

Vibrational Spectra and Force Constants of Bicyclic Molecules. I. Norbornane and Norbornane-*d*₄

Z. Meić, M. Randić*, and A. Rubčić*

Institute »Ruđer Bošković«, POB 1016, 41001 Zagreb, and *Faculty of Science and Mathematics, University of Zagreb, Marulićev trg 19/II, 41000 Zagreb, Croatia, Yugoslavia

Received September 10, 1973

Norbornane (bicyclo[2.2.1]heptane) and its derivatives have been extensively studied by chemical and physical methods. Since norbornane represents an important strained molecule, particular attention was paid to its geometry¹ and bonding properties². However, no vibrational analysis of norbornane or its derivatives has been undertaken. Only partly analysed vibrational spectra are reported³. Therefore we find desirable to undertake a complete vibrational analysis of norbornane and its deuterated species.

Norbornane belongs to the C_{2v} point group¹. The orientation of the molecule in cartesian coordinates, the numbering of carbon atoms, as well as all the bonds and angles with which the internal valence coordinates are associated are presented in Fig. 1. The $3N - 6 = 51$ fundamental vibrations are distributed among the irreducible representations of the C_{2v} point group as follows:

$$\Gamma_{\text{vib}} = 15 A_1 + 11 A_2 + 13 B_1 + 12 B_2$$

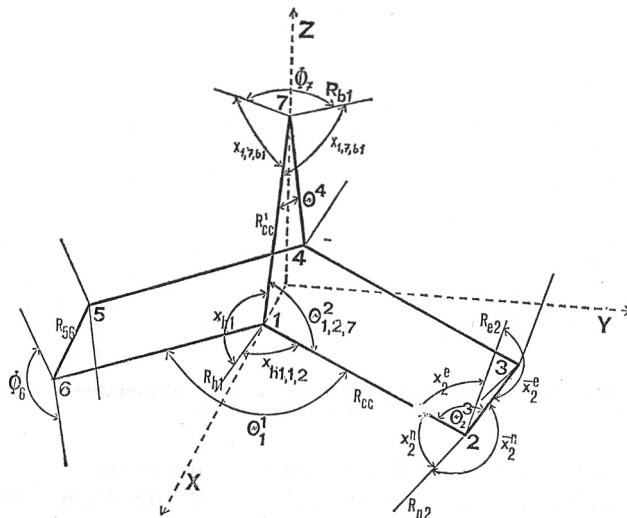


Fig. 1. Schematic view of norbornane molecule with the symbols of bond lengths, bond angles and orientation in the cartesian coordinate system.

Of these only A_1 , B_1 and B_2 modes are active in the infrared, but all the fundamentals are active in Raman spectroscopy. However, there are in all 62 internal coordinates, among which 11 redundancies exist. The redundant coordinates are distributed among the irreducible representations as follows:

$$\Gamma_{\text{vib}} = 5 A_1 + 1 A_2 + 3 B_1 + 2 B_2$$

The recognition of redundancy conditions is not trivial in molecules of such complexity. The local redundancies are easy to define. However, there is a number of cyclic redundancies which are not so obvious.

For instance, an unexpected condition is the linear dependence of the following internal coordinates: Θ^1 , Θ^2 , Θ^3 and Θ^4 in the A_1 species. Another example is the combination of R_{CC} , R'_{CC} and Θ^3 in the B_2 species. But it is not essential to solve all the redundancies, since in the calculation the corresponding frequencies appear as zeros, if all internal coordinates are used. The complete set of symmetry coordinates will be reported in a later paper⁴.

The standard procedure of Wilson⁵ and Eliashewich⁶ was followed in evaluating the G-matrix elements. The geometrical model used was based on electron diffraction data¹.

$$R_{\text{CC}} = R(C_1 - C_2) = R(C_2 - C_3) = 1.54 \text{ \AA} \quad R'_{\text{CC}} = R(C_1 - C_7) = 1.57 \text{ \AA}$$

$$\text{all } R_{\text{CH}} = 1.12 \text{ \AA} \quad \sphericalangle C_1 C_2 C_3 = 103^\circ \quad \sphericalangle C_1 C_7 C_4 = 93^\circ$$

$$\sphericalangle \text{HC}_1 \text{C}_2 = 119^\circ \quad \text{dihedral angle} = 113^\circ$$

