

Thus, the chemical shifts of H_a in the III, IV, and VI derivatives appear quite normal.

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Effects of Steric Compression on Coupling Constants^{1,2}

Sir:

Compounds with a half-cage structure related to the birdcage hydrocarbon are very useful for studying the effects of steric compression on chemical shifts.³ We now report that steric compression in this series of compounds leads also to unusual coupling constants and relaxation effects and that the results have an important bearing on the existence of a "through-space" mechanism⁴ for spin coupling.

The compounds with which we are concerned are half-cage O-inside derivatives I⁵ and II⁵ and the O-outside analogs III.⁵ In the O-inside alcohols I-OH and II-OH coupling between the inside H_b proton and the hydroxyl proton H_o (and perhaps even between H_b and the outside H_a α proton) is conceivable, as is also coupling⁶ between the two inside H_b and H_a protons in III.

Chemical shifts of H_a , H_b , and H_o in the various derivatives are summarized in Table I. For observation of H_b - H_o coupling, spectra were determined in acetone solution, conditions which are known to give very slow exchange of hydroxyl protons.⁷ The temperature-dependent bands clearly belong to H_o . The other bands can be assigned on the basis of the expected chemical shifts for inside and outside protons and on the expected relative complexity of the bands of H_a and H_b as a result of coupling of H_a to H_d , etc. Comparison of the hexachloro compounds with their unchlorinated analogs³ suggests that the deshielding of the inside protons tends to be even larger in the former derivatives than in the latter. In particular the deshielding of H_b on going from O-outside to O-inside compounds is

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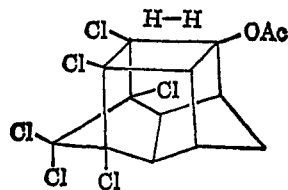
(2) Reported in part at the Symposium on Cagelike Molecules at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1, 1964.

(3) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5247 (1965).

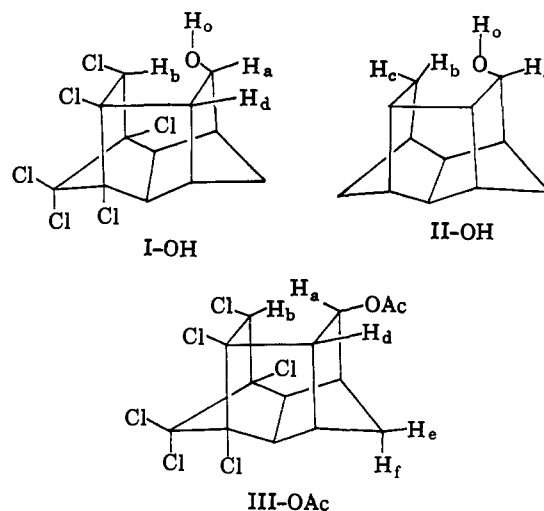
(4) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); S. Ng and C. H. Sederholm, *ibid.*, **40**, 2090 (1964); A. D. Cross, *J. Am. Chem. Soc.*, **86**, 4011 (1964); K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1339 (1965).

(5) S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *ibid.*, **82**, 5377 (1960).

(6) In valence-bond terms, this could occur as a result of a contribution of resonance structure IIIa to the resonance hybrid of III.



(7) J. R. Holmes, D. Kivelson, and W. C. Drinkard, *J. Chem. Phys.*, **37**, 150 (1962).



larger with the chlorinated materials than with their unchlorinated counterparts. Thus, $\Delta\delta$ is -2.0 p.p.m. between III-OH and I-OH, while it may be estimated to be *ca.* -1 p.p.m. with the unchlorinated alcohols.³

Regarding H_b - H_o coupling in I-OH, the band of H_o in this compound is a well-resolved 1:1:1:1 quartet, with spacings of 4.8 and 1.1 c.p.s., while the band of H_b is a doublet, with a splitting of 1.1 c.p.s. It is therefore obvious that H_o is coupled to H_b by 1.1 c.p.s.⁸ The various coupling constants between H_a , H_b , and H_o are shown in Table I; decoupling experiments confirmed these assignments. The value of J_{ab} was estimated from the sharpening of the H_b doublet upon strong irradiation of H_a . With the unchlorinated II-OH at -20° the band of H_o is a doublet ($J_{ao} = 4.8$ c.p.s., line width = 0.9 c.p.s.). Therefore the value of J_{bo} is less than *ca.* 0.5 c.p.s.

