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CARBON-13 CHEMICAL SHIFTS OF BICYCLIC COMPOUNDS

E. LIPPMAA and T. PEHK
Institute of Cybernetics of the Estonian Academy of Sciences, Tallinn, USSR

J. PAASIVIRTA
University of Jyväskylä, Jyväskylä, Finland

N. BELIKOVA and A. PLATÉ
Moscow State University, Moscow, USSR

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Abstract—^{13}C NMR absorption spectra of 50 bicyclic hydrocarbons, alcohols and ketones have been measured, in addition to some terpenes. The ^{13}C chemical shifts are approximately additive for similar compounds and can be used for the determination of molecular structure; they differ for *endo*- and *exo*-isomers, just as in proton spectra. These quite regular and predictable ^{13}C shift differences are much larger and are caused by the 1,4-nonbonded interaction between atoms heavier than hydrogen, not by magnetic anisotropy effects.

INTRODUCTION

BICYCLO [2.2.1]HEPTANE ring systems (derivatives of norbornane and norbornene) are rigid molecules of known and fixed geometry that have been very actively investigated by proton resonance methods[1 to 27] in order to study the influence of molecular geometry and polar substituents on proton chemical shifts and coupling constants. The general applicability of the Karplus relationships between vicinal proton-proton coupling constants and dihedral angles[28] and the 'W-letter' rule for couplings between distant protons,[29] as well as the linear variation of vicinal coupling constants with substituent electronegativities,[2] were all conclusively demonstrated on these and similar systems.[1] These relationships have been extremely useful in elucidating the structures of bicyclic and polycyclic compounds, particularly for the determination of substituent orientations. In addition to coupling constants, proton chemical shifts and their differences have been found to correlate well with molecular structure. It has been found that further to the usual inductive effects which are most apparent on the α-proton, many other analytically significant effects are present. Fraser,[5] Musher,[4] and Paasivirta[3] have pointed out that *exo*-protons in norbornane and norbornene derivatives are deshielded relative to the *endo*-protons at the same carbon atom. Additionally, in 2-substituted norbornanes the 2-*exo*-proton of the *endo*-isomer is deshielded relative to the 2-*endo*-proton of the *exo*-isomer.[15] This effect is similar to the well-known chemical shift difference between the diamagnetic axial and paramagnetic equatorial protons in cyclohexane derivatives.[30] Shift differences of this kind have generally been attributed to the diamagnetic anisotropy of the double bond or to the magnetic effect of the adjacent single bonds respectively. Similarly, substituents in the 2- and 3-positions cause a chemical shift difference of protons at the double bond.[10] A 2- or 3- *endo*-substituent leads to an increased shift difference of the 5- and 6- protons across the ring. This effect can be partially explained by the substituent anisotropy effect, but the influence of a —CN group is smaller than that of —OH and a good fit of the shifts with known group anisotropies could not be achieved.[3] Likewise, the shieldings of the 7-*syn* and 7-*anti* protons are not equal, the 7-*anti* proton being the more shielded one.[8,9] This result was at first unexpected, and Tori *et al.* in their first paper[6] assigned the 7-*syn* proton to the high-field multiplet because of the proximity of the double bond. In their second paper Tori and co-workers reversed this assignment on the ground of spin-decoupling experiments[7] and pointed out the possible significance of electronic effects which could cause such unusual shifts. All this has led to some controversy about the geometric (magnetic) versus electronic interpretation of differential proton shifts in norbornene derivatives.[8] It is usually assumed that inductive effects are transmitted along the chemical bonds only and must be equal for *exo*- and *endo*-protons at the same carbon atom. At present, the predominance of magnetic over electronic effects for *syn-anti* and *endo-exo* proton pairs in norbornene derivatives appears to be generally accepted,[8,9] although not proven.

The assumption that the 7-*syn* proton does not experience any unusual shielding effects in addition to the magnetic ones[8] is not in keeping with kinetic data[31] and the ^{13}C chemical shifts, where a very significant deshielding of the bridge carbon atom has been noted in norbornene and especially in norbornadiene.[32,33] This effect is clearly of electronic origin, since the measured ^{13}C chemical shifts correlate with atomic charges, calculated by the extended Hückel theory.[34] In addition to this, the ^{13}C chemical shifts which depend chiefly upon the electronic effects allow us to check the various interpretations of proton shifts. The relative magnitude of magnetic effects is the same as in proton spectra, but the total range of ^{13}C chemical shifts caused by electronic effects is about 30 times larger. The ^{13}C chemical shifts are known to be very sensitive to molecular geometry,[35 to 39] and so provide a new and sensitive technique for the determination of the orientation of substituents and even for the study of the structure of the alicyclic ring system itself. The applicability of proton resonance for these purposes is limited. Even if polar substituents are present in the molecule, the PMR spectra of these compounds are quite complex and double[7,11,13,21,22,23,40] or triple resonance,[26] spectra at 220 MHz,[40] deuterium labelling,[7,8,9,12,13] solvent effects,[1,19] and other special techniques are necessary for the determination of all the proton shieldings. Total spectrum analysis is usually a very difficult task and all proton chemical shifts have been measured for only a few norbornene derivatives.[3,8,9,27] To our knowledge no full analysis is available for norbornane derivatives (except the highly chlorinated ones), although the proton shifts of the symmetrical parent compound itself are known.[7]

In contrast to proton spectra, ^{13}C spectra registered with total decoupling of all hydrogen nuclei give only one line for each non-equivalent carbon atom in the molecule and so are inherently simple. The line intensity is roughly proportional to the number of equivalent carbon atoms, corresponding to a particular peak. Total interpretation of ^{13}C spectra of very complicated molecules, including steriods, is possible[38,68] and leads to useful empirical and semi-empirical relationships which can be employed for the determination of molecular structure.

The object of this paper is to present data about ^{13}C chemical shifts in norbornane and norbornene derivatives. These shifts can be used as increments for structural analysis, particularly for the determination of orientations of substituent groups, and provide a starting point for the estimation of the relative importance of electronic and magnetic effects in ^1H and ^{13}C NMR spectra.

EXPERIMENTAL

All experiments were performed on a frequency-swept universal spectrometer[41] at 15·1 MHz. Absorption spectra were registered in most cases, using a very strong unmodulated perturbing *rf* field for the total decoupling of hydrogen nuclei. Selective double resonance with a weaker *rf* field and off resonance decoupling[38,42] were used in some cases to facilitate spectrum interpretation. Off resonance experiments, where the perturbing *rf* field is weaker and displaced by about 200 to 300 Hz away from exact resonance with the protons connected to the carbon atoms being studied, provides multiplets with reduced (20 to

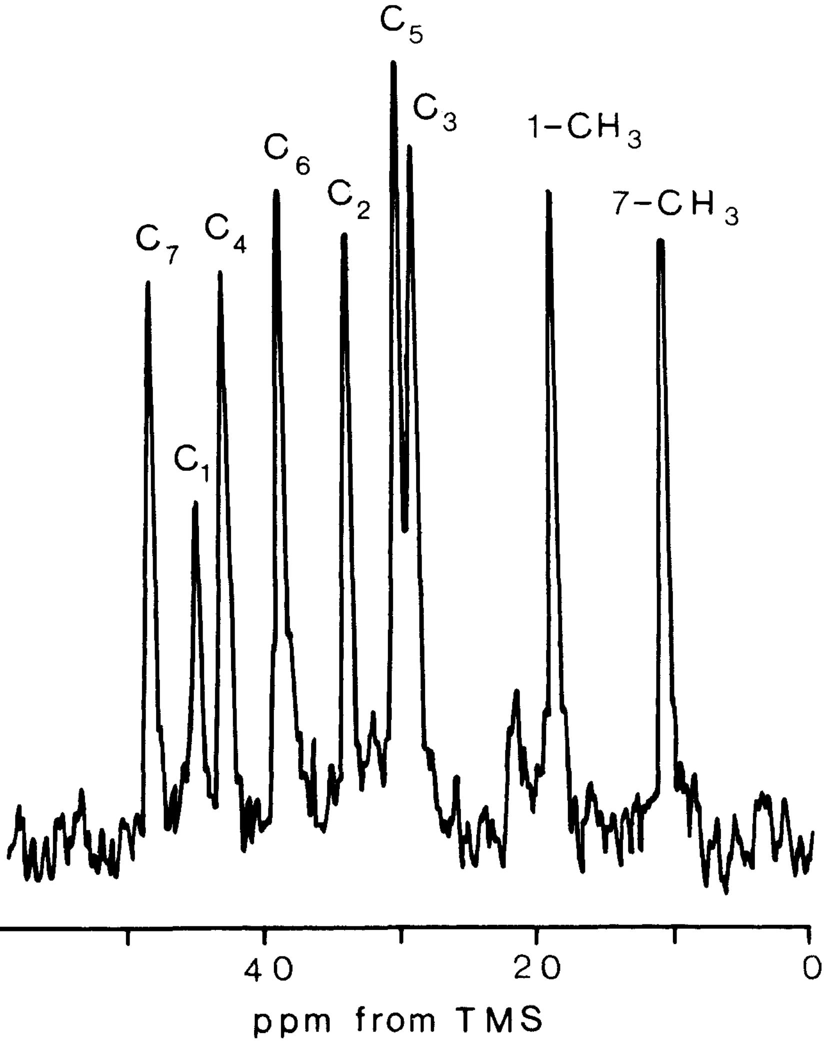


FIG. 1. Proton-decoupled ^{13}C absorption spectrum of 1,7-dimethylnorbornane.