All the HCH angles, however, were assumed tetrahedral. In addition to the parent compound, there are 15 distinct deuterated species possessing the same C_{2v} symmetry (Fig. 2). It is generally considered that the best available

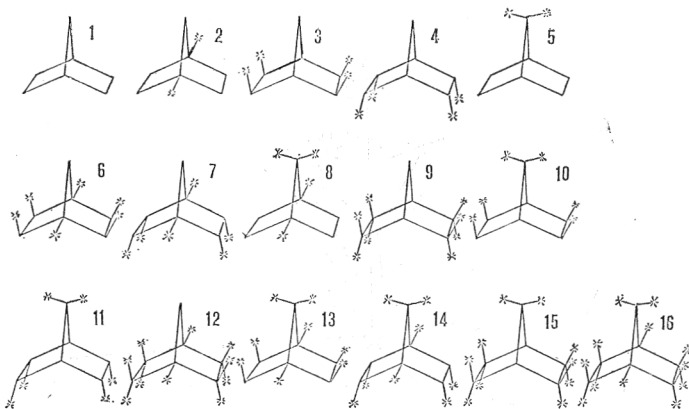


Fig. 2. The normal and all the possible symmetrically deuterated norbornanes belonging to the C_{2v} point group.

valence force field for saturated hydrocarbons is the one obtained by Snyder and Schachtshneider⁷. It was successively applied to several saturated cyclic molecules by the same authors⁷. Hence, we assumed it as the initial force fields for the moderately strained norbornane. In Table I are listed the signi-

ficant force constants taken from the paper of Snyder and Schachtschneider. Using the force constants of Table I we have calculated the vibrational fre-

TABLE I

$K_d = 4.554$ mdyn \AA^{-1}	(C,CH ₂ ,C)	C—H stretch
$K_s = 4.588$ „	(C,C,C,CH)	C—H „
$K_R = 4.387$ „	(H ₂ C,CH ₂)	C—C „
$K_{R'} = 4.337$ „	(H ₂ C,CH)	C—C „
$H_\delta = 0.550$ mdyn \AA^{-1} rad ⁻²	(C,CH ₂ ,C)	CH ₂ bend
$H_\gamma = 0.656$ „	(C,CH ₂ ,C)	CCH „
$H_\zeta = 0.657$ „	(C,C,C,CH)	CCH „
$H_\omega = 1.130$ „	(C,CH ₂ ,C)	CCC „
$H_\varphi = 1.084$ „	(C,C,C,CH)	CCC „
$F_R = 0.101$ mdyn \AA^{-1}	(C,C) (C,C)	stretch-stretch
$F_{R\gamma} = 0.328$ mdyn rad ⁻¹	(C,C) (C,C,H)	stretch-bend
$F_{R\omega} = 0.417$ „	(C,C) (C,C,C)	„
$F_{R\gamma'} = 0.079$ „	(C,C) (C,C,H)	„
$F_\gamma = -0.021$ mdyn \AA rad ⁻²	(C,C,H) (C,C,H')	bend-bend
$F_\varphi = -0.041$ „	(C,C,C) (C,C,C')	„
$F_{\gamma'} = 0.012$ „	(C,C,H) (C,C,H')	„
$F_{\gamma\omega} = -0.031$ „	(C,C,C) (C,C,H)	„

quencies for the molecules 1, 2, 3, 5 and 8 of Fig. 2. However, at present only infrared spectra⁸ of 1 and 3 are available for comparison with calculated values.

The observed, *i. e.* without the IR inactive A₂ species, and calculated fundamentals are listed in Table II.

