molecules, and its environment should be relatively unaffected by the addition of those electrolytes which are solvated preferentially by water. Addition of an electrolyte to an aqueous solution of an anhydride will alter the environment of the anhydride, either by direct interaction, or indirectly by changing the water structure.[34] At the same time the dioxane molecules will themselves change the structure of the water, and so further reduce the effect of added electrolytes.

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[34] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945); H. S. Frank and W.-Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957); O. Y. Samoilov, *ibid.*, **24**, 144 (1957); M. Kaminsky, *ibid.*, **24**, 171 (1957).

Studies on Cyclic Polyols. V. Long-Range Proton Spin Coupling and Other Features of Nuclear Magnetic Resonance Spectra of Substituted Cyclopentanes[1,2]

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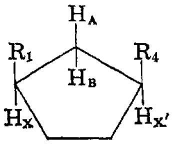
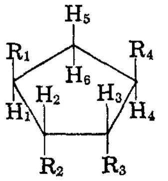
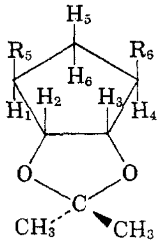
Received May 3, 1966

The proton magnetic resonance spectra of a large number of tetrasubstituted cyclopentanes have been examined. Compounds with the 1,4/2,3 configuration give spectra which can be rationalized by first-order analysis as AKX_2Y_2 systems. The signal for each methylene proton is a doublet of triplets. The higher field signal in this region represents the methylene proton *cis* to the 1,4 substituents, and always has wider lines than those seen in the lower field methylene multiplet. Similar line broadening and occasional line splitting are seen in the signal representing the protons attached to C_2 and C_3; these protons are *cis* to the methylene proton whose signal contains the broadened lines. Spin-decoupling experiments show that the line broadening is due to long-range spin–spin coupling (^4J). In all cases the four bonds have the M or W orientation which has been postulated as essential for such long-range coupling to be observed. ^4J has been measured for six compounds and varies from 0.5 to 1.5 cps. When the 2,3 substitution consists of an O-isopropylidene group (*i.e.*, in 2,4-dioxabicyclo[3.3.0]octane derivatives), ^4J is larger than ^3J. Certain other characteristics of the spectra of these compounds a represented, and some implications to the nmr spectroscopy of bicyclo[3.3.0]octane are discussed.





I a, $R_1 = R_4 = Br$; $R_2 = R_3 = OH$
b, $R_1 = R_2 = R_3 = R_4 = OH$
c, $R_1 = R_2 = R_3 = R_4 = OBz$



II a, $R_5 = R_6 = Br$
b, $R_5 = R_6 = OH$
c, $R_5 = R_6 = OBz$
d, $R_5 = Br$; $R_6 = OH$

We have described elsewhere[2] some of the characteristics of the nmr spectra of cyclitols and halocyclitols derived from cyclopentane. Because of the kind of symmetry present in many of the compounds studied, the A_2X_2 and ABX_2 (or AKX_2) approximations[4] could be used for first-order analysis of most of the signals representing the ring protons. Considerable information was obtained relative to the angular dependence of the internal chemical shift $\delta_X - \delta_A$ and $\delta_X - \delta_B$ in the ABX_2 systems studied, as well as of the influence of the electronegativity of the substituent on the magnitude of the internal chemical shift. The cyclopentane system was shown to be comparable in many ways to the substituted norbornanes and norbornenes[5] and the cyclohexane tetrols.[6] Compounds with the 1,4/2,3 configuration (structures I and II) usually had spectra which could be interpreted completely by first-order theory, with the further assumption that proton–proton spin couplings through four bonds (^4J) or more were too small to cause observable splitting of the spectral lines. Each of the methylene protons was represented by a doublet of triplets, the large doubling caused by the geminal coupling (J = 12–18 cps) and the smaller tripling due to coupling with the two flanking protons, H_1 and H_4. In many cases, however, the spectra showed certain additional features which could not be explained by the assumptions noted above. These anomalies always included slight widening and apparent "noisiness" of the signal of H_5 (which was always at higher field than H_6), and occasionally by widening or splitting of the H_2H_3 signal without any corresponding effect in the H_1H_2 signal (see Figures 1 and 2). In the present communication we present conclusive evidence for coupling through four bonds, involving H_5 and H_2,H_3. In all compounds with structure II, ^4J of H_2,H_3 is larger than ^3J, *i.e.*, $J_{25} > J_{12}$, whereas in series I, J_{12} is 2.5–4.5 cps. The deceptively simple[7a] nature of the spectra of many of the compounds is further emphasized by a previously unreported example.

