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The N.m.r. Spectra of Bicyclo[2.1.1]hexane Derivatives[1]

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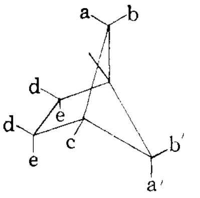
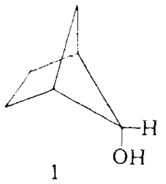
The n.m.r. spectra of a number of bicyclo[2.1.1]hexane derivatives have been examined and may be interpreted consistently using one set of coupling constants.

In the study of n.m.r. spectra, rigid systems such as that found in bicyclic compounds are of particular interest since they afford an opportunity to investigate the correlation between the spectral parameters and the geometry of the molecule. The bicyclo[2.1.1]hexane derivatives which were available from a previous investigation[2] have therefore been examined. For convenience in the following discussion, the various protons will be designated and the substituent will replace either or both of a′ and b′.



The spectra of key compounds, *endo*-bicyclo-[2.1.1]hexane-5-ol (1), *exo*-bicyclo[2.1.1]hexane-5-ol (2), bicyclo[2.1.1]hexane-5-one (3) and bicyclo-[2.1.1]hexane (4) are shown in Fig. 1. It will be convenient to consider the spectrum of 1 first. The doublet at $\tau = 9.40$ is the band shifted farthest upfield and has an area corresponding to one proton. This must correspond to a, b, or b′, for all other protons come in pairs. It cannot be b′ since this would be shifted down field due to the hydroxy group, and presumably appears at $\tau = 6.52$.

The band corresponding to the other member of the pair a and b appears at $\tau = 9.10$. It is a doublet, each member of which has been split further by the influence of other protons, presumably c ($\tau = 7.63$). It would be expected to give two triplets, but appears to have more components.



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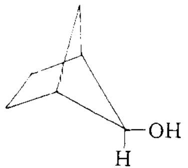

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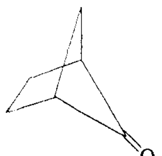

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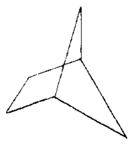

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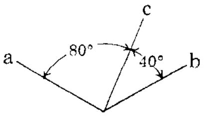
A confirmation of this assignment may be found in the relative intensities in the upfield doublet. The chemical shift between a and b is 18 sec.$^{-1}$ and the coupling constant is 7.6 sec.$^{-1}$. The relative intensity for the outside to the central line in an AB case is given by

$$\text{Rel. int.} = \frac{(\Delta\nu^2 + J^2)^{1/2} - J}{(\Delta\nu^2 + J^2)^{1/2} + J}$$

where $\Delta\nu$ is the chemical shift. Using the above values, the relative intensity was calculated to be 0.49, whereas the average ratio for several spectra taken at different times was 0.46.

A decision as to which band arises from a may be made by considering the geometry of the molecule as deduced from molecular models. Looking down the C_1–C_6 bond, the arrangement of a, b and c will be



The correlation between coupling constants and dihedral angles is well established: The coupling constant is maximum at 0° (~8 sec.$^{-1}$) and 180° (~10 sec.$^{-1}$) and minimum at 90° (~0 sec.$^{-1}$).[3] The coupling between a and c will then be negligible, and that between c and b will be on the order of 3–4 sec.$^{-1}$. The upfield doublet must then arise from a, and the split doublet arises from b. This analysis also shows that the band at $\tau = 7.63$ must arise from c, with $J_{bc} = 2.9$ sec.$^{-1}$. The A_2B_2 system arising from d and e appears at $\tau = 8.50$. The shape of the band indicates that at least one of the coupling constants between the four protons is large, but the spectrum is not well enough resolved to permit a detailed analysis.