60 Hz instead of the usual 120 to 170 Hz) splittings and only insignificantly reduced intensities. These modes of spectrometer operation allow the multiplicities of individual lines to be recognized because the usually very serious overlapping of spin multiplets is reduced. In particular the singlet lines of fully substituted quaternary carbon atoms stand out very clearly. Of course, such lines can be recognized by the reduced value of the nuclear Overhauser effect (and line intensity) just as well. Selective double resonance is useful for the determination of carbon atoms, adjacent (α-) to a double bond, because the corresponding proton resonance frequencies are strongly shifted. Noise decoupling was not used because it can create some additional noise in the measured spectrum and is useless for selective double resonance and off resonance experiments. The spectrometer was spin stabilized using a separate proton probe. A multichannel analyzer (Nokia LP 4050) was used for spectrum accumulation in some cases. Most samples were measured in 15 mm o.d. sample tubes as neat liquids or concentrated solutions in CS_2 at about 40°C, using a 15 to 40 Hz/sec sweep rate. The ^{13}C shifts were measured from external CS_2 or in some cases from dioxane (δ_{CS_2} = 125·9 ppm). The measured ^{13}C chemical shifts are reproducible to about $\pm 0{\cdot}2$ ppm.

All ^{13}C chemical shifts are now given on a new tetramethylsilane (TMS) scale with higher frequency (low field) shifts positive. This system is consistent with the δ-scale for protons and has the additional advantage that only one compound, available in any NMR laboratory (TMS) is used as a reference for three important nuclei (^1H, ^{13}C and ^{29}Si). CS_2 is a logical choice as a standard for ^{13}C if rapid passage single resonance spectra are being studied, but with the advent of double resonance and frequency sweep a proton-containing standard is a better choice, since it gives a much stronger double resonance signal and can be used for indirect measurement of ^{13}C chemical shifts by various methods of heteronuclear double resonance.[43 to 47] Benzene is not as suitable, because about half of the ^{13}C shifts are negative in any case, irrespective, whether the high or low field shifts are considered positive. In addition to this, benzene is not acceptable as an internal standard because of the strong solvent shifts. The new δ_{TMS} scale has been proposed informally many times, but tradition, and one of no long standing at that, has been holding it back. Within the new system larger and paramagnetic chemical shifts correspond to transitions with higher energies and this is certainly in keeping with the traditions of molecular spectroscopy, even to the point of having zero to the right, as in the optical spectra where frequency, wave-numbers and transition energies also increase to the left. All ^{13}C chemical shifts which were measured from CS_2 were converted to the new scale of proton-decoupled tetramethylsilane using the value $129{\cdot}0 + 64{\cdot}1 \pm 0{\cdot}1$ ppm for the chemical shift of CS_2,[44,48,49] so that $\delta_{TMS} = 193{\cdot}1 - \delta_{CS_2}$. Our own measurements give the same conversion factor.

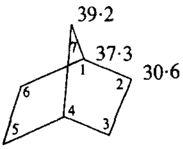
A decoupled ^{13}C spectrum of 1,7-dimethylnorbornane is shown in Fig. 1. The spectrum contains 9 lines that correspond to 9 non-equivalent carbon atoms. The line corresponding to C-1 is considerably weaker than other peaks.

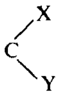
RESULTS

In addition to physical methods, described in the preceding section, approximate additivity of ^{13}C chemical shifts was widely used for the assignment of spectral lines to particular carbon atoms in the molecule. The increments of Savitsky and Namikawa[50] and those of Grant and Paul[51] are not directly applicable to bi- and polycyclic systems, as was shown in earlier papers.[33,41] The influence of substituents on the ^{13}C chemical shifts of norbornane and norbornene is quite regular, additive and predictable, however. Some increments that are generally valid for these systems are given in Table 1, but an even better fit can be achieved for very similar compounds. The effects of introducing a single methyl or hydroxyl group are predictable with high precision. Such analysis, using the very regular ^{13}C chemical shift changes on going from simpler to more complicated molecules in a systematic way was the most important single technique used for shift assignment in this study. The internal consistency of all shifts, as evidenced by the universal applicability of the increments given in Table 1 supplies additional proof to such procedure.

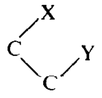
The parameters given in Table 1 must be added to the chemical shifts of norbornane to calculate the shifts of substituted derivatives. Positive parameter values

TABLE 1. SUBSTITUENT PARAMETERS FOR THE CALCULATION OF APPROXIMATE ^{13}C CHEMICAL SHIFTS OF NORBORNANE AND NORBORNENE DERIVATIVES





−4 ppm



−2·5 ppm[a]
0 ppm for *endo-exo* orientation of X and Y

Substituent groups	Changes of chemical shifts of the carbon atoms in the bicyclic ring system								
	C_1	C_2	C_3	C_4	C_5	C_5	C_6	C_6	C_7
	sp^3	sp^3	sp^3	sp^3	sp^3	sp^2	sp^3	sp^2	sp^3
1-CH_3	+6·1	+6·5	+1·5	0	+1·5	0	+6·5	+5·3	+6·2
2-*exo*—CH_3[b]	+5·5	+8·3	+10·4	0	−0·3	−0·3	+1·0	+1·6	−3·0
2-*exo*—OH[b]	+6·5	+44·9	+10·8	−0·5	−1·5	+3·6	−2·3	−0·4	−3·0
2-*endo*—CH_3[b]	+6·3	+6·9	+8·5	+0·5	0	+1·2	−7·0	−3·1	+2·0
2-*endo*—OH[b]	+7·2	+45·7	+11·3	0	−0·2	+2·8	−8·1	−2·0	+1·5
7—CH_3[c]	+3·6	−2·5	−2·5	+3·6	+0·5		+0·5	−6·3	+5·5
2=CH_2	+8·0	+121·0	+8·6	−1·0	−1·0	0	−0·5	−1·7	+0·5
2=O	+12·0	+176·0	+11·7	−1·3	−2·2		−5·2		−0·7
C_5=C_6[d]	+5·5	−3·5	−3·5	+5·5		+109·0		+109·0	+11·0

[a] Additional parameters for *gem*- and *vic*-disubstituted carbon atoms. These values are taken to be independent of bond angles between the —CH_3, —OH, C=O and C=CH_2 groups, but zero if no direct through-space interaction is possible. The resulting error is included in the ±4 ppm error of the calculated shifts.

[b] Introduction of methyl or hydroxyl groups into the 3-, 5- or 6- positions leads to symmetrical effects.

[c] *syn*- to the 2- and 3- positions.

[d] Introduction of one double bond between C_5 and C_6.

correspond to paramagnetic shifts. It is immediately apparent that all parameters have usual signs and magnitudes. The introduction of methyl groups or double bonds leads to a paramagnetic shift of the resonance of the substituted atom and its neighbours, but to a diamagnetic shift of atoms three bonds away which can be packed close together (1,4-nonbonded interaction). The values of some of the increments are close to those given by Grant for substituted cyclohexanes[37] which emphasises the universality of underlying shielding mechanisms. Of course, it could be possible to introduce more increments, such as different ones for 2,3-*exo*, *exo*-, 2,3-*exo*, *endo*- and 2,3-*endo*, *endo*- compounds, etc., but this is of little practical use since in any case these parameters are empirical ones of limited applicability and any further refinement only comes down to a more complicated method of presenting the data given in Tables 2 and 3. For structures of these compounds see Fig. 2.