TABLE II
Norbornane C₇H₁₂ (1)

No.	$\frac{\nu_{\text{exp.}}}{\text{cm}^{-1}}$	$\frac{\nu_{\text{calcd.}}}{\text{cm}^{-1}}$	$\frac{\Delta\nu}{\text{cm}^{-1}}$	No.	$\frac{\nu_{\text{exp.}}}{\text{cm}^{-1}}$	$\frac{\nu_{\text{calcd.}}}{\text{cm}^{-1}}$	$\frac{\Delta\nu}{\text{cm}^{-1}}$
	A ₁				A ₂		
1.	2950	2926	—	1.	—	2930	—
2.	—	2908	—	2.	—	2853	—
3.	—	2856	—	3.	—	1400	—
4.	2850	2853	—	4.	—	1319	—
5.	1455	1512	+ 57	5.	—	1288	—
6.	1450	1455	+ 5	6.	—	1176	—
7.	1310	1317	+ 7	7.	—	1124	—
8.	1252	1260	+ 8	8.	—	1017	—
9.	1138	1157	+ 19	9.	—	957	—
10.	1068	1068	0	10.	—	567	—
11.	948	967	+ 19	11.	—	93	—
12.	888	891	+ 3				
13.	815	807	— 8				
14.	752	689	— 63				
15.	390	397	+ 7				

No.	$\nu_{\text{exp.}}$ cm ⁻¹	$\nu_{\text{calcd.}}$ cm ⁻¹	$\Delta\nu$ cm ⁻¹	No.	$\nu_{\text{calcd.}}$ cm ⁻¹	$\Delta\nu$ cm ⁻¹	$\Delta\nu$ cm ⁻¹
B ₁				B ₂			
1.	2950	2937	—	1.	2950	2929	—
2.	—	2902	—	2.	—	2924	—
3.	2850	2858	—	3.	2850	2854	—
4.	1449	1457	+ 8	4.	1450	1453	+ 3
5.	1310	1302	— 8	5.	1310	1325	+ 15
6.	1310	1291	— 19	6.	1237	1246	+ 9
7.	1208	1225	+ 17	7.	1138	1149	+ 11
8.	1138	1159	+ 21	8.	1105	1117	+ 12
9.	1105	1093	— 12	9.	988	989	+ 1
10.	1020	1013	— 7	10.	920	912	— 8
11.	870	854	— 16	11.	797	800	+ 3
12.	—	707	—	12.	338	359	+ 21
13.	—	282	—				

Norbornane-d₄ C₇H₈D₄ (3)

A ₁				A ₂			
1.	2950	2908	—	1.	—	2897	—
2.	—	2892	—	2.	—	2139	—
3.	2850	2857	—	3.	—	1307	—
4.	2120— 2210	2138	—	4.	—	1301	—
5.	1455	1511	+ 56	5.	—	1259	—
6.	1325	1333	+ 8	6.	—	1122	—
7.	1273	1276	+ 3	7.	—	1010	—
8.	1235	1215	— 20	8.	—	908	—
9.	1149	1139	— 10	9.	—	862	—
10.	950	961	+ 11	10.	—	535	—
11.	883	900	+ 17	11.	—	84	—
12.	797	789	— 8				
13.	752	685	— 67				
14.	692	677	— 15				
15.	379	372	— 7				

B ₁				B ₂			
1.	2950	2904	—	1.	2950	2929	—
2.	2850	2895	—	2.	2850	2891	—
3.	2120— 2210	2148	—	3.	2120— 2210	2131	—
4.	1310	1312	— 3	4.	1310	1304	— 11
5.	1295	1292	— 3	5.	1273	1288	+ 15
6.	1254	1252	— 2	6.	1254	1243	— 11
7.	1202	1198	— 4	7.	1083	1118	+ 34
8.	1070	1096	+ 26	8.	1030	1004	— 27
9.	983	989	+ 6	9.	925	930	+ 5
10.	922	917	— 5	10.	810	815	+ 5
11.	775	773	— 2	11.	655	669	+ 14
12.	—	664	—	12.	347	347	0
13.	—	250	—				

Generally, the difference between experimental and calculated wavenumbers for most vibrational modes is within $\pm 20 \text{ cm}^{-1}$. However, several A_1 modes in the CH_2 deformation and skeletal bending regions show larger differences for both molecules 1 and 3. The preliminary investigation thus reveals that the force constants of Snyder and Schachtschneider are also fairly adequate for describing moderately strained polycyclic hydrocarbons. They may even be used for quantitative predictions, although some disagreement between the experimental and calculated frequencies should be expected for strained parts of a molecule.

