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METHYLENE PROTON COUPLING CONSTANT VARIATIONS IN 2-HALOETHANOLS AS A FUNCTION OF INTRAMOLECULAR HYDROGEN BONDING

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Recent pmr studies of alcohols have dealt with coupling constants involving the hydroxyl proton and the protons of an adjacent methylene or methine group.[1] One exception to this involved examination[2] of the vicinal methylene proton coupling constant variations of several alkyl-substituted phenylethanediols and propanediols in which it was found that an increase in size of the alkyl substituent resulted in increased coupling constants in the erythro isomers and diminished coupling constants in the threo isomers. These results were rationalized using conformational analysis on the basis of a Karplus-type[3] relationship between the observed vicinal methylene coupling constant (J_{HCCH}) and the corresponding dihedral angle.

It was our opinion that factors other than steric effects could in appropriate molecules cause changes in such dihedral angles and hence J_{HCCH}. One such factor to be considered was that of intramolecular hydrogen bonding. Krueger and Mettee[4] produced some evidence for intramolecular hydrogen bonding in CCl_4 solutions of the 2-haloethanols, but in other instances ir evidence for such an effect has been disputed[5]. Observation of a change in coupling constant with dilution in the 2-haloethanols and similar molecules would thus offer a novel method of studying intramolecular hydrogen bonding.

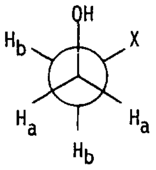
Table I indicates the observation of the above described effect, namely, a substantial decrease in J_{HCCH} of each 2-haloethanol over a dilution range of 100 to 0.1 mole percent. In order to verify that the apparent coupling constant changes were not the result of second order effects due to chemical shift variations during the dilution, computer simulated spectra[6] which reproduced the experimentally observed spectra in every detail were obtained using these data.

TABLE I

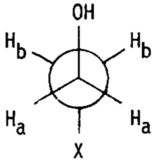
J_{HCCH} VARIATIONS (Hz) FOR THE ETHANOLS (XCH_2CH_2OH) AS A FUNCTION OF CONCENTRATION IN CCl_4[6]

X	Concentration (Mole %)				ΔJ_{HCCH}
	100	10	1.0	0.1	
I	6.40	6.40	6.10	6.00	-0.40
Br	5.85	5.80	5.50	5.20	-0.65
Cl	5.50	5.40	5.10	5.00	-0.50
F	4.30	4.30	4.20	4.00	-0.30
H	7.00	6.95	7.05	6.95	-0.05

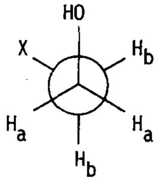
From a consideration of the primary rotamers 1a-c of a 2-haloethanol molecule, it becomes apparent that the vicinal methylene protons of mirror image rotamers 1a and 1c occupy one *trans* and three *gauche* relationships whereas rotamer 1b consists of two *trans* and two *gauche* methylene proton relationships. Since from the Karplus relationship $J_{trans} > J_{gauche}$ for vicinal methylene protons, the predicted order for the magnitude of the vicinal methylene proton coupling constants for conformers 1a-c would be $J_{HCCH\text{-}1b} > J_{HCCH\text{-}1a} = J_{HCCH\text{-}1c}$. Dilution of 2-haloethanol with an inert solvent such as CCl_4 should decrease the contribution of intermolecular hydrogen bonding and increase the contribution of intramolecular hydrogen bonding, resulting in an increase in the population of rotamers 1a and 1c relative to 1b, and hence a net decrease in J_{HCCH}.



1a



1b



1c

If the observed effect were a manifestation of intramolecular hydrogen bonding, a decrease in J_{HCCH} upon dilution in CCl_4 should not be observed for ethanol, since no mode exists for intramolecular interaction for this alcohol. The data for ethanol in Table I indicates that no J_{HCCH} variation outside the range of error for measurement of J_{HCCH} exists for ethanol upon dilution in CCl_4.

From a similar argument a decrease in J_{HCCH} would not be predicted upon dilution in DMSO^{d-6}. Since DMSO^{d-6} is a strong hydrogen bonding receptor, solvent-solute interactions would be expected to dominate intramolecular interactions[1] and an increase in the relative population of rotamer 1b at the expense of rotamers 1a and 1c due to the loss of intramolecular hydrogen bonding as well as a direct increase in the population of 1b due to steric interaction. Indeed the data in Table II indicates a slight but significant increase in J_{HCCH} for the 2-haloethanols upon dilution in DMSO^{d-6} suggesting that the population of all three rotamers is altered to the extent that a slightly larger net population of rotamer 1b results in the dilute solution in DMSO^{d-6} relative to neat alcohol.

TABLE II

J_{HCCH} VARIATIONS (Hz) FOR THE 2-HALOETHANOLS (X-CH_2CH_2OH) AS A FUNCTION OF CONCENTRATION IN DMSO^{d-6} [6]

	Concentration (Mole %)			
X	100	10	1.0	ΔJ_{HCCH}
I	6.40	6.60	6.60	+0.20
Br	5.85	5.90	6.10	+0.25
Cl	5.50	5.50	5.60	+0.10
F	4.30	4.30	4.40	+0.10

This study to our knowledge represents the first example of the observation of vicinal methylene proton coupling constant changes as an indicator of intramolecular hydrogen bonding. The effects of temperature and the effects of the various electronic and steric factors peculiar to the particular halogen atom under consideration will be the subject of continued interest in this field of study.

Acknowledgments

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References

1. cf. D. W. Slocum and C. A. Jennings, Tetrahedron Letters, preceding paper of this issue, and references therein.
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3. a) M. Karplus, J. Chem. Phys., 30, 11 (1959).
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   b) P. J. Krueger and H. D. Mettee, ibid, 42, 241 (1963).
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6. The nmr spectra were obtained on a Varian HA-100 Spectrometer at a probe temperature of 28°. Line frequencies were measured by the customary side-band technique using TMS as an internal standard. The coupling constants were obtained by averaging the data from at least two determinations at each concentration with an estimated precision of +0.05 Hz. The spectra of the haloethanols over the same concentration range were also obtained on a Varian HR-220 Spectrometer operating at 23° and nearly identical coupling constant values were obtained. The 100 Hz spectra of the 100 mole percent and 0.1 mole percent CCl$_4$ solutions were simulated using the LAOCOON III program to give traces superimposable on the experimentally determined spectra.

   The alcohols and the CCl$_4$ were dried over anhydrous MgSO$_4$ and anhydrous Na$_2$CO$_3$ and then distilled at ambient or reduced pressure.

   DMSO^{d-6} (Stohler) was used without further purification. Although hydroxyl proton multiplicity was obtainable for all the alcohols used in this study hydroxyl coupling could be eliminated by the addition of traces of HCl gas.