In the spectrum of 2, the proton band from a appears as a triplet, indicating coupling to two other protons. One of these is b and the other must be a′. In order to confirm this assignment, bicyclo[2.1.1]hexane-5-one[2] was reduced with lithium aluminum deuteride to give 2 having a deuterium in place of the proton at a′. The upfield band now was a doublet, and the doublet at $\tau = 6.30$ disappeared. The coupling constants are: $J_{aa'} = 6.8$, $J_{ab} = 6.8$ sec.$^{-1}$. A long-range coupling of the type found here has previously been reported by Meinwald and Lewis[4] for another bicyclo[2.1.1]hexane derivative.

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[1] This work was supported by the U. S. Army Research Office (Durham).

[2] K. B. Wiberg and B. R. Lowry, *J. Am. Chem. Soc.*, **84**, in preess (1962).

[3] *Cf.* H. Conroy in "Advances in Organic Chemistry, Methods and Results," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p. 260. The above values are for open-chain and large-ring compounds, but similar values are also found for cyclopropane and cyclobutane derivatives (unpublished results).

[4] J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961). A number of the features of the spectra of the *exo* derivatives has been noted by these authors.

It is also interesting to note that the band corresponding to the d and e protons in 2 is now a single sharp peak implying a negligible chemical shift between the two types of protons. At the same time, the band corresponding to b has shifted downfield from 9.10 τ in 1 to 7.41 τ in 2. This is in accord with the structural assignment, for in the *exo* isomer the hydroxy group will be away from the e protons but close to the b proton. The effect is also seen on the position of the a proton, but it is less marked than for the b proton as would be expected.

The spectrum of the ketone 3 confirms the assignment of the band due to the c protons, for this would be expected to be shifted downfield as a result of the introduction of a carboxyl group. More interesting, however, are the positions of the bands for the a and b protons. They are separated by 0.44 τ, which is similar to the separation in 1, which is 0.30 τ. The chemical shift for the a proton is, however, 0.68 τ greater than that for the a proton of 1. Thus, the carbonyl group, unlike the hydroxy group, shifts both the a and b proton bands by approximately an equal amount, and at the same time causes a larger chemical shift for the a proton than even the *exo*-hydroxy. The unusual geometrical relation of the chemical shift due to a carbonyl group has been noted previously, particularly in the case of cyclopentanone.[5]

Finally, in the spectrum of bicyclo[2.1.1]-hexane (4), the a protons are seen to give a quartet with spacings from left to right of 1.75, 1.90 and 1.75 sec.$^{-1}$. The corresponding band for the b protons is at approximately the same location as the d and e protons. Using 41.3 sec.$^{-1}$ as the chemical shift between the a and b protons, and assuming that $J_{bb} = J_{ab'} = 0$, the coupling constants were found to be $J_{aa'} = 6.7$, $J_{ab} = 5.4$ sec.$^{-1}$. The c proton band at 7.51 τ under high resolution is found to be a series of bands separated by about 1 sec.$^{-1}$. This results in part from the coupling between b and c, but must also result from coupling between c and d and e. The latter coupling constant is about 1 sec.$^{-1}$ which is approximately that expected for a dihedral angle of about 60°.

The spectra of the series of bicyclo[2.1.1]hexane derivatives are summarized in Table I. The values of chemical shifts show the expected trends with substitution of the proton at a' or b' and require no further comment. The spin coupling constants vary relatively little from compound to compound. The value of J_{bc} varies between 2.6–3.3 sec.$^{-1}$ in all compounds but one. In the *endo* series, the *gem* coupling constant J_{ab} has a value close to 6.5 sec.$^{-1}$ when there is a carbon substituent, and has a value close to 8 sec.$^{-1}$ when there is an oxygen substituent. The long range constant $J_{aa'}$ varies between 7–8 sec.$^{-1}$. Finally, the constants J_{cd} and J_{ce} are on the order of 0.5–1.0 sec.$^{-1}$. Except for $J_{aa'}$, the values of the coupling constants are in good accord with those expected for the geometry involved.[3]

There are two particularly interesting aspects of the spectra. First, it permits a rapid assignment of configuration of new compounds in the series. In order of increasing importance, this is based on the observation of a chemical shift between the d and e protons in many *endo* derivatives, but not *exo* derivatives; the observation of a larger chemical shift for the b proton in the *exo* series than the *endo* series; and, most important, the observation of a long-range coupling between the a and a' protons when both are present.

