Tetrahedron. Vol. 25, pp. 1261 to 1264. Pergamon Press 1969. Printed in Great Britain

THE EFFECT OF TEMPERATURE AND SOLVENT UPON GEMINAL PROTON–DEUTERON SPIN–SPIN SPLITTING

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(*Received in USA* 8 *May* 1968; *Received in the UK for publication* 15 *October* 1968)

Abstract—For a series of eight deuterated organic molecules it was shown that geminal proton–deuteron spin–spin splitting is both temperature and solvent dependent. Lowering of temperature leads to decoupling of the nuclei. This phenomenon is discussed in terms of the effect of molecular motion upon the efficiency of quadrupolar relaxation. Other dominant factors are molecular shape, intermolecular forces and solvent polarity.

THE temperature dependence of spin–spin splitting between a nucleus X with spin 1, possessing a quadrupole moment, and a nucleus Y with spin $\frac{1}{2}$ has already been demonstrated for the pairs ^{14}N–^{1}H,[1] and ^{14}N–^{19}F.[2] In both instances coalescence of the triplet pattern for the resonance of the nucleus Y was observed when the temperature was *lowered*. This phenomenon was attributed to more effective quadrupolar relaxation of nucleus X at low temperature.[3,4]

This behaviour is also expected for ^{2}H–^{1}H (D—H) coupling, and we wish to report observation of the disappearance of triplet structures in the resonances of protons geminal to one deutron (Table 1). At 54°, all resonances of such protons, and also of those geminal to two deuterons, showed sharp splittings attributable to D—H coupling. Lowering the temperature caused a progressive collapse of the multiplets (cf. Fig. 1) over a relatively narrow temperature range, i.e. $-6°$ to $-27°$ for compounds I–VII. The changes in line shapes† closely resemble those predicted theoretically.[5] Since addition of acid or base did not at all affect the line shapes, an exchange process is ruled out as a cause of coalescence. For molecules with deuterated Me groups (VIII and IX) the splitting patterns remained unchanged down to $-40°$, the lowest temperature attainable with the equipment on hand.

This difference in behaviour may be explained in terms of the rotational motions which these molecules undergo and which affect the quadrupolar relaxation.[3] The spin-lattice relaxation time T_1, when predominantly of quadrupolar origin, can be expressed as

$$T_1^{-1} \propto (e^2qQ)^2\,\tau_q(t), \quad \text{with} \quad \tau_q(t) \simeq \tau_q^{\circ}\, e^{E_a/kT}.$$

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[†] That no loss of resolution occurred at lower temperatures was indicated by the sharpness of other absorption peaks in the spectra.

TABLE 1[a]. PROTON–DEUTERON GEMINAL COUPLING CONSTANTS $2J_{HD}$ AND COALESCENCE TEMPERATURES t_c

Compound[b]	$^2J_{HD}$ (Hz)[c]	t_c (°C)	$^3J_{HH}$ (Hz)[d]
I. Me_2CH—CHDOH	1·5	−27	6·0
II. Me \\ CH—CHDOH / Et	1·4	−6	5·2
III. Me_3C—CHDOH	1·6	−27	—
IV. Ph_3SiCH_2—CHDOH	1·7	−20	—
V. Ph—CHD \\ CHOH*threo*) / Ph	1·8	−6	9·0[e]
VI. Ph—CHD \\ CHOH(*erythro*) / Ph	1·8	−6	4·9[e]
VII. Me \\ CH—CHD—OCONHPh / Et	1·5	−10	6·0
VIII. CHD_2—NO_2	1·9	[f]	—
IX CH_2D—Ph	2·2	[f]	—

[a] Spectra were determined at 60 MHz for 0·15M in $CDCl_3$ solns on a Varian A-60 spectrometer. J's are accurate to 0·05 Hz, and temps to 1°.

[b] $LiAlD_4$ reduction was used in the preparation of compounds 1–IV (from the corresponding aldehydes), and V and VI (from *cis*- and *trans*-stilbene oxide). VIII was prepared by decarboxylation of CH_2NO_2COOH in D_2O. IX was made by the reaction of $C_6H_5CH_2MgCl$ with D_2O.

[c] Measured at 54°. No further separation of peaks was observed at higher temps.

[d] These are coupling constants between protons in the —CH—CHD— portions of the molecules.

[e] The relative magnitudes of these J's suggest that the vicinal —CH— protons are *trans* to each other in threo- and *gauche* in the *erythro*-isomer.

[f] Spectrum remained unchanged between +54 and −40°.