TABLE 2. ^{13}C CHEMICAL SHIFTS OF HYDROCARBON DERIVATIVES OF NORBORNANE AND NORBORNENE

No.	Compound	^{13}C chemical shifts in ppm, measured to low field from external tetramethylsilane[a]								
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	Others	
(1)	Norbornane	37·3	30·6	30·6	37·3	30·6	30·6	39·2		
(2)	1-Methylnorbornane[90]	44·2	37·4	31·9	38·4	31·9	37·4	45·9	1-Me 21·4	
(3)	2-*exo*-Methylnorbornane[89]	43·7	37·0	40·4	37·5	29·3	30·7	35·4	2x-Me 22·8	
(4)	2-*endo*-Methylnorbornane[89]	42·1	34·5	38·9	38·1	30·6	22·3	40·7	2n-Me 17·5	
(5)	7-Methylnorbornane[95]	41·1	27·4	27·4	41·1	31·1	31·1	44·4	7-Me 12·9	
(6)	1,2-*exo*-Dimethylnorbornane[93]	45·7	41·0	40·4[b]	39·2	31·1	37·5[b]	41·6	1-Me 17·8;	2x-Me 19·9
(7)	1,2-*endo*-Dimethylnorbornane[93]	46·6	39·9	40·4	37·5	32·0	29·3	47·7	1-Me 19·5;	2n-Me 15·2
(8)	1,3-*exo*-Dimethylnorbornane[96]	44·9	47·5	38·3	45·3	32·0	36·2	42·0	1-Me 21·4;	3x-Me 22·8
(9)	1,3-*endo*-Dimethylnorbornane[96]	45·3	45·8	35·9	43·5	24·2	37·6	47·5	1-Me 21·9;	3n-Me 18·2
(10)	1,4-Dimethylnorbornane[92]	45·3	38·7	38·7	45·3	38·7	38·7	52·4	1,4-Me 21·9	
(11)	1,7-Dimethylnorbornane[93]	44·7	33·8	28·9	42·5	30·1	38·6	48·2	1-Me 18·6;	7-Me 10·7
(12)	2,2-Dimethylnorbornane[92]	48·1	36·9	47·2	38·8	28·7	25·1	38·8	2x-Me 31·7;	2n-Me 27·3
(13)	2-*exo*,3-*endo*-Dimethylnorbornane[92]	44·9	45·8	44·6	43·0	21·6	30·8	37·4	2x-Me 21·6;	3n-Me 16·1
(14)	Bornane[18]	46·9	37·3	29·4	46·9	29·4	37·3	45·5	1-Me 16·5;	7-Me 19·9
(15)	2-Methylenenorbornane[89]	45·6	154·3	38·4	37·0	28·6	29·9	39·2	2=CH_2 102·0	
(16)	1-Methyl-2-methylenenorbornane[93]	48·8	157·5	39·8	36·2	30·4	36·9	46·3	1-Me 17·5;	2=CH_2 100·6
(17)	2-*exo*-Methyl-3-methylenenorbornane[93]	42·6	43·3	161·3	45·8	28·8	28·8	35·3	2x-Me 19·7;	3=CH_2 101·6
(18)	2-*endo*-Methyl-3-methylenenorbornane[93]	41·1	42·6	161·3	46·3	30·4	21·2	39·2	2n-Me 14·6;	3=CH_2 100·9
(19)	2-Norbornene[c]	42·0	135·8	135·8	42·0	24·8	24·8	48·8		
(20)	2-Methyl-2-norbornene[91]	46·9	144·9	128·7	42·9	27·3	24·7	48·6	2-Me 15·1	
(21)	5-*exo*-Methyl-2-norbornene[89]	42·6	136·1	137·0	47·7	32·9	34·2	45·1	5x-Me 21·8	
(22)	5-*endo*-Methyl-2-norbornene[89]	43·5	137·0	132·5	48·7	32·9	35·0	50·6	5n-Me 19·6	
(23)	1,2-Dimethyl-2-norbornene[93]	50·9	146·2	129·5	41·8	29·6	31·8	54·7	1-Me 17·7;	2-Me 12·4
(24)	5-*endo*, 6-*exo*-Dimethyl-2-norbornene[92]	49·8	138·2	133·2	48·4	42·0	43·0	47·0	5n-Me 18·8;	6x-Me 20·4
(25)	*E*-5-Ethylidene-2-norbornene[d] [94]	42·2	135·9	134·9	51·0	142·0	31·4	50·6	$=\overset{*}{C}H$—Me 112·9;	Me 15·0
(26)	*Z*-5-Ethylidene-2-norbornene[e] [94]	42·0	136·1	133·7	45·3	141·2	34·0	49·9	$=\overset{*}{C}H$—Me 113·1;	Me 15·0
(27)	2,5-Norbornadiene[c]	50·4	143·2	143·2	50·4	143·2	143·2	75·2		

[a] $\delta_{TMS} = 193·1 - \delta_{CS_2} = 129·0 - \delta_{C_6H_6} = 67·2 - \delta_{dioxane}$.

[b] Tentative assignment.

[c] Commercial product.

[d] Low-boiling isomer.

[e] High-boiling isomer.

TABLE 3. ^{13}C CHEMICAL SHIFTS OF NORBORNANE AND NORBORNENE DERIVATIVES WITH POLAR SUBSTITUENTS

No	Compound	^{13}C chemical shifts in ppm, measured to low field from external tetramethylsilane[a]										
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	Others
(28)	2-*exo*-Norbornanol[16]	44·6	74·6	42·5	36·2	29·3	25·4	35·2				
(29)	2-*endo*-Norbornanol[16]	43·2	72·9	38·1	38·1	30·6	20·8	39·5				
(30)	2-*exo*-Hydroxy-2-*endo*-methylnorbornane[16]	50·1	77·8	49·5	38·2	29·0	24·9	38·2				2n-Me 26·3
(31)	2-*endo*-Hydroxy-2-*exo*-methylnorbornane[16]	49·4	77·2	47·6	38·3	29·3	23·1	39·5				2x-Me 31·1
(32)	2-*exo*-Norbornanemethanol	38·4	45·3	34·7	36·9	29·7	30·6	35·6				CH_2OH 66·7
(33)	2-*endo*-Norbornanemethanol	38·8	42·9	34·4	37·5	30·6	23·1	40·5				CH_2OH 64·6
(34)	Isoborneol[c] [97]	49·4	79·8	41·3	46·1	28·3	34·9	46·9	21·1	21·1	12·2	
(35)	Borneol[bc]	50·1	77·5	39·8	46·4	29·4	27·0	48·6	19·6	21·1	14·3	
(36)	2-*exo*-Chlorobornane[c] [17]	49·8	67·6	42·8	46·4	27·3	36·6	47·5	20·4	20·4	13·6	
(37)	2-*endo*-Chlorobornane[c] [83]	50·6	67·1	40·2	45·3	28·3	28·3	47·7	18·4	20·5	13·2	
(38)	2-Norbornanone	50·3	217·7	45·6	36·2	27·8	24·9	38·1				
(39)	Camphor[bc]	57·1	215·4[d]	43·2	43·5	27·6	30·3	46·6	20·0	19·4	9·8	
(40)	3-*endo*-Bromocamphor[bc]	57·6	210·1	54·8	50·3	23·2	31·1	46·1	20·3	20·3	10·1	
(41)	1,3,3-Trimethyl-2-norbornanone[b]	53·7	219·3[e]	46·9	45·5	25·1	31·8	41·6	23·5	21·9	14·8	
(42)	2-*exo*-Hydroxy-5-norbornene[10]	49·8	71·8	36·5	40·7	139·7	133·1	45·6				
(43)	2-*endo*-Hydroxy-5-norbornene[10]	49·1	72·6	38·1	44·2	139·4	132·4	49·1				
(44)	1-Methyl-2-*exo*-hydroxy-5-norbornene	53·8	74·6	38·9	41·1	140·2	139·4	50·9				1-Me 14·7
(45)	1-Methyl-2-*endo*-hydroxy-5-norbornene	54·3	77·1	40·7	43·3	139·2	136·8	54·3				1-Me 17·0
(46)	2-*exo*-Methyl-2-*endo*-hydroxy-5-norbornene[10]	54·2	78·0	49·3	43·2	138·1	134·5	44·5				2x-Me 29·5
(47)	2-*exo*-5-Norbornenemethanol	43·9	41·9	30·0	41·9	136·7	136·7	45·4				
(48)	2-*endo*-5-Norbornenemethanol	44·3	43·1	29·8	42·3	137·1	132·9	50·2				CH_2OH 66·1
(49)	Norbornen-2-one[11]	55·8	212·8	36·7	40·0	143·0	130·8	50·8				
(50)	1-Methylnorbornen-2-one[11]	59·3	213·5	37·8	38·6	143·0	135·6	56·1				1-Me 12·0
(51)	Ethylidenecyclopentane	132·1	28·3	26·6	26·4	33·5						$=\overset{*}{C}H{-}Me$ 114·2 —Me[f] 14·3

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[a] $\delta_{TMS} = 193·1 - \delta_{CS_2} = 129·0 - \delta_{C_6H_6} = 67·2 - \delta_{dioxane}$.

[b] Commercial product.

[c] Concentrated solution in CS_2.

[d] 219·4 ppm in $CHCl_3$ solution.[72]

[e] 219·2 ppm.[14]

[f] *cis*- to the C_2 methylene group of the ring.

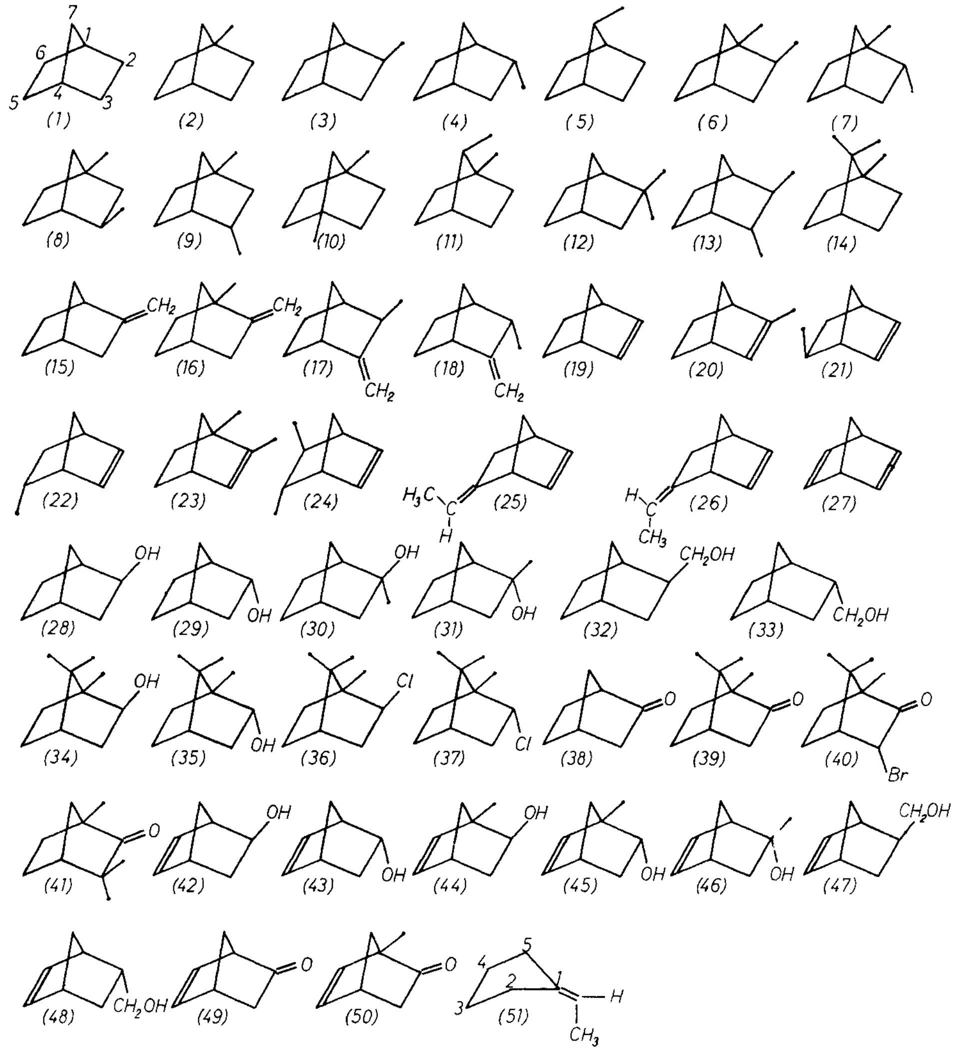

FIG. 2. The structures of all norbornane and norbornene derivatives described in Tables 2. and 3.