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[1] (a) Supported in part by U. S. Public Health Service Grant AM-07719 from the National Institute of Arthritis and Metabolic Diseases. (b) Presented before the Division of Organic Chemistry at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[2] Part IV: H. Z. Sable, W. M. Ritchey, and J. E. Nordlander, *Carbohydrate Res.*, **1**, 10 (1965).

[3] Author to whom communications should be addressed at the Department of Biochemistry, Western Reserve University, Cleveland, Ohio.

[4] 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, p 98.

[5] (a) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963); (b) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2709 (1963); (c) *ibid.*, **86**, 1171 (1964).

[6] G. E. McCasland, S. Furuta, L. F. Johnson, and J. N. Shoolery, *J. Org. Chem.*, **28**, 894 (1963).

[7] (a) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961); (b) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (c) R. U. Lemieux, J. D. Stevens, and R. R. Fraser, *Can. J. Chem.*, **40**, 1955 (1962).

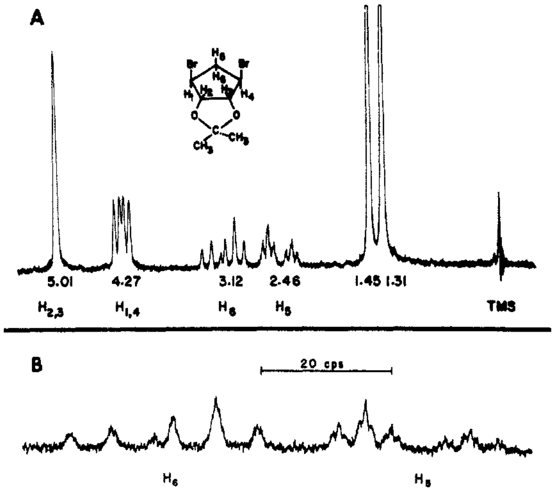

Figure 1.—60 Mc/sec nmr spectrum of IIa, normal sweep rate (A); H_5 and H_6 signals of IIa, slow sweep (B).

Results

Spectral Evidence for Long-Range Coupling.—The spectra of IIa and IIb are shown in Figures 1A and 2. The basis for assignment of the signals at δ 2.46 and 3.12 to H_5 and H_6 of IIa was discussed fully in the previous publication.[2] The doublet of doublets at δ 4.27 shows major splitting due to $J_{1,6}$ of 6.2 cps equal to the tripling in the signal at δ 3.12, and minor splitting due to $J_{1,5}$ of 3.2 cps equal to the tripling in the signal at 2.46; consequently the signal at δ 4.27 represents H_1,H_4 and the tall singlet at 5.01 represents H_2,H_3. Similar arguments apply to the assignment of signals in all the other compounds. The values for J_{12} observed in Ia and Ib (Table I) are of the correct order of magnitude[5a,7b,7c] for the expected dihedral angle of approximately 120°. The much smaller $J_{1,2}$ for the four compounds with structure II is not readily explicable. The observed difference in coupling constants doubtless has a conformational basis, but the conformational properties of these compounds are insufficiently understood at present to permit a precise interpretation.