Table I. Summary of Chemical Shifts and Coupling Constants

Compound	Solvent	Chem. shifts (τ values)		
		H_a	H_b	H_o
I-OH ^a	Acetone	5.70	2.05	4.22 ^d
I-OH	CDCl ₃	5.83	2.60	
I-OAc	CDCl ₃	5.12	3.45	
II-OH ^b	Acetone	6.00	6.03	5.90 ^{d,e}
II-OH	CDCl ₃	5.05	4.60	
III-OAc ^c	CDCl ₃	4.20	4.52	

^a $J_{ad} = 5.5$, $J_{ao} = 4.8$, $J_{bo} = 1.1$, $J_{ab} = 0.24$ c.p.s. ^b $J_{ao} = 4.8$, $J_{bo} < 0.5$ c.p.s. ^c $J_{ab} < 1$ c.p.s. ^d Temperature dependent. ^e 5.4 p.p.m. at -20° .

It is extremely unlikely that the coupling of H_b with either H_a or H_o proceeds by a through-bond mechanism, as the protons are separated by five and six single bonds, respectively.⁹ Therefore the coupling most probably takes place *via* the unshared electrons of the oxygen atom. In both I-OH and II-OH one can consider the possibility that the H_b -O interaction partakes of the character of a hydrogen bond. Certain polyhalogenated hydrocarbons, *e.g.*, chloroform, are well known

(8) Not only is H_b coupled to H_o , but a "long-range" isotope effect (0.5 c.p.s. upfield) is observed for the chemical shift of H_b in I-OD. This isotope effect is rather remarkable in light of the fact that the isotope effects in CHD groups and in HDO⁷ are only *ca.* 0.7 and 1.8 c.p.s., respectively.

(9) Coupling between OH and CH protons has not been reported even through four single bonds [S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964)].

to form¹⁰ hydrogen bonds; on the other hand, saturated hydrocarbons or their monohalo derivatives do not form hydrogen bonds. However, the special proximity effects in I-OH may well be favorable to weak internal hydrogen bonding, and this may help explain the larger value of J_{bo} in I-OH than in II-OH. It is also likely that the chlorine atoms give rise to a buttressing effect, thus forcing H_b closer to the oxygen atom in I-OH than in II-OH and thereby causing a larger J_{bo} in I-OH than in II-OH. This would be in line with the larger deshielding effects observed with the chlorinated than with the unchlorinated derivatives.

Since II-OH has in its infrared spectrum an abnormally high frequency C-H stretching band, presumably corresponding to C- H_b , and since hydrogen bonding leads to a low-frequency shift, most of the H-O interaction is repulsive, and this is probably also true of I-OH. At least formally then, the coupling of H_b with H_o can be termed as of the "through-space" type.

As regards H_a - H_b coupling in III-OAc, this is evidently quite small. Of the two low-field bands of equal intensity, the broader band (τ 4.2) is assigned to H_a (unresolved coupling to H_d , H_f , etc.) and the sharper band (τ 4.52, width 1.0 c.p.s.) to H_b . Therefore the value of J_{ab} must be considerably less than 1 c.p.s. In attempting to detect an unresolved H_a - H_b coupling in III-OAc by double resonance we observed that, although the band of H_b did not change in width on irradiation of H_a , the area of the band increased by about 45%. This unexpected nuclear Overhauser effect is discussed in more detail in another paper.¹¹ Suffice it to mention here that the observation of this effect is a reflection of a very efficient mutual relaxation of H_a by H_b , and *vice versa*, by the direct dipole-dipole mechanism. In fact, the bands of H_a and H_b are already broadened at room temperature by an unusually short spin-lattice relaxation time¹² (T_1) of these protons. The broadening is greatly magnified at -60° . Whereas other bands in the spectrum change little, the band of H_a , which has a width of 3.6 c.p.s. at 35° , now has a width of 5.2 c.p.s. Similarly, H_b increases in width from 1.0 c.p.s. at 35° to 3.3 c.p.s. at -60° . At both temperatures the line width of internal tetramethylsilane is 0.5 c.p.s.

The present work shows that "through-space" coupling is negligible when the interaction is directly between two nonbonded protons, but that an interaction through an oxygen atom can lead to appreciable H-H coupling. It is therefore likely that appreciable "through-space" coupling will be found for H-F and F-F interactions provided that the nuclei are sufficiently close to one another.

