

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_{b_0} 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_{b_0} 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_a 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_a , 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.

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(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

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

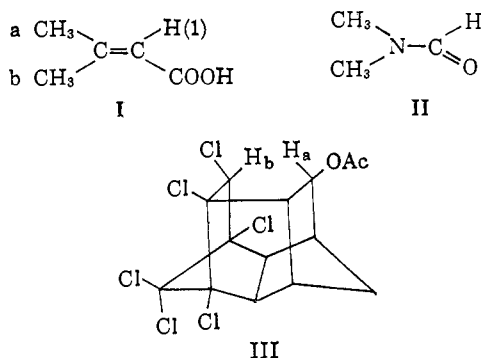
(4) R. J. C. Brown, H. S. Gutowsky, and K. Shimomura, *ibid.*, **38**, 76 (1963).

(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).

nuclei will be correspondingly reduced. Thus, it is possible to determine experimentally from NOE values which nuclei in a molecule are responsible for the relaxation of any particular nucleus. Also, since the relaxation is very strongly dependent on the distance between a pair of nuclei, studies of NOE's under the conditions described above should be of considerable stereochemical and conformational interest in organic chemistry.



As an illustration, we can take β,β -dimethylacrylic acid (I) and consider which protons are likely to contribute to the intramolecular relaxation of H(1). The carboxyl proton is not very close to H(1) since I probably exists largely as a cyclic hydrogen-bonded dimer. Of the two methyl groups, b is so much further from H(1) than is a that it should not contribute appreciably to the relaxation of H(1). Thus H(1) should be relaxed largely by the protons in a. Therefore, saturation of the protons in a should give a NOE for H(1), whereas saturation of the protons in b should do nothing to the intensity of the band of H(1). The problem is complicated by small long-range couplings of H(1) to both a and b. Complete saturation of either a or b protons can be achieved by double irradiation,⁷ but only under conditions that decoupling occurs. However, the decoupling is an extra phenomenon that does not affect integrated intensities provided that the spectrum is observed by means of a frequency sweep.⁸

The spectrum of I, as a 9% solution in benzene- d_6 , was observed by a frequency sweep⁸ method with 9% benzene in the solution as a reference line for a field-frequency lock.⁸ The methyl groups gave two well-separated doublets ($J = 1.3$ c.p.s. for both doublets); the upfield doublet (τ 8.58) can be assigned⁹ to the methyl group a and the downfield doublet (τ 8.03) to methyl group b. The band of H(1) was approximately a 1:6:15:20:15:6:1 septet (τ 4.34), owing to the virtually equal coupling to each of the methyl groups. Irradiation of either of the two methyl bands resulted in the band of H(1) changing to a 1:3:3:1 quartet, but, more important, the integrated intensity of the quartet was higher when the high-field methyl group was irradiated (relative intensity = 117 ± 1) than when the low-field methyl group was irradiated (relative intensity = 96 ± 1) or than when the irradiation frequency was offset from the methyl groups (relative intensity = 100 ± 2). Thus it is the upfield methyl group which is *cis* to H(1), in agreement with the

previous assignment⁹ based on chemical shifts. Saturation of H(1) did not result in any significant change in the intensity of either methyl group. Thus, the protons of a methyl group relax one another, and outside protons contribute little by comparison.

A similar experiment carried out on an 8% solution of dimethylformamide (II) in deuterium oxide gave the following results for the changes in integrated intensity of the formyl proton over that observed without double irradiation: $+18 \pm 1\%$ (low-field methyl saturated), $-2 \pm 1\%$ (high-field methyl saturated). Thus the low-field methyl is *cis* to the formyl hydrogen, in agreement with previous, but not entirely unambiguous, assignments.¹⁰

If a molecule has two protons which are particularly close together (*e.g.*, the half-cage acetate¹¹ (III)), then of course these two protons will relax one another very effectively. So effective is the dipolar interaction of H_a with H_b in III that an increase in the intensity of the band of either of these protons was observed when the other band was saturated, even when oxygen was not removed from the solution.

The present method seems to be of wide applicability, but care must be taken in interpreting small changes in intensities.¹² A differential effect, as observed for I and II, is unambiguous.

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(12) Overloading of the audio phase-sensitive detector can easily occur when an intense line is irradiated, but such effects can be overcome by (a) using a more dilute sample, (b) decreasing the input to the detector, or (c) removing the unwanted frequency by filtering. In any case, spurious effects generally cause a decrease in the intensity of a band and thus cannot be confused with a NOE. The present experiments were carried out at 60 Mc.p.s. on a modified⁵ Varian HR60 spectrometer.

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A New Type of Cyclic Transition Metal Complex, $[\text{Ni}(\text{SC}_2\text{H}_5)_2]_6$

Sir:

We wish to report the structure and stereochemistry of a nickel mercaptide hexamer which has been definitely established by a single-crystal X-ray analysis as the first representative of a new type of transition metal cluster.

Nickel mercaptides have previously been reported as *insoluble* high polymers,^{1,2} but through the use of organotin-sulfur compounds which react with metal halides to form metal mercaptides by cleavage of the Sn-S bonds,³ we have prepared in 53% yield a *soluble*, diamagnetic, purplish black crystalline product from the reaction of nickel(II) chloride and bis(ethylthio)-dimethyltin in alcohol. Molecular weight measure-

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