TABLE I

Compd	$J_{1,2}$, cps[a]	$J_{2,5}$, cps[a]
Ia	4.5	0.55
Ib	Not measurable	Not measurable
Ic	2.8	0.74
IIa	0.8	0.9
IIb	~0	1.1
IIc	0	1.5
IId	Uncertain, probably ~0	$J_{2,5} = 1.4$ cps $J_{3,5} = 0.8$ cps

[a] Except in case IId it is assumed that $J_{1,2} = J_{3,4}$ and $J_{2,5} = J_{3,5}$. The values reported were obtained by direct measurement of expanded spectra recorded at slow sweep rates.

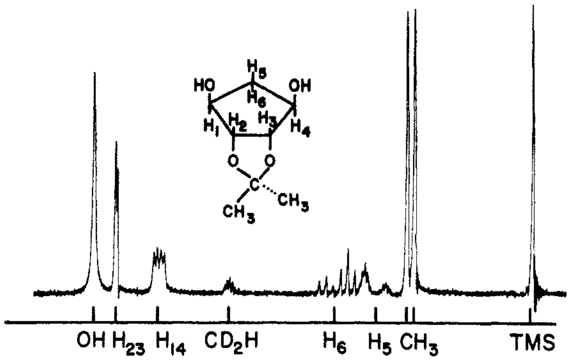

Figure 2.—60 Mc/sec nmr spectrum of IIb. The chemical shifts of the signals indicated follow: CH_3, δ 1.28 and 1.37; H_5, δ 1.70; H_6, δ 2.13; CD_2H, δ 3.29; H_{14}, δ 4.09; H_{23}, δ 4.56; OH, δ 4.79.

Evidence that the apparent noisiness of the H_5 signal is not an adventitious effect but is due to some nuclear spin–spin interaction is obtained when the signal is recorded on an expanded scale at a much slower sweep rate (Figure 1B). Each of the six lines of the signal is now seen to be itself a symmetrical triplet, with an average splitting of 0.9 cps. A first-order interpretation suggests that this tripling is due tointe ractions with two equivalent nuclei not already assigned and the only two such nuclei are H_2 and H_3. Since no corresponding splitting was observed in the H_2,H_3 signal, the assignment of the fine tripling in the H_5 signal to $J_{2,5} = J_{3,5}$ had to be substantiated by an unequivocal method. Proof of this postulation was obtained by spin–spin decoupling[8] achieved by nuclear magnetic double resonance. Each of the substances listed in Table I except compound Ib was examined by this technique, and in each case "decoupling frequencies" for the second irradiation were found, which converted the split signals of H_2,H_3 into singlets, or which made existing moderately sharp singlets into even taller, narrower signals. When the H_5 signal was observed, the double irradiation narrowed and heightened the individual lines of the doublet of triplets. In no case was the doubling or tripling of the H_5 signal, which is due to the interactions $J_{5,6}$, $J_{1,5}$, and $J_{4,5}$, affected by irradiation at the resonance frequency of H_2,H_3. Compound Ib could not be examined in this way because all of the O–C–H protons gave a poorly resolved multiplet in which the individual resonance frequencies could not be assigned. Some of the "decoupling frequencies" are indicated in Table II and these frequencies (actually frequency differences) correspond to frequency differences between lines in the signal being irradiated and the signal being observed. In all six compounds studied there is therefore unequivoca lproof of long-range coupling of H_5 with H_2 and H_3.

In some of the spectra the individual lines of the H_5 signal could not be discerned readily, but instead the signal consisted of two envelopes showing clearly only the geminal coupling $J_{5,6}$ (*e.g.*, see Figure 2). Even in these cases, however, irradiation at the frequency of the H_2,H_3 signal caused some improvement in the resolution of the H_5 signal. Fortunately in these cases ^4J was large enough to cause splitting of the H_2,H_3 signals, and the long-range coupling was proved because irradiation at the frequency of the H_5 signal collapsed the H_2,H_3 doublets to singlets. The magnitude of the coupling constants was measured directly from the spectra, usually with an expanded scale and very slow sweep rate. Since in all cases the ratio $(\nu_p - \nu_q)/J_{pq} > 100$, the line separation is almost certainly an accurate measure[9a,b] of the coupling constant ^4J. In none of

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(8) (a) W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956); (b) L. F. Johnson, "Varian Associates Technical Information Bulletin," Vol. 3, No. 3, 1962, p 5.