1. Hydrocarbon derivatives of norbornane

1.1. *Norbornane* (**1**). The assignment of all shifts is self-evident. It is interesting to note that it proved impossible to distinguish between C-1, C-4 and C-7 using only INDOR spectra.[25] The systematic difference about 1·8 ppm between our data and the data of Olah and White[25] may be caused by some systematic error that does not show up between similar compounds in one series of experiments.

1.2. 1-*Methylnorbornane* (**2**). In accordance with the data for cyclohexane derivatives[36,37] the methyl group is considered to exert a pronounced paramagnetic influence on the shifts of the substituted atom and its neighbours and so the shifts of

C-2 and C-6 must be larger than the shifts of C-3 and C-5. The assignment of all other shifts according to line multiplicities is unambiguous.

1.3. *2-exo-Methylnorbornane* (**3**) *and 2-endo-Methylnorbornane* (**4**). The assignment of methyl resonance is unambiguous and leads to a significant shift difference $\Delta = 5{\cdot}3$ ppm. The same difference equals $\Delta = 4{\cdot}4$ ppm in 2,2-gem-dimethylnorbornane (**12**) and so must in both cases be caused by the 1,4-nonbonded interaction with C-7·and C-6 respectively. The difference of *endo-exo* proton shifts of partly magnetic origin is only 0·31 ppm. Using the known properties of the 1,4-interaction and of the methyl group it is possible to assign all other resonances so that an internally consistent system, both for all chemical shifts and for the substituent parameters, is formed for **3**, **4**, **6**, **7**, **8**, **9**, **12** and **13**.

1.4. *7-Methylnorbornane* (**5**). The C-2, C-3 and C-5, C-6 peaks of equivalent carbon atoms with double intensity have been assigned by considering the atoms *syn-* to the methyl group to be the more diamagnetic ones. All other assignments are self-evident and unambiguous.

1.5. *1,2-exo-Dimethylnorbornane* (**6**) *and 1,2-endo-Dimethylnorbornane* (**7**). All chemical shifts in these compounds have been assigned using the generally additive influence of the two methyl groups. If the additional parameter for two vicinal substituents $-2{\cdot}5$ ppm is taken into account, then the difference between shifts calculated from **2**, **3** and **4** and the experimental ones is less than 1·0 ppm in most cases. The assignment of methyl resonances is unambiguous because of the large shift difference; analogy with **3** and **4** was used for this purpose.

1.6. *1,3-exo-Dimethylnorbornane* (**8**) *and 1,3-endo-Dimethylnorbornane* (**9**). The assignment followed as in the previous case, but was, of course, facilitated by the absence of vicinal substituents which leads to a better shift additivity. The shifts were calculated from the data for **2**, **3** and **4**. Assignment of the methyl resonance was likewise simplified by the absence of interactions between methyl groups that leads to a constant shift of the 1-methyl group. The shift difference between *endo-* and *exo-* methyl groups is $\Delta = 4{\cdot}6$ ppm in this case.

1.7. *1,4-Dimethylnorbornane* (**10**). Only line intensities were necessary for unambiguous assignment of all spectral peaks in this case. Of course, line multiplicities provided an additional check. It is interesting to note that the measured shifts agree very well with the calculated ones, using the data for **2** to calculate the influence of one additional methyl group. Apparently the interaction between the distant methyl groups is very weak in this molecule.

1.8. *1,7-Dimethylnorbornane* (**11**). The data for **2** and **5** were used for the assignment. As in the case of **5**, it was assumed that the *syn*-methyl group leads to a diamagnetic shift of C-2 and C-3 resonances. The very large difference of methyl shieldings made possible an unambiguous assignment of these lines. Both are slightly more shielded than in **2** and **5**, as is usual for flexible groups in 1-4 position to each other. This increase is accounted for by the *vic*-increment.

1.9. *2,2-Dimethylnorbornane* (**12**). All carbon shifts were assigned using the data for **3** and **4**. If the *gem-* increment is taken into account, then a fair additivity is achieved. The methyl resonances were assigned by analogy with the other 2- and 3-substituted norbornanes and the quite large shift difference lends support to this procedure.

1.10. *2-exo, 3-endo-Dimethylnorbornane* (**13**). As in the previous case, the data for **3** and **4** were used for the assignment, but in a different combination. Additivity is very good in this case and introduction of the *vic*-parameter would only lead to an additional error. This parameter is clearly significant only for close interacting groups. The difference of methyl resonances is $\Delta = 5{\cdot}3$ ppm in this case and by analogy with **3**, **6** and **8**, the *endo*-methyl group is assigned to the more diamagnetic line.

1.11. *Bornane* (**14**). Only tentative assignment is possible for singlet lines of fully substituted carbon atoms in this case. The shift differences are too small and the influence of substituents at C-7 upon molecular geometry is too large for an unambiguous assignment. The assignment of all other lines, however, is simplified by molecular symmetry and unequivocal. It is interesting to note that the introduction of a second methyl group at C-7 has a strong influence upon the shift of the first methyl group, but only little effect on C-7 itself.

1.12. *2-Methylenenorbornane* (**15**). For the assignment of both unsaturated carbons the increments of Savitsky and Namikawa[50] can be used. The very large shift difference simplifies the use of these parameters. Of course, the parameters in Table 1 lead to the same result. C-1 and C-4 could be assigned by analogy with **1**, using the doublet character of these signals as a reconfirmation. Since the protons connected to C-3 have a resonance frequency quite different from those at C-7 (about 0·5 ppm to low field),[15] selective double resonance could be used to assign these carbon atoms. The remaining C-5 and C-6 were assigned by analogy with **16**, because it is well known that the influence of the double bond is very weak when several bonds away[35] and the influence of a methyl group at C-1 always leads to a small paramagnetic shift at C-5.

1.13. *1-Methyl-2-methylenenorbornane* (**16**). Signal multiplicities and comparison of the measured shifts with those calculated from the data for **2** and **15** is sufficient for an unambiguous assignment.

1.14. *2-exo-Methyl-3-methylenenorbornane* (**17**) *and 2-endo-Methyl-3-methylenenorbornane* (**18**). All chemical shifts in these compounds have been assigned using the data for **1**, **3**, **4** and **15**. The additivity of substituent influences is very good and for only two carbons in **18** does the difference between measured and calculated shifts exceed 1 ppm. Use of the additional *vic*- parameter is justified for these compounds. The difference of methyl resonances is $\Delta = 5{\cdot}1$ in this case, the *endo*-group being, as always, the more diamagnetic one.

2. Hydrocarbon derivatives of norbornene

2.1. *2-Norbornene* (**19**). The assignment of all resonances is straightforward and unambiguous. The bridge methylene resonance shows a significant paramagnetic shift, an effect which is even more significant in **27**.[32]

2.2. *2-Methyl-2-norbornene* (**20**). The olefinic carbon atoms could be recognized by signal multiplicities, since C-2 gives a singlet, but C-3 a doublet line. The shift of C-1 must be more paramagnetic than that of C-4; compare with the data for substituted cycloalkenes.[52] The shift of C-7 is very different from those of C-5 and C-6, and virtually unchanged as compared with **19**. The assignment of C-5 and C-6 rests on the comparison with **23**, where the 1-methyl group leads to very regular and predictable changes of these shifts.

2.3. *5-exo-Methyl-2-norbornene* (**21**) *and 5-endo-Methyl-2-norbornene* (**22**. Since only a mixture of these compounds could be used because of difficulties with isomer separation the assignment of some lines was difficult. The methyl groups are easily recognized and show the usual difference of chemical shifts, only slightly smaller than in norbornane derivatives. The substituted C-5 carbons could be assigned through the use of selective double resonance. This shift is equal in both isomers, although it is slightly different in **3** and **4**. The assignment of C-6 and C-7 was simplified by the large shift difference. The shifts of C-7 in both isomers show the usual pattern of 1,4-interaction with the methyl groups, the shift in **21** being the more diamagnetic one. The shifts of the methyl-substituted atom and the adjacent methylene carbon atom are usually also more diamagnetic in *endo*-isomers. The assignments are consistent with this trend. The influence of a 2- (or 5-) methyl group on the resonance of the adjacent bridgehead carbon is sufficiently pronounced to allow an unambiguous assignment of these resonances (compare with **3** and **4**). The data for **24** were used to help in the assignment of C-2 and C-3 resonances. Because of the closeness of some of the shifts these assignments must be considered only tentative for **21**. Just as in proton spectra,[3] the difference of these shifts is larger in *endo*-isomers than in *exo*-isomers, but the effect is so large [4·5 ppm in the *endo*-isomer (**22**), 0·9 ppm in the *exo*-isomer (**21**)] that it cannot be of magnetic origin. These effects are even larger in norbornenols (**42**) and (**43**).