The forms of normal modes and the potential energy distribution (PED) show, for instance, that the largest deviations are associated with ν_5 of both isotopes corresponding to the CH_2 scissoring at the bridge position, and ν_{14} of 1 as well as ν_{13} of 3, which correspond to the $\text{C}_1\text{C}_7\text{C}_4$ deformation respectively. The most important force constants for these vibrations are $H_8 = 0.550$ and $H_{10} = 1.130 \text{ m dyn } \text{Å}^{-1} \text{ rad}^{-2}$. Because of the geometry used ($\Theta^4 = 93^\circ$ and not tetrahedral for which the force constant H_{10} is applicable) force constant H_{10} has to be increased to the value of $2.13 \text{ m dyn } \text{Å}^{-1} \text{ rad}^{-2}$, thus increasing the wavenumber $\nu_{14} = 685$ to 752 cm^{-1} , and H_8 has to be decreased from 0.550 to $0.490 \text{ m dyn } \text{Å}^{-1} \text{ rad}^{-2}$ thus decreasing the wavenumber $\nu_5 = 1512$ to 1455 cm^{-1} . The complete refinement of the original force field will be reported later.

A more detailed study of these molecules should be supported by the assignment of numerous bands in the CH stretching region, which are still ambiguous. The synthesis of molecules 2, 5 and 8 is in progress and the band contour analyses of the gas phase infrared spectra, as well as the depolarisation degrees of the Raman bands⁸, will provide sufficient experimental data for the complete and accurate vibrational analysis. This work will be reported in future.

Acknowledgement. We are indebted Prof. D. E. Sunko and Mr. M. Tomić, Zagreb, for the samples of norbornane and norbornane-d₄. Our thanks are also due to Prof. D. Hadži, Ljubljana, who enabled the recording of IR spectra on Perkin-Elmer M521 in his laboratory.

REFERENCES

1. Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Jap.* **40** (1967) 1552; G. Dallinga and L. H. Toneman, *Rec. Trav. Chim. Pays-Bas* **87** (1968) 795; J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.* **90** (1968) 3149; A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jap.* **44** (1971) 2356, and references cited therein.
2. e.g. G. Klopman, *J. Amer. Chem. Soc.* **91** (1969) 89; N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.* **92** (1970) 4270; M. Randić and D. Stefanović, *J. Chem. Soc. A* (1968) 755; Z. B. Maksić and M. Eckert-Maksić, *Croat. Chem. Acta.* **42** (1970) 433.
3. D. Roberts, W. Bennet and F. Armstrong, *J. Amer. Chem. Soc.* **72** (1950) 3329; D. Kivelson, S. Winstein, P. Bruck and R. L. Hansen, *J. Amer. Chem. Soc.* **83** (1961) 2938; M. Avram, G. D. Mateescu and I. I. Pogany, *Rev. Chim. Acad. Repub. Pop. Roum.* **7** (1962) 665; V. T. Aleksanyan, Z. B. Barinova, G. N. Zhizhin, Kh. E. Sterin, N. A. Behkova and A. F. Plate, *Zh. Strukt. Khim.* **4** (1963) 28.
4. Z. Meić, A. Rubčić and M. Randić, in preparation.
5. E. B. Wilson, Jr., J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York 1955.

6. M. V. Volkestein, M. A. Eliashevich and B. I. Stepanov, *Kolebanya Molekul*, GITTL, Moscow 1949.
7. R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta* **21** (1965) 169.
8. Z. Meić, D. E. Sunko and M. Tomić, in preparation.

SAŽETAK

Vibracijski spektri i potencijalne konstante bicikličkih molekula. I. Norbornan i norbornan-d₄.

Z. Meić, M. Randić i A. Rubčić

Analizirana su svojstva unutrašnjih koordinata norbornana na temelju simetrije C_{2v}. Primjenom prosječnoga potencijalnog polja za zasićene ugljikovodike Snyder-Schachtschneidera izračunane su vibracijske frekvencije za više različitih izotopa norbornana. Raspoloživi eksperimentalni podaci infracrvenih spektara zadovoljavajuće se slažu s izračunanim vrijednostima.

INSTITUT »RUĐER BOŠKOVIĆ«

i

PRIRODOSLOVNO-MATEMATIČKI FAKULTET,
SVEUČILISTA U ZAGREBU,
41000 ZAGREB

Primljeno 10. rujna, 1973.