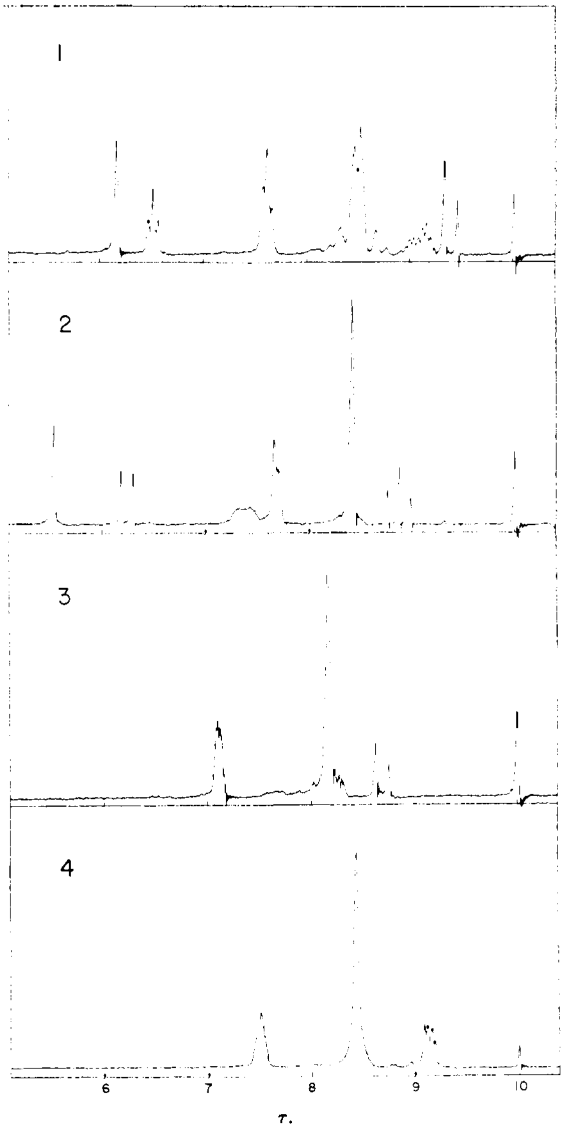

Fig. 1.—N.m.r. spectra of bicyclo[2.1.1]hexane derivatives.

The other interesting aspect of these spectra is the occurrence of a long-range coupling between a and a', whereas the coupling between b and b' appears to be negligible (probably less than 0.5 sec.$^{-1}$). One may first ask if the strained ring which is present is a principal contributing factor. In this connection, the observation of a ong-range spin–spin coupling[6] in methyl α,β-dibromoisobutyrate (5) is of interest. One of the two hydrogens marked a and b is spin coupled with the

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(5) *Cf.* K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961); L. M. Jackman, "Applications of Nuclear Magnetic Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp. 121–125.