(9) (a) In this expression ν_p and ν_q are the chemical shifts of two nuclei in cps, and J_{pq} is the true coupling constant, also in cps; (b) T. J. Flautt and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 3212 (1963); (c) "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectra 10 and 14.

TABLE II

DECOUPLING FREQUENCIES FOR LONG-RANGE COUPLING OF H_2H_3 WITH H_5

Compd	Unperturbed spectrum, δ (ppm)[a]		Signal		Δν, irradiated − obsd,[b] cps	Appearance of signal	
	$\nu_{H_2}\nu_{H_3}$	ν_{H_5}	Obsd	Irradiated		Without irradiation	With irradiation
Ia	4.37	2.34	H_5	H_2H_3	−114 or −130	Doublet of triplets, lines appear "noisy"	Lines of the lower field triplet higher and narrower
			H_2H_3	H_5	+112.5	Doublet, W_h = 3.1 cps[c]	Lines narrower and taller
Ic	6.03	2.2	H_5	H_2H_3	−228	Doublet of triplets lines wide and "noisy"	Lines of lower field triplet sharpen, taller
					−241		Lines of higher field triplet sharpen, taller
			H_2H_3	H_5	+228 or +241	Doublet, lines have "shoulders"	Lines narrower and taller
IIa	5.01	2.46	H_5	H_2H_3	−144	Doublet of triplets, lines appear "noisy," W_h = 2.0 cps	Lines of lower triplet sharp and taller
					−162		Lines of higher field triplet sharp and taller
			H_2H_3	H_5	+143	Singlet	Signal becomes taller
IIb	4.56	1.70	H_5	H_2H_3	−162.5	Doublet of unresolved multiplets, W_h = 4.7 cps	Lower multiplet resolved to a triplet
					−173		Higher field multiplet is resolved to a triplet
			H_2H_3	H_5	+164 or +174.5	Doublet	Collapses to a narrow singlet
IIc	4.85	2.27	H_5	H_2H_3	−144	Doublet of triplets; lines irregular	Lines of lower field triplet narrow and taller
					− 161		Lines of higher field triplet narrow and taller
			H_2H_3	H_5	+143	Doublet	Tall singlet
IId	4.76 5.09	2.24	H_2H_3	H_5	+152	"AB quartet" with splitting or widening of each line	All four lines become narrow singlets[d]

[a] The following line separations in cps, ascribed to $J_{5,6}$ are measured in the spectra: Ia, 15.0; Ic, 15.6; IIa, 16.1; IIb, 14.2; IIc, 15.8; IId, 15.4 cps. [b] Δν is indicated as positive when the "irradiated signal" is at higher frequency than the observed signal, and is negative when the reverse is true. [c] W_h, width of a line or signal at half-height. [d] See text for a detailed explanation.

the examples reported was there any evidence of long-range coupling of H_6 with H_2 and H_3.