2.4. *1,2-Dimethyl-2-norbornene* (**23**). Comparison with the shifts of **20** and **2** allowed all lines to be assigned. The effect of one additional methyl group in the 1-position is small on the unsaturated carbon atoms, but analytically significant at C-5 and C-6. Both methyl groups are diamagnetically shifted as compared with **2** and **20**, but the difference is large enough for unequivocal assignment.

2.5. *5-endo-6-exo-Dimethyl-2-norbornene* (**24**). The assignment followed the same reasoning that was used for **21** and **22**. Since the methyl groups are located far from each other, the additivity is excellent and the difference between calculated (using **19**, **21** and **22**) and experimental shifts does not exceed 0·9 ppm. Just as in the case of **13**, the *vic*-parameter was taken to be zero in this case. The methyl resonances follow the characteristic pattern with different shifts for *endo*- and *exo*-methyl groups, but the difference is smaller than in **13**.

2.6. *E-5-Ethylidene-2-norbornene* (**25**) *and Z-5-Ethylidene-2-norbornene* (**26**). For the nomenclature of *cis-trans* isomers of this type see Lit.[53,54] Chemical shifts of C-1, C-4, C-6 and C-7 can easily be assigned by comparison with **15** and taking into account the different signal multiplicities for C-4 and C-7. The only difficulty is the assignment of C-2 and C-3. Comparison of the shifts of pentene-1 and pentadiene-1,4[55] shows that in unconjugated dienes C-2 is diamagnetically and C-1 paramagnetically shifted relative to the corresponding carbon atoms in pentene-1. The resonances of C-2 and C-3 have been assigned by assuming the same to be the case in **25** and **26**. Even though shift differences between the isomers are generally small, the resonances of C-4 and C-7 are very characteristically shifted showing that in **25** the methyl group must be closer (and in 1,4-non-bonded interaction) with C-6, but in **26** with C-4. It follows that the lower boiling **25** must be the *E*- and the higher-boiling **26** the *Z*-isomer. In this case ^{13}C resonance was used as a structure determination tool for compounds that had not been investigated before.

2.7. 2,5-*Norbornadiene* (**27**). The ^{13}C spectrum is very simple and assignment of all chemical shifts straightforward. The most important feature of this compound is the unusually large paramagnetic shift of the C-7 bridge carbon.[32,33] This shift may be caused by some electron delocalisation to the double bonds that leads to changes of atomic charge densities[34] and to an increased reactivity. Kinetic measurements show an unusually strong influence of far-away substituents,[31] which can only be possible if there is some electron delocalization between C-7 and the double bonds.[12]

3. Derivatives of norbornane with polar substituents and terpenes

3.1. 2-*exo-Norbornanol* (**28**) *and* 2-*endo-Norbornanol* (**29**). The proton spectra of stereoisomeric norbornanols are so complicated that a full analysis is hardly possible. Carbon spectra are also complex, but still tractable, even though selective double resonance is of only limited utility in this case. C-1, C-2 and C-4 resonances can be unambiguously assigned from line multiplicities and from the known influence of a hydroxyl group upon carbon shifts in alicyclic and aliphatic compounds.[36,56] It follows from these data as well as from the shifts of **1**, **3** and **4** that the shifts of C-4 and C-5 must remain practically unchanged upon the introduction of a hydroxyl group. A 1-4 diamagnetic shift of the C-6 resonance is expected in both compounds, and that of C-7 in **28** as well. This leaves only C-1 and makes a full interpretation possible. Of course, comparison with **30**, **31**, **34**, **35**, **42**, **43**, **44** and **45** proves that the influence of a hydroxyl group in bicyclic systems can be modelled along these lines. The C-2 resonance is different in an *endo-exo* pair of isomers. The difference ($\Delta = 1{\cdot}7$ ppm) is much larger than that for H-2 in proton spectra and is similar to the orientation effects in cyclohexane derivatives[57] and possibly of the same nonmagnetic origin.

3.2. 2-*exo-Hydroxy*-2-*endo-methylnorbornane* (**30**) *and* 2-*endo-Hydroxy*-2-*exo-methylnorbornane* (**31**). The interpretation of these spectra follows the same reasoning as was used in the case above. The introduction of an additional methyl group leads to an additional paramagnetic shift of C-1 and C-3 resonances and accentuates the shift difference between C-1 and C-4. The very wide 25 ppm range of methylene shifts makes possible an unequivocal assignment of C-3 (the most paramagnetic one), C-7, C-5 and C-6 (the most diamagnetic one). As in the previous cases, the introduction of a methyl group at C-2 leaves the C-5 shift practically unchanged and increases by a few ppm the screening of C-6 in **30** and C-7 in **31** respectively. It is important to note that the 1,4-nonbonded interaction of methylene carbons with closely spaced hydroxyl groups is slightly more pronounced than that with methyl groups. The C-6 resonance is more diamagnetic in the *endo*-hydroxyl compound (**31**) and the C-7 resonance in the *exo*-isomer (**30**).

3.3. *2-exo-Norbornanemethanol* (**32**) *and 2-endo-Norbornanemethanol* (**33**). Most of the carbon chemical shifts in these compounds are very close to those of **3** and **4** as expected. The influence of a hydroxymethyl group upon the chemical shifts of ring carbons is only slightly stronger than that of a methyl group. Line multiplicities supply some additional proof and the assignment of the *exo*cyclic methylene resonances is unambiguous.

3.4. *Isoborneol* (**34**), *Borneol* (**35**), *2-exo-Chlorobornane* (**36**) *and 2-endo-Chlorobornane* (**37**). The carbon spectra of these compounds consist of 2-singlets, 2 doublets, 3 triplets and 3 quartets each. The spin multiplicities of all lines were determined from off decoupled spectra. Out of the two quaternary carbon atoms, C-1 must be the less shielded one, because the shifts of C-1 and C-7 are nearly equal in **14**, but the presence of polar substituents leads to an additional paramagnetic shift of the C-1 resonance. Assignment of the C-2 and C-4 doublets is unambiguous because of the large paramagnetic shift of the substituted carbon atom C-2. In accordance with the data for **28**, **29**, **30** and **31**, C-3 must be the least and C-6 the most shielded one of the three methylene groups. This leaves only C-5 whose shift does not change much upon substitution at C-2. An additional shielding and diamagnetic shift of the C-6 resonance is very apparent in the spectra of *endo*-isomers, the difference being $\Delta = 7{\cdot}9$ ppm in the first and $\Delta = 8{\cdot}3$ ppm in the second pair of isomers. Of the three methyl groups the assignment of C-10 is straightforward, since comparison with **14** shows it to be the most diamagnetic one—an effect that can only be enhanced by the substituents at C-2. The chemical shifts of C-8 and C-9 resonances coincide in the *exo*-compounds and are slightly paramagnetic relative to those of **14**. This behaviour is in accord with data for the paramagnetic 1,5-interaction in hydrocarbons.[58] We demonstrated paramagnetic shift resulting from steric interaction of crowded groups in carbon spectra of methoxybenzenes.[59] Since there is at present no sure way to assign the methyl resonances, the more diamagnetic shift is tentatively assigned to C-8 of the *syn*-methyl group in the *endo*-isomers, that occupies a position which is sterically similar to that of C-5 in *exo*-isomers where the shift change is always slightly diamagnetic and no direct through-space interaction is possible. In proton spectra the shift difference of *syn*- and *anti*-methyl groups is larger in the *exo*-isomers and the shift of C-8 is slightly paramagnetic relative to C-9. This circumstance is not contradictory, as such reversed shift differences in ^1H and ^{13}C spectra are rather common and were substantiated in camphor (**39**) by selective double resonance.

3.5. *2-Norbornanone* (**38**). The ^{13}C chemical shifts of 2-norbornanone were measured using a mixture, consisting of 60 per cent **29**, 20 per cent **28** and only 20 per cent of **38**. The assignment of spectral lines is quite straightforward, because the general trends in some cyclic ketones are known[60] and it is apparent from other data that shift changes of C-4 and C-5 relative to (**1**) must be relatively small. Significant paramagnetic shifts were found for C-1 and C-3, as is usual in ketones, as well as diamagnetic shifts for C-6 and C-7, as in usual for methylene groups three bonds away from the carbonyl oxygen atom.

3.6. *Camphor* (**39**). The chemical shifts of camphor can be estimated from those of **14** and **38**. The assignment of singlet lines is unambiguous because of the large paramagnetic influence of the adjacent carbonyl group. The same influence permits C-3 to be distinguished from C-5 and C-6, which have been assigned by comparison with **38**. The shift of C-10 is more diamagnetic than in **14** because of the 1,4-influence of the carbonyl oxygen atom. Selective double resonance was used to assign the C-8 and C-9 methyl carbons and the *syn*-group (C-8) proved to be the less shielded one, contrary to proton spectra where the opposite is true.[61 to 66] The proton shift difference is only 8 Hz at 60 MHz and room temperature in a concentrated CS_2 solution, but this was just enough for selective decoupling.