(6) D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

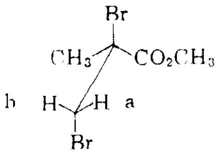
TABLE I

N.M.R. SPECTRA OF BICYCLO[2.1.1]HEXANE DERIVATIVES^{a}

Compound	a	b	b′(a′)	c	d,e	Other protons	J_{ab}	J_{bc}	J_{aa}
endo-5-	^{a}								
$-\mathrm{COOH}$	9.12(d)	~8.57(b)	7.54(t)	7.24(t)	8.32(m)	$-\mathrm{COO}H$ −1.60(s)	6.6	2.9	
$-\mathrm{COCH_3}$	9.25(d)	~8.63(b)	7.68(b)	7.30(t)	8.53(s)	$-\mathrm{COC}H_3$ 8.12(s)	6.6	3.8	
$-\mathrm{COCl}$	9.17(d)	8.52(bd)	~7.14^{a}	~7.14^{b}	8.31(m)		6.6	^{d}	
$-\mathrm{CO_2CH_3}$	9.22(d)	8.62(b)	7.26(b)	7.30(t)	8.37(m)	$-\mathrm{CO_2C}H_3$ 6.46(s)	6.3	2.9	
$-\mathrm{CON(CH_3)_2}$	9.22(d)	8.65(b)	7.67(b)	7.31(t)	8.38(m)	$-\mathrm{CON(C}H_3)_2$ 7.06, 7.21	6.6	3.0	
$-\mathrm{CH_2OH}$	9.25(d)	8.68(b)	~8.3(b)	7.61(b)	8.56(s)	$-\mathrm{C}H_2\mathrm{OH}$ 6.89(d), $J = 7.2$ $-\mathrm{CH_2O}H^{c}$ 6.31(s)	6.0	^{d}	
$-\mathrm{CH_2OCOCH_3}$	9.18(d)	8.58(b)	~8.05^{b}	7.54(t)	8.43(s)	$-\mathrm{C}H_2\mathrm{OCOCH_3}$ 6.31(d), $J = 6.6$ $-\mathrm{CH_2OCOC}H_3$ 8.05(s)	6.6	^{d}	
$-\mathrm{CH_2Br}$	9.21(d)	8.63(b)	~7.94(b)	7.52(b)	8.47(s)	$-\mathrm{C}H_2\mathrm{Br}$ 6.98(d), $J = 8.4$	6.6	^{d}	
$-\mathrm{OH}$	9.40(d)	9.10(m)	6.52(t)	7.63(t)	8.50(m)	$-\mathrm{O}H^{c}$ 6.3-6.6(s)	7.6	2.9	
$-\mathrm{OCOCH_3}$	9.22(d)	~8.85(bd)	5.81(t)	7.40(t)	8.48(s)	$-\mathrm{OCOC}H_3$ 8.10(s)	7.8	2.6	
$-\mathrm{OCOCF_3}$	9.06(d)	8.73(m)	5.57(t)	7.21(m)	8.36(s)		8.4	2.7	
$-\mathrm{OSO_2C_6H_4CH_3}$	9.24(d)	8.97(m)	6.00(t)	7.50^{b}	8.48(m)	$-\mathrm{C_6}H_4$ 2.30, 2.74 $-\mathrm{C}H_3$ 7.55(s)	7.8	2.7	
$-\mathrm{Br}$	9.47(d)	~8.5	~5.59(m)	7.82(b)	8.26(m)		6.0	^{d}	
$=\mathrm{O}$	8.72(d)	~8.28(m)		7.15(m)	8.22(s)		7.2		
$-\mathrm{H}$	9.13(q)	~8.44^{b}		7.51(m)	8.42(s)		5.4		6.7
exo-5-									
$-\mathrm{OH}$	8.90(t)	7.41(b)	6.30(d)	7.72(d)	8.43(s)	$-\mathrm{O}H^{c}$ 5.5–5.6(s)	6.8	2.8	6.8
$-\mathrm{OH}$-5-*d*	8.90(d)	7.42(b)		7.73(d)	8.43(s)	$-\mathrm{O}H^{c}$ 5.5(s)	6.8	2.7	
$-\mathrm{OSO_2C_6H_4CH_3}$	8.90(t)	~7.51^{b}	5.87(d)	~7.51^{b}	8.40(s)	$-\mathrm{C_6}H_4$ 2.68, 2.24 $-\mathrm{C}H_3$ 7.55(s)	7.1	^{d}	8.1
$-\mathrm{Br}$	8.83(t)	~7.22(b)	6.32(d)	7.32(s)	8.20(s)		8.1	^{d}	8.1
1-Chloro-*endo*-5-									
$-\mathrm{COOH}$	8.52(d)	~8.3	7.39(d)	7.23(b)	8.07(m)		6.6	3.3	
$-\mathrm{COCl}$	8.48(d)	8.27(m)	7.00^{b}	7.00^{b}	8.05(m)		6.6	^{d}	
$-\mathrm{CO_2CH_3}$	8.54(d)	~8.36(b)	7.47(d)	7.31(b)	~8.14(m)	$-\mathrm{CO_2C}H_3$ 6.36(s)	6.4	^{d}	
$-\mathrm{H}$	8.44(q)	~8.27(b)		7.51(b)	8.17(s)				