The Deceptively Simple Spectrum of Bromohydrin IId. A. Assignment of the Spectral Lines.—We have pointed out previously[2] that the spectra of many of the compounds in this series are deceptively simple.[7a] This feature is seen in the spectrum of the bromohydrin IId, shown in Figure 3. As usual the higher field signal in the methylene region is assigned to H_5, and the lower field signal to H_6 ($J_{5,6}$ = 15.7 cps). The value of $J_{1,5}$ has not been determined. H_1 and H_4 are represented by four lines of approximately equal height in the region of δ 4.3. The relative intensities prove that this multiplet is not an AB system, but actually consists of two overlapping doublets, one centered at δ 4.30 and the other at 4.35, representing H_1 and H_4. Line separation ascribable to $J_{1,5}$ is not seen in this multiplet. The first-order interpretation of this pattern is shown in the expanded partial spectrum in the upper part of the figure. Confirmation of this analysis was obtained from a spin-decoupling experiment which showed that the nuclei represented by the multiplet labeled H_1,H_4 are indeed coupled to H_6. It is not clear which doublet belongs to H_1 and which to H_4, but in general Br–C–H protons appear at higher field than corresponding O–C–H protons. As one example the α-proton chemical shifts[9c] of ethyl bromide (δ 3.43) and ethanol (δ 3.70) may be cited. Furthermore the O–C–H signal of Ia is at δ 4.37 and the Br–C–H signal is at δ 4.14. On the other hand H_1,H_4 of IIb appear at δ 4.09, whereas the corresponding signal of IIa is at δ 4.27.

A similar uncertainty exists in the assignment of the H_2 and H_3 resonances. These nuclei form an AB system of two doublets centered at δ 4.76 and 5.09, with $J_{2,3}$ = 5.65 cps. Although assignment of the signals is indicated in Figure 3, we must emphasize that this is only speculative and is based on the following argument. Deshielding of a nucleus H by a vicinal electronegative substituent R is greater when R and H are transoid rather than cisoid,[2,5] and the inductive effect of the neighboring Br and OH groups probably is not the sole cause of the different resonance frequencies of H_2 and H_3. An important contribution must be ascribed to the anisotropy of the C–Br and C–OH bonds,[10] because the internuclear distances involved are

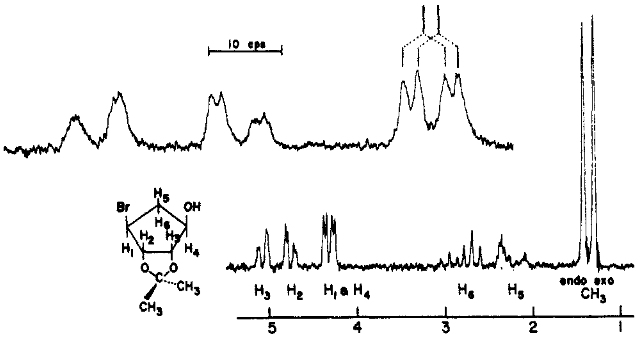

Figure 3.—60 Mc/sec nmr spectrum of IId. The upper part of the figure is an expanded spectrum at slow sweep rate, of the portion between δ 5.5 and 4.0, and a first-order analysis of the four principal lines in the H_1–H_4 multiplet.

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(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, Chapter 7.

small. However, accurate assessment of these relative anisotropy effects is not possible at present.

Two singlets at δ 1.31 and 1.43 represent the methyl groups on the dioxolane ring. The basis for assigning these to the *endo* and *exo* methyl groups, respectively, will be presented in a later communication.[11] The expanded partial spectrum in the figure shows the H_1, H_2, H_3, and H_4 signals. Each of the four lines of the H_2,H_3 "AB quartet" is split. The splitting might be ascribed to vicinal proton coupling, *i.e.*, $J_{1,2}$ and $J_{3,4}$, but this explanation is unlikely because there is no corresponding splitting in the H_1 and H_4 signals, and because double irradiation at a frequency $\Delta\nu = +152$ cps (see Table II) decouples H_2 and H_3 from H_5, collapsing each of the lines to a sharp singlet. Decoupling of all four lines by double irradiation at the same $\Delta\nu$ is explained as follows: when the lower doublet (H_3) is being observed, the decoupling frequency coincides with the lower band of the H_5 signal, and, when the higher doublet (H_2) is observed, the decoupling frequency corresponds to the upper band of the H_5 signal.

