13}C_1$, and -7-$^{13}C_1$ with freshly prepared sodium amalgam.[23,24] Norbornadiene-$d_1$ isotopomers: Cyclopentadienylthallium was prepared in a solution of $Tl_2SO_4$ and NaOH.[22] It was reacted with dilute $D_2SO_4$ in $D_2O$ back to pentadiene-5-$d_1$. Norbornadiene-7-$d_1$ was obtained by cycloaddition as described above for the $^{13}C$ species. A mixture of norbornadiene-1-$d_1$, -2-$d_1$, and -7-$d_1$ was prepared along the same line, but the deuterium substitution of cyclopentadiene-5-$d_1$ was first again randomized.[22]

**MWFT Spectrometer.** All measurements were carried out with an Ekkers–Flygare-type[25] MWFT spectrometer operating over 12-25 GHz with 2–6-m waveguide cells. The details of the design of our spectrometer were reported elsewhere.[26] Only a short description of the operating conditions is given here. Microwave pulses of 300–500-ns duration with a peak power of 10 W polarized the molecules in the cell. The transient molecular emission signal was amplified and down-converted to the frequency range 0–10 MHz. The signal was digitized at a rate of 20 MHz and transferred to a 512-channel analyzer. The pulses were repeated at a rate of 25 kHz. Up to 10 million individual coherent emission signals were accumulated over a period of 7 min for signal-to-noise ratio enhancement. The power spectrum was recovered with 256 points over a 10-MHz range after Fourier transformation. The spectra were recorded at sample pressures of 1–3 Pa and a temperature of −65 °C.

## Results

**Assignments and Analysis.** By starting from a preliminary model of the geometrical structure for **3** (structure I of ref 5) and including corrections from the results of the previous microwave study[16] of **3**, the rotational constants for the isotopomers were calculated to within 1 MHz of the finally observed constants. Rotational transitions were readily identified near the predicted values from the rotational constants. Only $\mu_c$-type transitions were observed as in the parent species. Finally, six to eight R-branch transitions with $J$ values up to 3 and between 17 and 26 Q-branch transitions with $J$ values ranging from 5 to 35 were assigned and their frequencies measured with an accuracy of better than 10 kHz. Tables with listings of all measured transition frequencies are available as supplementary material.

Three rotational constants and five quartic centrifugal distortion constants were adjusted to the measured transition frequencies in an iterative least-squares fit for each of the isotopomers. The results are listed in Table I together with the estimated uncertainities. The latter represent one standard deviation calculated in the least-squares fit. The centrifugal distortion constants are defined according to Watson's asymmetric reduction in the prolate $I^r$ basis.[27] Their variations among the isotopomers comply with the expected mass dependence.

**Molecular Structure.** A complete set of rotational constants or moments of inertia for all singly isotopically substituted species of **3** was available by combining the newly observed data with the previously determined values of the parent species. The coordinates of each substituted nucleus were calculated in the principal axis system of the parent norbornadiene. The differences of the moments of inertia between an isotopomer and the parent species were evaluated with the help of equations given by Rudolph[28] and Kraitchman.[29] The three-dimensional equations of Kraitchman were applied for C and H in position 2. The equations of Rudolph are better adapted to isotopic substitutions of nuclei located on symmetry planes. This is the case for positions 1 and 7. These equations avoid the calculation of coordinates perpendicular to symmetry planes. Such coordinates often result in small imaginary values due to zero-point vibrational effects instead of exactly zero. The results of the substitution coordinates are collected in Table II. Bond lengths, bond angles, and dihedral angles of norbornadiene were calculated from the substitution coordinates. They are listed in Table III.

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**Table III.** Structural Parameters of Norbornadiene[a]

| parameter | substitution structure[b] | least-squares fit of differences of: moments of inertia | modified moments[c] | rotational constants |
|---|---|---|---|---|
| $r(C_1–C_2)$ | 1.5363 | 1.5349(41) | 1.5304(42) | 1.5439(41) |
| $r(C_1–C_7)$ | 1.5597 | 1.5584(41) | 1.5561(42) | 1.5607(24) |
| $r(C_2–C_3)$ | 1.3376 | 1.3387[d] | 1.3368[d] | 1.3448[d] |
| $r(C_1–H)$ | 1.0887 | 1.0896(17) | 1.0901(17) | 1.0934(19) |
| $r(C_2–H)$ | 1.0797 | 1.0801(16) | 1.0810(16) | 1.0846(23) |
| $r(C_7–H)$ | 1.0951 | 1.0949(14) | 1.0946(14) | 1.0979(21) |
| $\angle(C_1C_2C_3)$ | 107.16 | 107.12(11) | 107.12(12) | 107.06(8) |
| $\angle(C_1C_7C_4)$ | 92.03 | 92.01(25) | 91.95(25) | 92.29(12) |
| $\angle(C_2C_1C_6)$ | 107.20 | 107.40[d] | 107.55[d] | 106.90[d] |
| $\angle(C_2C_1C_7)$ | 98.35 | 98.34[d] | 98.31[d] | 98.48[d] |
| $\angle(C_7C_1H)$ | 117.70 | 117.76(38) | 117.78(38) | 118.21(25) |
| $\angle(C_3C_2H)$ | 127.94 | 127.88(11) | 127.94(12) | 128.15(19) |
| $\angle(HC_7H')$ | 112.11 | 112.08(17) | 111.86(18) | 111.98(18) |
| $\delta_1$[e] | 122.60 | 122.51(25) | 122.43(26) | 122.82(7) |
| $\delta_2$[f] | 176.28 | 176.10(38) | 176.07(37) | 176.69(20) |