[a] The abbreviations are: s, singlet; d, doublet; t, triplet; q, quarter (arising from the A part of an A_2B_2 case); m, partially resolved multiplet; b, broad. [b] The peak position is uncertain since it is very close to a more intense band. [c] The hydroxyl proton band position is concentration dependent. [d] The spectrum was not well enough resolved to permit a determination of the coupling constant.

methyl group with a coupling constant of 0.8 sec.$^{-1}$. The geometry[7] of the pertinent parts of compounds 2 and 5 are shown in Figs. 2 and 3, respectively. For 5, the geometry is shown in a planar projection for the more favored conformation. It is assumed that the bromine is above the plane at the center carbon, and below the plane at the right hand carbon.



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It may be noted that the geometry is quite similar, suggesting that proton a of 5 is the one which is spin coupled with the methyl group. The coupling in 5 will be smaller than that in 2 since it is probable that at any one time only one hydrogen of the methyl group will be strongly spin coupled with a and that the coupling will be averaged over all three protons. It would also be reasonable to expect that the coupling constant would decrease with an increase in the distance between the centers to which the hydrogens are attached. In 2, the distance is 2.13 Å.[7] whereas in 5 it is about 2.6 Å. In view of these two differences, a factor of 9 between the two long-range spin–spin coupling constants is not unreasonable, and therefore it does not appear necessary, in view of the limited data presently available, to consider the strained four-membered ring in 2 other than in its effect on the geometry of the molecule.

It is generally assumed that the Fermi or contact potential gives the principal contribution to the proton spin–spin coupling.[8] The magnitude of the coupling has been considered in terms of deviation from perfect pairing in which extra bonding possibilities such as hydrogen–hydrogen and carbon–carbon bonding for two adjacent carbon–hydrogen bonds are included.[9] The inclusion of these alternate bonding possibilities decrease the repulsive interaction of the wave functions for the two C–H bond orbitals, and at the same time introduce

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(7) The dimensions for bicyclo]2.1.1]hexane are based on the geometry proposed by C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).

(8) *Cf.* the discussion in J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, pp. 184–192.

(9) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

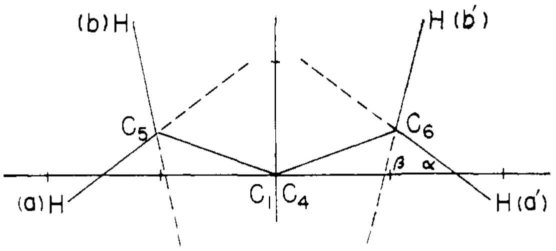

Fig. 2.—Geometrical arrangement of hydrogens at carbons 5 and 6 in bicyclo[2.1.1]hexane. The scale marks are at 1-Å. intervals.

correlation between the spins of the electrons at the hydrogens. This serves in a sense to "transmit" information concerning the nuclear spins of the hydrogens. Molecular orbital treatments of spin–spin coupling have also appeared.[3,10] In either case, the coupling constant would be expected to be approximately proportional to the square of the overlap integrals for the two carbon–hydrogen bond orbital wave functions.[3] The same should also be true for the present case.