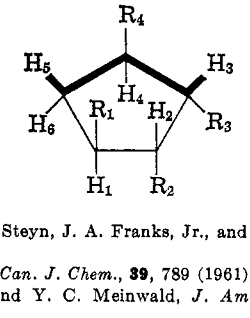
B. The Apparent Equality of $J_{1,6}$ and $J_{4,6}$.—The signal of H_6 is a doublet of triplets resembling those of H_6 in the symmetrical compounds of this series. First-order interpretation suggests that the tripling is a consequence of the fortuitous equality of $I_{1,6}$ and $J_{4,6}$, but this interpretation is probably wrong. These couplings should be compared with those of the corresponding protons of IIa and IIb. $J_{1,6}$ for the dibromo compound IIa is 6.2 cps and for the dihydroxy compound IIb $J_{1,6}$ is 4.7 cps. The tripling in the H_6 signal in the present case is 5.5 cps, and if this splitting represents $0.5\ (J_{1,6} + J_{4,6})$ the values taken from IIa and IIb make $0.5\ (J_{1,6} + J_{4,6}) = 5.45$ cps, in excellent agreement with the observation. Flautt and Erman[9b] have emphasized that, in an ABX system when $\Delta\nu_{AB}$ is small compared to the mutual coupling constant J_{AB}, the spacings are not equal to J_{AX} and J_{BX} but to $0.5\ (J_{AX} + J_{BX})$. The present case is different, since it is an AXY rather than ABX system, and J_{XY} is probably negligible. However δ_X and δ_Y are very close, and this may lead to the same averaging of coupling constants J_{AX} and J_{AY} to produce the equal spacing in the H_6 multiplet. The spacings of the two doublets in the H_1 and H_4 signals are not identical; the frequencies of the first and third lines (numbering from lower to higher field) differ by 7.0 cps, and the second and fourth lines by 5.5 cps. It is tempting to assign the signals on the basis of these spacings, but in view of the inconsistencies in the spectrum, *e.g.*, the apparent equivalence of $J_{1,6}$ and $J_{4,6}$ in the H_6 signal, and nonequivalence in the H_1,H_4 signal, reliance on first-order analysis for this decision is unwarranted.

C. The Inequality of $J_{2,5}$ and $J_{3,5}$.—The spacings assigned to $J_{2,5}$ and $J_{3,5}$ are not equal. The inequality may be the result of the differing electronegativity of the substituents on the adjacent carbon atoms,[5] or of differences in orientation of H_2 and H_3 due to a preferred conformation of IId. This aspect of the problem is difficult to assess: the infrared spectrum of IId has O–H stretching bands characteristic of both free and intramolecularly H-bonded hydroxyl groups;[12,13] since there is only one OH group and the compound is pure,[14] an appreciable fraction of the molecules must have an average conformation determined by three rings (the third bridge is C_1–Br·····HOC_4), whereas the remainder of the molecules do not have the additional constraint of the third ring. In the molecules which are H bonded, the average vectorial relation between the molecular orbitals C_2–H_2 and C_5–H_5 will be substantially the same as the relation of C_3–H_3 and C_5–H_5, whereas in the nonbonded molecules a preferred conformation may exist in which these relations are not the same. Obviously these relations between the molecular orbitals must exert a profound influence on the magnitude of the coupling constant. Unlike the case of $J_{1,6}$ and $J_{4,6}$, there is no mixing of $J_{2,5}$ and $J_{3,5}$ because $\nu_2 - \nu_3$ is 15 to 20 times as large as $J_{2,5}$ or $J_{3,5}$, and about four times as large as $J_{2,3}$.