(10) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp. 197-201; A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1715 (1963).

(11) F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5250 (1965).

(12) The contribution to the line width (*i.e.*, $1/T_1$) is proportional to the inverse sixth power of the distance between two nuclei.

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Nuclear Magnetic Resonance Spectral Assignments from Nuclear Overhauser Effects¹

Sir:

Assignments in proton high-resolution nuclear magnetic resonance spectra are usually made on the basis of chemical shifts and coupling constants. We now show that additional valuable information can sometimes be obtained by a consideration of the intramolecular spin-lattice relaxation paths for the various protons in a molecule.

With most organic compounds the main relaxation mechanism contributing to T_1 is the direct dipole-dipole interaction.² Intermolecular contributions by this mechanism can be made very small by dissolving the compound to be studied in a magnetically inert solvent,³ or at least in a solvent not containing fluorine nuclei or protons (*i.e.*, nuclei with high magnetic moments). A further important condition is that paramagnetic species, including molecular oxygen,⁴ be present in only extremely small concentrations since such species are very efficient in relaxing protons.

The contribution to T_1 from the intramolecular dipole-dipole interaction of nuclei A and B (spin $1/2$) is given by² $1/T_1^{AB} = \hbar^2 \gamma_A^2 \gamma_B^2 \tau / d^6$, where T_1^{AB} is the contribution to T_1 for nuclei A or B, τ is the correlation time for random molecular rotation,⁵ d is the internuclear distance between A and B, and the other symbols have their usual significance. If several nuclei are present, the contributions to T_1 for each nucleus may be added in the usual way, *i.e.*, $1/T_1^A = 1/T_1^{AB} + 1/T_1^{AC} \dots$. If A and B are both protons and $1/T_1^A = 1/T_1^{AB}$, it can be shown² that complete saturation of the B nuclei will result in a 50% enhancement of the integrated intensity of the band of the A nuclei. This is a nuclear Overhauser effect^{2b,6,7} (NOE). If other nuclei contribute appreciably to the relaxation of the A nuclei, the increase in intensity of the band of the A

(1) This investigation was supported by National Science Foundation Grant No. GP 3780.

(2) (a) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948); (b) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, New York, N. Y., 1961, p. 264; (c) J. G. Powles, *Ber. Bunsengesellschaft*, **67**, 328 (1963).

(3) G. Bonera and A. Rigamonti, *J. Chem. Phys.*, **42**, 171 (1965).

(4) R. J. C. Brown, H. S. Gutowsky, and K. Shimomura, *ibid.*, **38**, 76 (1963).

(5) Different correlation times may be required for different pairs of nuclei if the molecule is not a rigid sphere. This may be quite important in the case of a rapidly rotating methyl group attached to a large organic molecule. If the resonance frequencies of A and B are the same, the contribution² to the relaxation time is 50% greater than that given in the formula.

(6) The original Overhauser effect (A. W. Overhauser, *Phys. Rev.*, **91**, 476 (1953)) is a manifestation of electronic-nuclear cross-relaxation. The NOE (I. Solomon, *ibid.*, **99**, 559 (1955); I. Solomon and N. Bloembergen, *J. Chem. Phys.*, **25**, 261 (1956)) is the nuclear-nuclear analog of the Overhauser effect. To our knowledge, the only example of an NOE in a strictly proton system is the very recent work of R. Kaiser (*ibid.*, **42**, 1838 (1965)) in which intermolecular cross-relaxation effects were studied. Two other phenomena which, however, are not dependent on cross-relaxation are known as "general NOE's," and are as follows: (a) a redistribution of the intensities of the lines of a proton on saturation of one line of a multiplet of another proton, or group of protons (W. A. Anderson and R. Freeman, *ibid.*, **37**, 85 (1962); R. Kaiser, *ibid.*, **39**, 2435 (1963)) (if cross-relaxation is important, an increase in the total intensity should also occur, but no example of this is known as yet); (b) a decrease in the intensity of a line of a proton when another line belonging to the same proton is saturated, where the splitting of the proton resonance is caused by spin coupling to a nucleus whose relaxation time is comparable to or shorter than that of the proton (the situation is more complex when several nuclei are involved) (K. Kuhlman and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **85**, 1010 (1963); F. A. L. Anet, *Tetrahedron Letters*, **46**, 3399 (1964)).

(7) J. D. Baldeschwieler and E. W. Randall, *Chem. Rev.*, **63**, 81 (1963).