τ_q is a composite of correlation times τ_c for molecular reorientations which would lengthen with decreasing temperature. Thus the longer τ_q is, the shorter will be T_1 and the lifetime of a quadrupolar nucleus X in a given spin state. If $1/\tau$ becomes of the order of the spin coupling constant J_{XY}, the spin coupling patterns disappear,[5] that is, "spin decoupling" takes place.

For deuterium-substituted methanes which are spherical molecules and undergo facile overall reorientation, including tumbling about the C—D bond(s), the presence of D—H splittings was reported,[6,7] these measurements were carried out at room temperature in carbon tetrachloride solution. Molecules VIII and IX have a relatively regular shape and are thus expected to undergo frequent reorientations at low temperature; this is borne out experimentally through the persistence of the splitting patterns down to −40°. In these cases one must also consider the obviously facile intramolecular rotation of the deutero-methyl group. However, molecules I–VII have relatively irregular shapes, and their tumbling will be more restricted than that of VIII and IX.

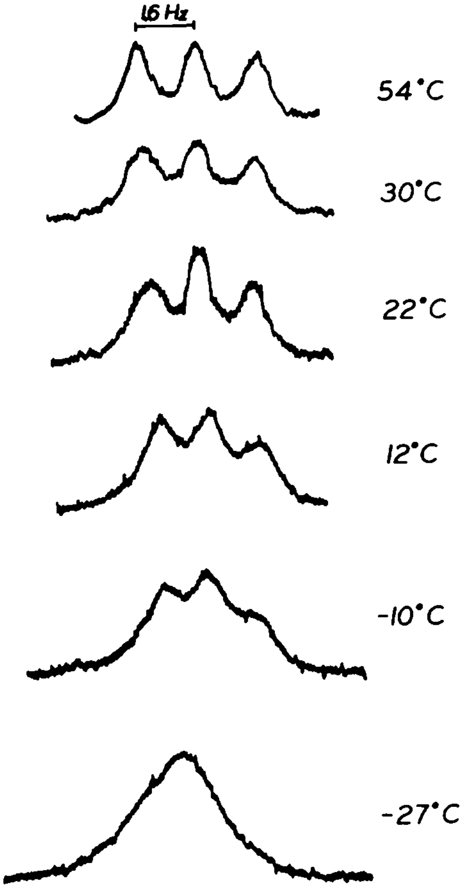

FIG. 1 Spin–spin coupling behaviour with decreasing temperature for the CHD group of $Me_3C—CHDOH$ (III).

Finally, the field-gradient at the deuterium nucleus should also be affected by the electronegativity of neighboring substituents.

One would further predict that in addition to changes of τ_q due to thermal motion the same effect would result from dilution of the H-bonded solute with a non polar solvent. Molecular movement would be freer and the situation at higher temperatures would be approximated, i.e. $1/\tau \ll J_{HD}$.

At room temperature $Me_2CHCHDOH$ as a pure liquid shows a simple doublet for CH—CH—D—OH. Dilution with carbon tetrachloride, carbondisulfide, or chloroform, caused a gradual transformation of the doublet into a doublet of triplets. The concentration at which this change occurred varied from solvent to solvent. For example, with pyridine and trifluoroacetic acid the change from doublet to doublet of triplets occurred at concentrations as low as 5% of solvent while with carbon tetrachloride, no change in the simple doublet was observed until 75% by volume of solvent was added. No change in the doublet CH—$\underline{\text{CHD}}$—OH was observed upon dilution to the lowest observable concentrations with either cyclohexane or benzene.

Clearly the strongest force inhibiting rapid molecular motion for the pure alcohol is the presence of intermolecular H-bonding. Solvents such as CCl_4, CS_2 and $CHCl_3$ act to break up this bonding by forming by forming solvent solute molecules. The fact that much lower percent concentrations of C_5H_5N and CF_3COOH bring about the doublet to doublet of triplet change is not readily explained. The effect is not simply one of acid or base catalysis since other acids and bases at comparable concentrations do not cause the same change.

These decoupling effects may find application in spectral analysis. Although the spectra of proton-containing molecules can often be simplified by deuterium substitution, line broadenings and/or splittings due to D—H coupling sometimes remain. Such "residual" D—H coupling may, in favorable cases, be removed by a modest decrease in temperature.

Acknowledgements—We are grateful to Dr. J. J. Eisch (Catholic University of America) for supplying compound IV, and to Dr. W. B. Moniz (U.S. Naval Research Laboratory) and to Dr. G. Fraenkel (Ohio State University) for helpful criticism. Fruitful discussion with Dr. J.-M. Lehn, Institute of Chemistry, Strasbourg, and Dr. I. O. Sutherland, University of Sheffield, are gratefully acknowledged. The phenomenon reported in this paper has been observed by both these workers.

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