Discussion

Long-range coupling has been found in the spectra of many classes of saturated compounds: bornanes,[9b,15] norbornanes,[5c,16] bicyclo[2.1.1]hexanes,[17] steroids,[18] 2,3-disubstituted butanes,[19] 1,2-dibromo-2-phenylpropane,[20] 1,6-anhydrohexapyranoses,[21] and miscellaneous cyclic structures.[22] In most of the cases mentioned the observed magnitude of $^4J_{HH}$ was about the same as that seen in the cyclopentane compounds which are the subject of this communication. An exception is the bicyclo[2.1.1]hexane series[17] in which $^4J_{HH}$ for the *endo*-C_5 and *endo*-C_6 protons is 7 cps, a value much larger than most of the vicinal coupling constants in the same molecules. In the bicyclo[2.2.1]heptane series ^4J values of 1–4 cps are found for *endo* H-*anti* H, and *exo* H-*exo* H′ interactions, which also are larger than $^3J_{HH}$ for the *endo* H-bridgehead H coupling.[5c,16] Meinwald and Lewis[17] rationalized the long-range coupling by assuming fairly extensive overlap of the small lobes of the orbitals directed away from the C–H bonds in question. Rassat, *et al.*,[22] Shoppee, *et al.*,[18d] and Sternhell[18e] have defined the geometric conditions for such couplings as the "tail-to-tail", "M" or "W" rule.

All the examples reported in this paper obey the "W" rule, and in the bicyclic systems the bridgehead hydrogens have $^4J_{HH} > {}^3J_{HH}$. The present study is the first



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[11] H. Z. Sable, W. M. Ritchey, and J. E. Nordlander, to be published.

[12] (a) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); (b) *ibid.*, **76**, 4323 (1954); (c) *ibid.*, **80**, 5950 (1958).

[13] J. A. Franks, Jr., B. Tolbert, R. Steyn, and H. Z. Sable, *J. Org. Chem.*, **30**, 1440 (1965).

[14] B. Tolbert, R. Steyn, J. A. Franks, Jr., and H. Z. Sable, to be published.

[15] F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

[16] J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

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[18] (a) Y. Osawa and M. Neeman, *ibid.*, **85**, 2856 (1963); (b) D. H. Williams and N. S. Bhacca, *ibid.*, **85**, 2861 (1963); (c) N. S. Bhacca, J. E. Gurst, and D. H. Williams, *ibid.*, **87**, 302 (1965); (d) C. W. Shoppee, F. P. Johnson, R. Lack, and S. Sternhell, *Tetrahedron Letters*, 2319 (1964); (e) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

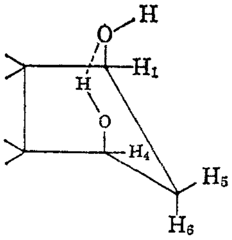
[19] (a) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **84**, 743 (1962); (b) F. A. L. Anet, *ibid.*, **84**, 747 (1962).

[20] D. R. Davis and J. D. Roberts, *ibid.*, **84**, 2252 (1962).

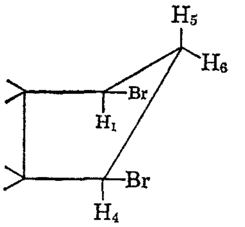
[21] L. D. Hall and L. Hough, *Proc. Chem. Soc.*, 382 (1962).

[22] A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, 233 (1964).

in which it is possible to compare mono- and bicyclic systems with ostensibly the same geometry and substituent electronegativity. The steric relation of H_1 and H_2 in Dreiding models seems very little altered between series I and series II, but the conformational mobility of II is greatly diminished. In conformationally mobile systems such as the unbridged cyclopentanes the dihedral angles for HCCH may be constantly changing and the ^3J values measured are therefore time averaged. Because the possible excursion of the atoms in the unbridged systems is larger than in the bridged systems and $J_{120°}$ is quite small, it is reasonable that the average value of J_{trans} (*i.e.*, $J_{1,2}$ in this case) will be much smaller in the bridged systems in spite of no apparent change in the dihedral angle seen in molecular models. Eventually the influence of conformational factors on ^4J may be evaluated. The infrared spectrum of IIb shows two O–H stretching bands at 3603 and 3536 cm^{-1}, characteristic of one free and one intramolecularly H-bonded OH group. The $C_1OH \cdots OC_4$ hydrogen bond ($\Delta\nu = 67$ cm^{-1}) is of the same strength as the corresponding bond in 1,3-cyclopentanediol.[23] The formation of this bond results in an envelope conformation E_5, in which C_5 is displaced "below" the plane of the rest of the ring, *i.e.*, away from R_1 and R_4 (the nomenclature is that of Hall[24] and Bishop and Cooper[24]). The conformation of IIa and IIc is less certain. Presumably replusion between the bulky groups at C_1 and C_4 would lead to the conformation E^5, but mutual complexing between the two benzoyl residues in IIc cannot be excluded *a priori.*