3.7. 3-*endo-Bromocamphor* (**40**). In this compound most carbon chemical shifts are close to those of camphor. There is no ambiguity about the assignment of methyl groups and the singlet resonances of C-1, C-2 and C-7. The C-3 and C-4 resonances were assigned by selective decoupling and the C-5, C-6 methylene carbons by comparison with the shifts of camphor (**39**), where the shielding of C-6 is not expected to change on bromine substitution at C-3. The slight diamagnetic shift of C-5 in **40**, caused by the 1,4-interaction as in **37** provides an additional check.

3.8. 1,3,3-*Trimethyl*-2-*norbornanone* (*fenchone*) (**41**). Line multiplicities and shifts calculated on the basis of **2**, **12**, **38** and **39** were used for the assignment. Proximity of the carbonyl group decreases all methyl shifts by about 6·8 ppm. Such an effect would be expected on the basis of the 1,4-interaction. The shift difference of the methyl groups at C-3 is diminished in fenchone ($\Delta = 4{\cdot}4$ ppm in **12**; $\Delta = 1{\cdot}6$ ppm in **41**), but the diamagnetic shift of C-5 resonance tends to confirm an assignment of the more diamagnetic shift to the *endo*-methyl group. The assignment of other shifts is quite unambiguous because lines with the same multiplicities have very different shifts and a fair fit between the experimental and calculated values (including the *vic*- and *gem*-parameters) was achieved with the maximum error not exceeding 4 ppm.

4. Derivatives of norbornene with polar substituents

4.1. 2-*exo*-*Hydroxy*-5-*norbornene* (**42**), 2-*endo*-*Hydroxy*-5-*norbornene* (**43**), 1-*Methyl*-2-*exo*-*hydroxy*-5-*norbornene* (**44**) *and* 1-*Methyl*-2-*endo*-*hydroxy*-5-*norbornene* (**45**). In addition to selective double resonance and off resonance double resonance a pairwise comparison of methylated and unmethylated derivatives was used for the interpretation of these spectra. C-5 and C-6 were assigned by selective double resonance, using the results of some earlier measurements of proton shifts.[3,10,27] On the other hand, it follows from the data for hydrocarbons (**1**) and (**2**), (**20**) and (**23**) that the 1-methyl group has a paramagnetic influence on C-1, C-2 and C-6 only, which confirms the assignments made above. Of course, because of the closeness of shieldings, this assignment is only tentative for **44**. The assignment of C-1, C-2 and C-3 shifts is simplified by the paramagnetic influence of the hydroxyl group.[36,66,67] The shift of C-4 is fairly constant in all these compounds. A strong 1,4-nonbonded interaction with the hydroxyl oxygen is also very apparent in all these spectra. The resonance of C-7 is always more diamagnetic in *exo*-isomers ($\Delta = 2{\cdot}5$ ppm for the first pair of compounds and 3·4 ppm for the second). The difference of C-5 and C-6 shieldings in **42** and **43** must be attributed to the same cause because it is 20 to 30 times larger than the difference between H-5 and H-6 shieldings in proton spectra and of opposite sign.

4.2. *2-exo-Methyl-2-endo-hydroxy-5-norbornene* (**46**). Spectrum interpretation follows the reasoning given above, but comparison with the ^{13}C shifts of **21** and **43** was used as well. As was also the case for **30** and **31**, a double substitution at C-2 diminishes the shift difference of C-5 and C-6.

4.3. *2-exo-5-Norbornenemethanol* (**47**) *and 2-endo-5-Norbornene-methanol* (**48**). As was shown earlier for **32** and **33**, the inductive influence of a hydroxymethyl group upon the C-1, C-2 and C-3 shifts is only slightly more pronounced than that of a methyl group, but considerably weaker than for hydroxyl. This fact is well illustrated by the equality of the C-5 and C-6 shifts in **47**, where only a weak and paramagnetic influence upon the C-6 shift may be operative, but no inductive effect. This shift difference is likewise small in **21** and much larger both in **22** and **48**, where through-space nonbonded interactions are possible. The C-1 and C-4 resonances were distinguished from that of C-2 by selective double resonance, using the results of measurements of proton spectra.[20] From the two bridgehead carbons C-1 must be the more paramagnetic one because of the proximity of the hydroxymethyl group. As in the previous cases, the relative screening of C-7 is diamagnetic (Δ = 4·8 ppm) in the *exo*-isomer.

4.4. *Norbornen-2-one* (**49**) *and 1-Methylnorbornen-2-one* (**50**). Assignment of the C-2 resonance is unambiguous in both compounds because of the very large paramagnetic shift of any carbonyl carbon. The unsaturated C-5 and C-6 carbons were assigned on the basis of selective decoupling experiments, using the results of earlier measurements of proton spectra.[11] In this case both H-6 and C-6 are the more diamagnetic ones of the two methine groups in the double bond of **49**. The introduction of a methyl group at C-1 leads to a relative diamagnetic shift of H-6 in **50**, but to a paramagnetic shift of C-6. The last-mentioned effect is in accordance with all previous data about the influence of the 1-methyl group in **23**, **44** and **45**. The assignment of all other resonances is straightforward because the line multiplicities are different for carbons with close chemical shifts. Of the two bridgehead carbons the one closest to the carbonyl group must be the more paramagnetic one. The assignment of C-3 is confirmed by comparison with the C-2, C-4 carbon shifts of cyclopentanone.[68]

DISCUSSION

It is immediately apparent from all the data presented that the ^{13}C chemical shifts are very sensitive to changes in molecular geometry. In particular the differences between ^{13}C chemical shifts of *endo*- and *exo*-isomers are analytically significant. The shifts exhibit surprisingly good additivity and both the position and orientation of methyl and hydroxyl substituents can be accurately determined, even if only one isomer is available out of several possibilities. Quantitative analysis of isomer mixtures and the proof of chemical homogeneity of synthesis products is also possible. Such novel uses of ^{13}C resonance can be rather important, because some mixtures of very close-boiling isomers are hard to separate even on the best of GLC columns and the detector sensitivity is usually different also for different isomers. Of course, ^{13}C NMR spectra allow the isomers to be structurally identified as well and this is not possible by GLC methods alone.

All substituent influences and other regularities are given in a condensed form in Table 1 for the universal substituent parameters that can be used to calculate approximate values of ^{13}C shifts in bicyclic systems. The calculated shift values agree with the experimental values within ±1 ppm in more than half of the cases and the error only rarely exceeds 4 ppm, particularly for carbonyl and some other sp^2-type carbons as well as in *gem*-disubstituted compounds. Savitsky and Namikawa[69] give the same ±4 ppm upper limit for the difference between calculated and experimental shift values. Of course, to be of any practical value for structure determination purposes, these parameters must be universal and cannot contain much information about molecular geometry, because if bond angles and atomic distances are already known, then the molecular structure is known also. A much better fit can be achieved if the influence of substituents is deducted from closely similar compounds with similar geometry. Such an approach can be useful for the study of isomer mixtures and was used in this work in many cases.

If one takes into account all the various factors that can influence ^{13}C chemical shifts, then the possibility of introducing additive parameters for the calculation of even very approximate shift values is surprising. The main reason for it seems to to be the fact that the influence of all substituents is confined to the closest carbon atoms only (the substituted atom, its immediate neighbours and the fourth atom that can assume a close *gauche*- 1,4-position to the substituent).

As usual in ^{13}C NMR spectrometry, the influences of hybridization and atomic charge are the most apparent. Both unsaturation (sp^2-hybridization) and increased positive charge lead to large paramagnetic shifts. The introduction of both hydroxyl and carbonyl groups lead to paramagnetic shifts of α-carbons that are slightly larger than in aliphatic compounds,[56] (see Table 4). As can be seen from Table 4, there is only a very rough correlation of the ^{13}C shifts with group electronegativities. The influence of both 2-OH and 2-CH_3 groups is strongly asymmetric in bicyclic systems and much more pronounced on C-3 than on C-1. This shows that even the

TABLE 4. CHANGES OF ^{13}C CHEMICAL SHIFTS IN NORMAL ALIPHATIC COMPOUNDS UPON INTRODUCTION OF POLAR SUBSTITUENTS.[56] POSITIVE INCREMENTS CORRESPOND TO PARAMAGNETIC SHIFTS

Substituent groups	Carbon atoms in the normal aliphatic chain		
	α-CH_2	β-CH_2	γ-CH_2
—OR[a]	+43	+2	−3
—OH	+40	+1	−3
—OCOR	+36	−0·5	−3
—NH_2	+29	+12	−4
—Cl	+23	+2	−1
—Br	+12	+3	0
—I	−14	+5	+3
—COH	+12	−7	0
—COR	+12	−5	0
—COO^-	+8	−2	0
—COOR	+5	−4	0
—COOH	+3	−4	0

[a] R = any normal alkyl group

usual inductive influences are modified in bicyclic systems, as such effects are more symmetrical in aliphatic compounds. The observed substituent effects are similar to those found in cyclohexanone and cyclohexanol, where the effects on α-carbons are also larger than in aliphatics.