[a] Bond lengths in Å, angles in deg. Numbers in parentheses represent one standard deviation from least-squares fit. [b] Calculated from the substitution coordinates of Table I. [c] Corrected moments of inertia according to the method proposed by Harmony, see text. [d] Dependent parameter calculated from fitted parameters. [e] Dihedral angle between the planes of $C_1C_7C_4$ and $C_1C_2C_3$. [f] Dihedral angle between the planes of $C_1C_2C_3$ and $C_2C_3H$ measured on the side opposite to the bridge.

As an alternative, the bond lengths and angles were determined directly in two least-squares fits.[30] The differences of moments of inertia between the isotopomer and parent molecule were minimized in the first fit. In the second fit, the differences of rotational constants were treated similarly. The center-of-mass condition and the vanishing of nondiagonal moments of inertia are fulfilled strictly during the fits which compensate zero-point vibrational contributions to first order. The results are included in Table III with estimated errors in parentheses. The standard deviations from the fits provide some measure of the uncertainities of the structural parameters. The residual deviations between observed and calculated differences in the fits are much larger than their standard deviations from the spectroscopic analyses. Thus the uncertainities of the structural parameters must be treated with caution.

The substitution coordinates $r_s$ were determined according to the procedure of Costain[31] from the differences of ground-state moments of inertia between parent species and all singly substituted isotopomers. He noticed that the $r_s$ coordinates are about halfway between the $r_0$ and $r_e$ coordinates in linear molecules. The $r_0$ coordinates follow directly from the ground-state moments of inertia and suffer strongly from uncompensated vibrational contributions. The $r_e$ coordinates characterize the hypothetical vibrationless state, i.e. the minimum on the Born–Oppenheimer potential surface. The observation of Costain[31] was further corroborated by theoretical considerations of Watson.[32] Recently, Harmony[33] proposed to apply these ideas also to asymmetric tops. The moments of inertia were scaled by a factor determined from the ratio between the moments of inertia calculated from the $r_s$ coordinates and the observed ground-state moments of inertia. The larger vibrational effects in deuterated isotopomers were further compensated by a small elongation of 0.002 81 Å of a C–D bond length compared to a C–H bond.[34] The scaled moments of inertia were finally subjected to a least-squares fit of the structural parameters as carried out above. The results shown in Table III should approximate the equilibrium structure $r_e$. The approximation was claimed to reproduce the $r_e$ structure for several examples to 0.001 Å for bond lengths and to 0.1° for angles in ref 34.

**Table IV.** Comparison of Structural Parameters[a] of Norbornadiene

| parameter | this work[b] | electron diffraction[c] | ab initio calculations: STO 3G[d] | 3-21G[e] | 6-31G*[f] |
|---|---|---|---|---|---|
| $r(C_1–C_2)$ | 1.5304(31) | 1.5332(14) | 1.548 | 1.550 | 1.5395 |
| $r(C_1–C_7)$ | 1.5567(28) | 1.5711(31) | 1.556 | 1.566 | 1.5505 |
| $r(C_2–C_3)$ | 1.3362(30) | 1.3387(12) | 1.311 | 1.319 | 1.3192 |
| $r(C_1–H)$ | 1.0903(13) | 1.1094(47) | 1.088 | 1.076 | |
| $r(C_2–H)$ | 1.0809(13) | 1.0896 | 1.080 | 1.069 | |
| $r(C_7–H)$ | 1.0954(12) | 1.1094(47) | 1.087 | 1.081 | |
| $\angle(C_1C_2C_3)$ | 107.13(9) | | 107.4 | 107.5 | |
| $\angle(C_1C_7C_4)$ | 91.90(17) | 92.2(4) | 92.0 | 92.0 | 91.87 |
| $\angle(C_2C_1C_6)$ | 107.58(25) | | 106.5 | 106.2 | 107.45 |
| $\angle(C_2C_1C_7)$ | 98.30(14) | | 98.3 | 98.3 | 98.31 |
| $\angle(C_7C_1H)$ | 117.66(26) | | 118.0 | 118.2 | |
| $\angle(C_3C_2H)$ | 127.84(10) | 125.2(14) | 128.8 | 128.1 | |
| $\angle(HC_7H')$ | 111.99(14) | 114.7(30) | 110.0 | 111.7 | |
| $\delta_1$[g] | 122.40(19) | 122.65(15) | 122.9 | 123.0 | 122.46 |
| $\delta_2$[g] | 175.94(28) | 180 | 177.7 | 177.9 | |

[a] Bond lengths in Å, angles in deg. [b] Pseudoequilibrium structure with estimated uncertainties in parentheses, see text. [c] Structure I of ref 5, which depends on several assumptions. [d] Reference 12. [e] References 2 and 13a. [f] Reference 14. [g] Definitions of these dihedral angles are given in Table III.