The wave function for a carbon–hydrogen bond orbital may be written as

$$\psi_{\mathrm{CH}} = \frac{1}{\sqrt{2 + 2s_{\mathrm{CH}}}}\left({}^{1}/{}_{2}\phi_{2\mathrm{s}}^{\mathrm{C}} + \frac{\sqrt{3}}{2}\,\phi_{2\mathrm{p}}^{\mathrm{C}} + \phi_{1\mathrm{s}}^{\mathrm{H}}\right)$$

where s_{CH} is the overlap integral between the hydrogen 1s orbital and the carbon sp^3-orbital. The overlap integral would then be

$$s_{\mathrm{CH.CH}} = \frac{1}{2 + 2s_{\mathrm{CH}}}\left({}^{1}/{}_{4}s_{\mathrm{ss}}' + \frac{3}{4}\,s_{\mathrm{pp}}' + s_{\mathrm{HH}}' + s_{\mathrm{sH}}' + \sqrt{3}s_{\mathrm{pH}}' + \sqrt{\tfrac{3}{2}}s_{\mathrm{sp}}'\right)$$

where s and s' refer to carbon 2s-orbitals on the two centers, p and p' refer to the carbon 2p-orbitals, and H and H′ refer to the two hydrogens.

The necessary values of the overlap integrals are available from the tables of Kopineck[11] (2s- and 2p-hydrogenic wave functions) and of Mulliken, Reike, Orloff and Orloff[12] (1s with 1s, 2s and 2p Slater wave functions). Using the geometry shown in Fig. 2,[7] with $\alpha = 37.2°$ and $\beta = 77.1°$, the overlap integral for the CH bonds to a and a′ was found to be 0.007, and that for the CH bonds to b and b′ was found to be 0.056. The latter is the larger because of the magnitude and negative sign of $s_{\mathrm{sp}'}$ for the bonds to a and a′ which nearly cancells the contribution of $s_{\mathrm{pp}'}$ and because of the larger overlap integral between H$_b$–H$_b$′ than between H$_a$–H$_{a'}$. To facilitate a comparison, the components of the overlap integral are given in Table II.

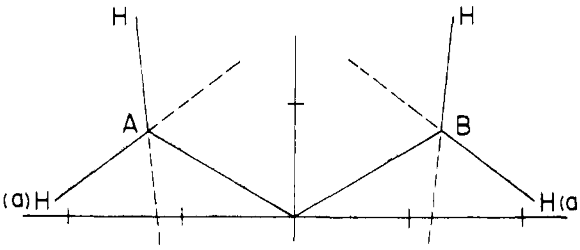

Fig. 3.—Geometrical arrangement of hydrogens at the methyl group (A) and the bromomethyl group (B) of methyl α,β-dibromoisobutyrate.

TABLE II

OVERLAP INTEGRALS

Bond	Length, Å.	Overlap integral
C–C	2.13	0.219(σ,σ), 0.069(π,π), 0.221(s,s), 0.189(σ,s)
H$_a$–H$_a$′	3.89	.006
H$_b$–H$_b$′	2.60	.048
C–H$_a$′	3.08	.035(σ,s), 0.000(π,s), 0.027(s,s)
C–H$_b$′	2.60	.078(σ,s), 0.000(π,s), 0.062(s,s)
C–H	1.09	.687

$Z(\mathrm{C}) = 3.18$; $Z(\mathrm{H}) = 1.2$

On this basis, one would have predicted that the coupling between b and b′ would have been much larger than that between a and a′ which is contrary to observation. Small modifications of the assumed geometry will not change this result. It would therefore appear that either the Fermi contact potential is not the most important contributor to the long-range spin coupling, or that the simple wave function used above is a very poor approximation to the true wave function.

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(10) H. M. McConnell, *J. Phys. Chem.*, **24**, 460 (1956).

(11) H. J. Kopineck, *Z. Naturforsch.*, **56**, 420 (1950).

(12) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).