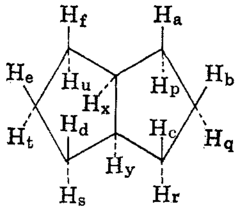
E_5



E^5

Virtual coupling[25] cannot be involved in the coupling of H_5 with H_2 and H_3, since $J_{1,2}$ and $J_{3,4}$ are small or zero. Furthermore, when both $J_{1,2}$ and $J_{2,3}$ are measurable, spin decoupling of H_5 does not affect the spacing ascribed to $J_{2,3}$, and in the converse experiment spin decoupling of H_2,H_3 does not affect the spacings in the H_5 signal ascribed to $J_{1,5}$. H_5 is coupled with H_6, equally with H_1 and H_4 and equally with H_2 and H_3. By the first-order approximation the H_5 signal should represent the A portion of an AKX_2Y_2 system, with 18 lines expected. All 18 lines are easily discernible in Figure 1B.

On the basis of the consistent presence of measurable long-range coupling, predictions may be made concerning the spectra of bicyclo[3.3.0]octane derivatives[26] whose structure closely resembles that of II. The unsubstituted hydrocarbon III has five groups of geometrically equivalent protons: H_x,H_y, H_b,H_e, H_q,H_t, H_a,H_c,H_d,H_f, H_p,H_r,H_s,H_u. All the members of a group have the same chemical shift. The chemical shift differences among the methylene protons should be small, but the bridgehead protons are appreciably different from the methylene protons. In spite of the steric equivalence the members of any group are not magnetically equivalent,[27] *e.g.*, since H_q and H_t are differently coupled to H_b. As a result there are many magnetically nonequivalent nuclei with nearly identical chemical shifts, and well-resolved spectral lines should not be expected. Some examples of nonzero coupling expected in III are the following: H_y is coupled strongly (^3J) to H_r and H_s, and less strongly (^4J) to H_p,H_q,H_t,H_u. Furthermore, because of the expected strong coupling $J_{x,y}$, H_y is virtually coupled[25] to protons coupled to H_x. (By analogy with II we are assuming that $J_{yc} = J_{yd} = 0$.) This combination of real and virtual coupling can only result in spectra which will be extremely difficult to analyze. The expected complexity is indeed seen in the recorded spectrum[26] of III.



III

Experimental Section

Nmr spectra were recorded with Varian Associates DP-60 and A-60 spectrometers. Nuclear magnetic double resonance experiments were performed with an NMR Specialities HD-60A spin decoupler in conjunction with the DP-60 instrument. All compounds were studied as 10% solutions with tetramethylsilane (TMS) as internal reference (except when D_2O was the solvent, in which case trimethylsilylpropane 3-sulfonate was used). Ia was dissolved in acetone-D_6, Ic in D_2O, IIb in CD_3OD, and the other substances in $CDCl_3$. Ia, Ib, Ic, and IIa were prepared as described elsewhere;[28] IIb, IIc, and IId were prepared[14] from known compounds by unequivocal routes, gave correct elemental analysis and were considered pure by other criteria.

Acknowledgment.—We thank Herbert Grossman for assistance in recording some of the spectra and in the spin-decoupling experiments.

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[26] (a) W. B. Moniz and J. A. Dixon, *J. Am. Chem. Soc.*, **83**, 1671 (1961); (b) A. D. Ketley and J. L. McClanahan, *J. Org. Chem.*, **30**, 940 (1965).

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