In addition to the usual inductive effects, polarization of double bonds and homoconjugation between the carbonyl group and a β, γ-double bond occurs, as was pointed out by Gurudata and Stothers.[70] This polarization is very apparent in norbornenone (**49**) and 1-methylnorbornenone (**50**), where the chemical shift difference of the unsaturated carbon atoms is of the same sign as in proton spectra,[11] but from 10 to 15 times as large. This paramagnetic influence is largest on the 5-CH group, both in the ^1H and ^{13}C spectra. Such a large shift difference between the C-6 and C-5 resonances ($\Delta = 12{\cdot}2$ ppm in **49**) cannot be a consequence of the 1,4-nonbonded interaction only, which does not exceed $\Delta = 2{\cdot}9$ ppm in the saturated compound (**38**) and is always weaker for sp^2-hybridized carbon atoms. A similar polarization effect may be active in norbornenols, where the C-5 resonance is likewise always at a much higher frequency (more paramagnetic) than in the parent compound. At the same time it should be pointed out that the difference between the chemical shifts of carbonyl groups in the saturated and β, γ-unsaturated bicyclic ketones is not caused only by the interaction of the carbonyl group with the doubly bonded carbons. The large difference between the chemical shifts of C-2 and C-3 of norbornene and norbornane must also be taken into account in comparing the C-2 shieldings in **38** and **49**. If this is done, a trend opposite to that given in[70] is arrived at. The carbonyl shifts are strongly paramagnetic in bicyclic compounds. These shifts have been measured and discussed in terms of changes of ΔE[71] in some earlier reports by other authors.[71,72,73]

The gross atomic charges can also change as a result of electron delocalization. This effect is very pronounced on the C-7 methylene carbon resonance, which is paramagnetically shifted to higher frequency upon the introduction of double bonds into the molecule.[32] There is also some correlation[41] with the charges that were calculated by the extended Hückel theory for **1**, **19** and **27**.[34] Such delocalization is present in nonclassical ions,[12] and kinetic data for the solvolysis of some substituted 7-brosylates[31] illustrate this point especially well. Different non-conjugated substituents lead in this case to 1000-fold changes in the reaction rate. It seems that the same effect is active in non-ionized molecules as well and leads to changes of gross atomic charges, but possibly also to a decrease of ΔE.[12] The proton shifts of this methylene group are also so unusual,[1,4,7,12] that it lead to a wrong assignment of the *syn*- and *anti*- proton resonances.[6,75 to 78] Attempts to explain these effects by double bond anisotropy[8] have not been convincing because it leaves chemical kinetic data unexplained and does nothing to rationalize the very large paramagnetic ^{13}C shifts that are accompanied by only moderate proton shifts ($\Delta = 1{\cdot}67$ ppm in ^1H spectra and $\Delta = 35{\cdot}8$ ppm in ^{13}C spectra for the bridge methylene group in **1** and **27**). It is important to note that in other compounds where hyperconjugation of the methylene group is possible (cyclopentadiene, 9,10-dihydroanthracene), no unusual deshielding effects appear either in the ^{13}C or in the ^1H spectra.[33] The very large differences in the behaviour of ^1H and ^{13}C shieldings in norbornane and norbornene show that magnetic effects cannot be very important in ^{13}C spectra. At the same time there are many effects that are similar to those in proton spectra where they are usually ascribed to magnetic influences of nearby bonds or cycles. The most important of these are the shift differences between *exo*- and *endo*-oriented substituents (methyl or hydroxymethyl groups) and the relationship between the difference of C-5 and C-6 respectively H-5 and H-6 shieldings and the orientation of substituents at C-2 or C-3.[3,12] These effects are of such a magnitude in proton spectra that magnetic bond anisotropy appears to be the most probable cause. The difference of *exo*- and *endo*-proton shieldings at the same C-2 or C-3 carbon atom is about 0·5 to 1·3 ppm, but the difference of methyl ^{13}C shifts at the same positions ranges from 4 to 5 ppm in norbornane derivatives and is somewhat smaller in norbornenes. At the same time the chemical shift of the substituted carbon atom is also dependent upon the orientation of the substituent, exactly as in substituted cyclohexanols.[57] Just as in the proton spectra, even the substituted carbon (C-2) resonance itself is more paramagnetic in the *exo*-isomer (high-frequency shift). Fraser[5] has suggested that the shift difference in proton spectra may be caused by the magnetic anisotropy of the $C_5{=}C_6$ double bond. This assumption is clearly untenable,[3] also in view of the ^{13}C-resonance data, as the positions of the corresponding hydrogen and methyl carbon atoms cannot be very different, yet the shift difference is large.

The inverse effect, difference of C-5 and C-6 shifts caused by the substituents at C-2 or C-3,[3,10] is also present in ^{13}C spectra. This difference ranges from 0·04 to 0·34 ppm in proton spectra, but up to 7 ppm in ^{13}C spectra. In general the ^{13}C effect is from 20 to 40 times larger and usually of opposite sign to the proton shift difference (compare **42, 43, 47, 48**; for proton shifts see Lit.[3,10,20,27]). The magnitude and especially the reverse order of the ^{13}C shifts shows that such differences can hardly be caused by magnetic effects alone. In the ^{13}C spectra at least the electronic effects must be much more significant. This point is further confirmed by the comparison of norbornane and norbornene derivatives with identical orientations of substituents at C-2. The C_5-C_6 shifts difference is very different for the sp^2 and sp^3 hybridizations and no simple relationship exists between these two sets of shielding differences.

Since magnetic effects can hardly be the cause of such long-range influences of substituents in ^{13}C spectra, the *gauche*- or 1,4-nonbonded interactions provide the most probable mechanism. Such steric interactions always lead to diamagnetic (upfield, low-frequency) shifts in ^{13}C spectra[35,36,43,74] and occur only between atoms heavier than hydrogen that are three bonds apart (in 1- and 4-positions of a chain) and can occupy positions close to each other in space. These upfield shifts are not significant for proton resonance, but are very large in fluorine spectra, the difference of *syn*- and *anti*-7-fluorine shifts in 7-fluoro-2-oxanorcarane derivatives being up to 30 ppm.[80] This relationship is very general and many other examples from fluorine spectra of alicyclic compounds can be found.[81] Such upfield shifts have been explained by the steric interaction of hydrogen atoms which would have the same spatial orientation as proximate hydrogens in the completely staggered structure of *gauche* butane.[37] The sign and magnitude of this effect have been discussed, assuming that the C—H bond polarizability is the underlying mechanism.[74] The argument, is not quite convincing, however, because the necessary parallelism between the bond polarizabilities and differential shieldings is not very good.[39] It seems that changes in carbon hybridization[51] and correspondingly in ΔE can also be an important cause for diamagnetic shifts caused by the 1,4-interaction,[35] all the more so as differences exist between the ultraviolet spectra of *n*-butane conformers.[82] Difference between the longer-wavelength $\sigma \rightarrow \sigma^*$ transitions in the *transoid*- and *gauche*-conformers of *n*-butane is equal to 0·56 eV. The *gauche* conformation is close to the ethylenic *cis*-configuration, and in some extent also to the relative orientation of C-6 and the 2-*endo*-methyl group, or C-7 and the 2-*exo*-methyl group.

Since it is most probable that in addition to differences between the molecular ground state wave functions, the excited states may be involved as well, there is at present scarely any hope for exact calculations of ^{13}C chemical shifts of bicyclic compounds. Various empirical methods must be used and information gathered about such analytically important but little known shielding mechanisms as the 1,4- or *gauche*-interaction. The most important manifestations of the 1,4-nonbonded interactions in ^{13}C spectra of 2-substituted derivatives of bicyclic compounds are the very characteristic shifts of C-6 and C-7 resonances. There is a diamagnetic shift of the bridge methylene (C-7) resonance in all *exo*-isomers, and a similar shift of the C-6 resonance in *endo*-isomers, both in comparison to the parent compound and to the other isomer. The influence of *endo*-CH_3 to the C-7 and of *exo*-CH_3 to the C-6 resonance is much smaller and paramagnetic. In the case of hydroxyl groups the influence upon the C-6 resonance is diamagnetic in both cases, being only much more pronounced for an *endo*-substituent. Such strongly polar groups may have in addition to the steric through-space influence some special through-bonds interaction with the third carbon atom as well. The high-field shifts of C-4 resonances in both norbornanols and the inability of an intervening methyl group to shield the 1,4-interaction of a 2-hydroxyl or carbonyl group with the C-6 carbon atom in **35** and **50** certainly point in this direction, but at present it is not possible to separate these effects. The problem is somewhat similar to that of the interpretation of some long-range spin-spin couplings.