## Discussion

Norbornadiene is an ideal case for the structure determination from spectroscopic data of isotopic species. No nucleus is located near a principal inertial axis except those on inertial planes by symmetry. A comparison of the structural parameters in Table III which were determined with different procedures reveals substantial variations only in the bond lengths $C_1–C_2$ and $C_2–C_3$. The remaining bond lengths are within the combined uncertainities of the fits. The angles are remarkably consistent among the different determinations in Table III. The bond lengths from the fit of the differences of rotational constants are on the average 0.005 Å longer than the other results. Rudolph[35] investigated the origins of structural variations of fits to the differences of moments of inertia ($r_{\Delta I}$) or of rotational constants ($r_{\Delta B}$). He showed that $(r_{\Delta I} + r_{\Delta B})/2 \approx r_0$ holds. This relation was used to estimate the $r_e$ bond lengths from the approximate relation $(r_e + r_0)/2 \approx r_s$. The results of the estimation agree to within 0.002 Å with the bond lengths obtained from the procedure of Harmony if a lengthening of the C–D bonds of 0.0028 Å is included. The average of these two pseudoequilibrium structures, which is listed in Table IV, was considered to represent the best estimate of the structure of norbornadiene. The uncertainities of the bond lengths and angles were estimated from the combined standard deviations of the fitted structures in Table III. The corresponding coordinates of the nuclei were calculated in the principal axis system of the parent molecule. They are listed in Table II for comparison with the substitution coordinates.

Structural parameters obtained from different experimental methods are based on different operational definitions which do not fully compensate for inherent zero-point vibrational contributions. They must be compared with caution. Our results of the structure of **3** agree much better with structure I than with structure II of the electron diffraction study of Yokozeki and Kuchitsu.[5] They had to make several assumptions regarding the parameters of the hydrogens. Their longer C–H bond lengths and different C–H bond angles are not regarded as crucial in view of the assumptions. The most striking difference, however, is the long bond length $C_1–C_7$ of 1.571 Å compared to our result of 1.557 Å whereas the other C–C bond lengths are within the

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estimated uncertainities. It was noticed by Kuchitsu and Cyvin[36] that the $r_g$ lengths for C–C bonds from electron diffraction are systematically longer by 0.009 Å than the $r_s$ lengths. The results of the NMR studies[9,15] vary considerably among themselves and do not match well with our structure.

It is instructive to compare our pseudoequilibrium structure to that of several ab initio calculations. The most obvious difference to our structure is the short bond length $C_2$–$C_3$ common to all ab initio results. The exceptionally long observed bond length $C_1$–$C_7$ was confirmed in all ab initio calculations. The observed variations among the different C–H bond lengths are well reproduced in the calculations of refs 2 and 13 although the absolute values are smaller by 0.012 Å compared to the pseudoequilibrium values. The decrease is consistent with the tests of Schäfer et al.,[37] who found that C–H bond lengths of ab initio calculations with the 4-21G basis set are on the average 0.013 Å shorter than the $r_s$ values. The angles calculated in refs 2, 12, and 13 agree within 2° with the experimentally determined angles. Those of the carbon skeleton from the calculations with the 6-31G* basis set[14] reproduce our results even within 0.2°, which might be fortuitous. Such an agreement is quite remarkable considering the large deviations of some angles from their standard values in the highly strained framework of **3**. The endo displacement of the ethylenic hydrogens as measured by the difference of the dihedral angle $\delta_2$ (defined in footnoote *f* of Table III) from 180° was found experimentally to be almost twice as large as the ab initio values.[2,12,13] Our result confirms the endo displacement derived from the combined analysis of NMR and ED data.[15]

The pseudoequilibrium structure from spectroscopic data gives a reliable picture of the molecular geometry of **3**. Details like unusual bond angles or the tilt of the ethylenic hydrogens are unambiguously verified. Some remaining discrepancies with ab initio calculations require further studies.

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**Supplementary Material Available:** Listings of measured rotational transition frequencies of norbornadiene-1-$^{13}C_1$, -2-$^{13}C_1$, -7-$^{13}C_1$, -1-$d_1$, -2-$d_1$, and -7-$d_1$ (Tables V-X) (8 pages). Ordering information is given on any current masthead page.

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(36) Kuchitsu, K.; Cyvin, S. J. In *Molecular Structure and Vibrations*; Cyvin, S. J., Ed.; Elsevier: Amsterdam, 1972; p 183.

(37) Schäfer, L.; Van Alsenoy, C.; Scarsdale, J. N. *J. Mol. Struct.* (THEOCHEM) 1982, *86*, 349–364.