The 1,4-interaction is not reciprocal. In the case of 2-methyl substituents the effect is strongest on C-6. It is considerably greater, about twice as strong as for C-7 and for the methyl carbon itself; the diamagnetic shift of the C-6 resonance is about twice as small for an *sp*^{2}-hybridized carbon atom. The unequal mutual influences are especially apparent in the case of *exo*cyclic methylene groups as in **16**, **17** and **18**. In general the 1,4-influences of methyl and hydroxymethyl groups are of similar magnitude, the effect of a hydroxyl group being slightly stronger. The latter point is well ilustrated by the fact that there is a diamagnetic shift of the C-6 resonance both in the *endo*- and the *exo*-isomer of norbornanol. This is not the case for methyl or hydroxymethyl groups. Likewise, the 2-carbonyl group has a strong diamagnetic influence on C-6, but the similar effect of an *exo*cyclic methylene group as in **15** or **16** is only weak. The characteristic differences of the C-5 and C-6 resonance frequencies are likewise best interpreted on the basis of the 1,4-interaction. The lower sensitivity of *sp*^{2}-hybridized carbon atoms leads to smaller shift differences in norbornene derivatives (about 60% of those in substituted norbornanes). Also, it makes understandable how the interplay of various substituent effects, including the paramagnetic shift of the C-6 resonance caused by a 1-methyl group, can lead to a very small shift difference of this type in **44** or to a complete absence of it as in **37**. Of course, all these facts as well as the magnitudes and the inverse order of ^1H and ^{13}C shifts serve as a good illustration to the belief that the diamagnetic shift of the C-6 resonance frequency in *endo*-isomers must be of electronic origin. The reason for the decreased sensitivity of the sp^2-hybridized atoms, which is especially pronounced in *exo*cyclic methylene carbons (compare **15**, **16**, **17** with **3**, **4**, **6**, **7** and **13**) may be found in the different electronic structures, but steric differences may also play a minor part because the shift differences of the substituted C-2 carbon atoms are larger in *endo-exo* pairs of norbornane derivatives as compared to those of norbornene. All the data obtained thus suggests that for a successful 1,4-interaction it must be possible for the interacting atoms to come close together. Diamagnetic shifts of methyl resonances are very small or absent in 2,3-*endo, exo* isomers (**13**) and (**24**), but large in other cases. The only true exception is the more active carbonyl group (see Table 3 and **50**) where considerable 1,4-interaction is possible even under adverse geometrical conditions, as in **38** and **39**. Of course, as in several instances discussed above, this effect may be partly caused by an overall change of molecular geometry, but the much smaller changes of similar structure in **15** do not confirm this. The 1,4-interaction leads to most significant shift changes on both ends of the interacting chain, but the middle atoms are also involved, as in cyclohexane derivatives.[18] This influence is absent if the interaction itself is absent, as in 2,3-*endo, exo*-isomers and is taken into account by the *vic*-increment (see Table 1.). Any *gem*-disubstituted carbon atoms are also additionally shielded, but the influence upon the substituent groups themselves is paramagnetic, as in **12**, **14**, **30** and **31**. In this case the influence of a *gem*-hydroxyl group is smaller than that of a *gem*-methyl group. Just as the influence of a methyl group upon the adjacent groups is complicated—paramagnetic for ^{13}C and diamagnetic for the ^1H resonance—the trends for ^{13}C and ^1H resonances of methyl groups do not coincide. The proton ^1H resonance of the *syn*- (C-8) methyl group in camphor (**39**) is the more diamagnetic of the two, but the ^{13}C resonance peak of this group is the more paramagnetic one. The inverse order of chemical shifts was proven unequivocally by selective double resonance experiments. In addition to this, while in ^1H spectra the 1-methyl (C-10) resonance is close to those of the other two methyl groups in neutral solvents,[61 to 66] the ^{13}C resonance of this group shows a very strong diamagnetic shift in **39**. Likewise the ^1H chemical shifts of both *geminal* methyl groups are practically equal in fenchone (**41**) as befits their symmetrical orientation relative to the carbonyl group,[64,66] but the corresponding ^{13}C shifts differ by 4·4 ppm. This shift difference is a clear manifestation of the 1,4-nonbonded interaction in ^{13}C spectra. What part similar interactions may play in proton spectra is completely unknown at present, but it is clear that such possibilities must not be ignored. At any rate it is not sound to assign all differences in the chemical shifts of *endo*- and *exo*- protons to the magnetic influences of nearby bonds or cycles.[8] The failure of bond anisotropy as a mechanism for the widely different ^{13}C chemical shifts in hydrocarbons is best illustrated by the fact that bond anisotropies up to $\chi_{c-c} = 416 \cdot 10^{-6}$ cm^3/mole must be used in such a case.[51] If one adheres to the magnetic anisotropy theory, then it appears that carbon behaves as if it had an 'effective atomic susceptibility' at least an order of magnitude greater than that of the hydrogen atoms.[79] This is quite impossible, and as shown by Spiesecke and Schneider for methyl iodide,[79] other additional contributions must be present.

The very complicated interplay of many long-range effects makes some assignments difficult, such as those for the *geminal* methyl groups (C-8 and C-9). Just as in the proton spectra,[85] the α-methyne resonance is characteristic for *endo*-, *exo*-isomers of terpenes [compare the ^{13}C shifts of C-2 in the isomeric pairs (**34**), (**35**) and (**36**), (**37**)], but the ^{13}C shift difference is usually quite small for methyl groups as the very characteristic 1,4-interaction is not effective in this case. The proton shifts of these methyl groups are also different, but although these lines have been proposed as suitable for structure determination,[86] these shifts are clearly not regular enough for this purpose. Owing to the ASIS phenomenon[64,65,87] the assignment of methyl groups is somewhat simpler in ketobornanes, but nevertheless the preliminary assignment for camphor[62] was later found to be erroneous.[65] The final assignment was confirmed only through the use of deuterated compounds.[65,66] The proposed use of ^1H line-widths for this assignment[66] is not quite convincing, and so the equally complicated situation with the ^{13}C shift deserves some attention.

If one considers the weak 1,5-interaction[62] to be paramagnetic as in hydrocarbons,[58] then the C-8 resonance must be slightly more paramagnetic in 2-*exo*-isomers as compared with the corresponding *endo*-isomers. At the same time the spatial relation of a 2-*exo*-substituent to C-5 is similar to that of a 2-*endo*-substituent to the *syn*-carbon C-8. The first influence is certainly slightly diamagnetic and the second one may be as well. These assumptions are not contradictory with the data for the few compounds studied, but additional measurements on doubly substituted bornane derivatives are needed for confirmation.

It is also clear that the weak paramagnetic 1,5-interaction does not play an important role in ^{13}C-spectroscopy of alicyclic compounds. This is clearly apparent from the practically equal ($\Delta < 0{\cdot}2$ ppm) chemical shifts of *syn*- and *anti*-methyl carbons in **34**, **36** and **39**. The quite different ($\Delta = 5{\cdot}0$ ppm) chemical shifts of the α-methylene carbons C-2 and C-5 adjacent to the *exo*cyclic double bond and the near equality of the β-methylene shifts in ethylidenecyclopentane (**51**) provide another example for the importance of the 1,4-nonbonded interactions as well as for the relative unimportance of the 1,5-interactions. If the last-mentioned effect is present at all in bicyclic compounds, then it must consist of a paramagnetic through-space and a diamagnetic through-bonds component, but it is at present impossible to distinguish between such effects and the influence of changes in molecular geometry.

This leads us to the question of the influence of molecular geometry, particularly the bond angles upon ^{13}C chemical shifts. The data for cycloalkanes,[88] bicyclic ketones,[71] alkyl-substituted cyclopentenes and cyclohexenes,[60] as well as adamantane derivatives[84] show that this influence may be very significant, but the absence of necessary X-ray data for bicyclic compounds makes such analysis impossible at present. Good linear correlations have been found between *J*(CH) and the corresponding bond angles in unsaturated systems.[1] Since this effect was caused by a change of carbon hybridization it is quite possible that similar relationships may hold for ^{13}C chemical shifts as well.

CONCLUSION

^{13}C resonance provides a new and promising technique for the study of molecular structure of substituted bicyclic compounds. The chemical shifts of all carbon atoms can easily be determined and assigned even for quite complicated molecules with 10 and more carbon atoms—a task that is very difficult for ^1H nuclei in proton spectra of the same compounds. The carbon shifts are predictable and provide numerous simple rules for the determination of the position and orientation of substituents. In general all important effects are of electronic nature and the influence of diamagnetic anisotropy of nearby chemical bonds and cycles is negligible. This important circumstance is caused by the wide range of ^{13}C shifts, about 30 times that of the ^{1}H shifts, where the magnetic effects (usually about 1 ppm in magnitude) cannot play any significant part. A very important effect, specific for spectra of heavier nuclei, is the *gauche* 1,4-nonbonded interaction which always leads to diamagnetic (low frequency) shifts that are most useful analytically. Although both ^{13}C and ^{1}H shifts correlate with gross atomic charges, changes in bond order and hybridization, and even though the directions of these trends are the same, the presence of the 1,4-nonbonded through-space effects and the relative insignificance of magnetic effects in ^{13}C spectra leads to a lack of direct parallelism between the ^{1}H and ^{13}C chemical shifts. Indeed, the relative order of these shieldings may be inverted in many cases. Since the full interpretation of ^{13}C spectra is much simpler than that of proton spectra, and the relationships between ^{13}C shifts in similar compounds are also inherently simple, these shifts could be used even for the interpretation of very complicated proton spectra, using double resonance methods. In addition to this, ^{13}C shifts provide a method for the determination of molecular structure, particularly that of substituent orientation, for heavily substituted compounds where there are no protons with characteristic shifts left. This problem is similar to that of acrylic acid derivatives, where ^{13}C resonance proved to be a useful analytical method.[39]

Carbon resonance was used in this study for the determination of molecular configuration of isomeric 2-ethylidene-2-norbornenes. The influence of an ethylidene group upon the ^{13}C resonances is well illustrated by the shifts in ethylidenecyclopentane (**51**), which indicate the importance and magnitude of the 1,4-interaction. Using this method, it was shown that the low-boiling isomer has *E*-structure (**25**), and the high-boiling one the *Z*-structure (**26**).

In addition to the elucidation of molecular structure, ^{13}C resonance can also be used for quantitative analysis of isomer mixtures which are hard to separate by existing methods. Of course, this is practical only if proton spectra cannot be used for any reason (over-lapping multiplets, too complicated spectra, etc.).

In addition to the analytical use, ^{13}C spectra of rigid bicyclic molecules provide a good starting point for a more thorough understanding of all the factors that influence ^{13}C chemical shifts. In particular, rigid structures are useful for the study of various electron delocalization and through-space effects that are as yet little understood.

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