A CONCENTRATION EFFECT ON THE MAGNETIC NONEQUIVALENCE

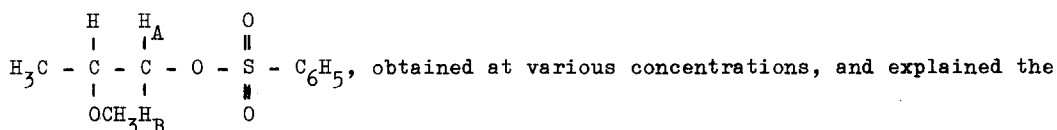OF THE BENZYLIC PROTONS OF 1-PHENYLPROPANOL-2

by

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It is known that magnetic nonequivalence of protons in NMR, with respect to chemical

shift (1, 2) and coupling constants (3, 4) may show a concentration dependence.

Csckvary and Gagnaire (2) analysed the NMR spectrum of

$$H_3C - \underset{\underset{OCH_3}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{H_B}{|}}{\overset{\overset{H_A}{|}}{C}} - O - \underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}} - C_6H_5,$$ obtained at various concentrations, and explained the

concentration dependence of the magnetic nonequivalence of the protons H_A and H_B by a

variation of solute-solute interaction. Jackman and Bowman (5) found that the methylene

protons of 2-butanol are magnetically nonequivalent and that the extent of nonequivalen-

ce decreases on dilution. In this connection we want to report a strong concentration

dependence of the magnetic nonequivalence of the benzylic protons of 3,3,3-trideutero-

-1-phenylpropanol-2. The spectrum was recorded on a Varian A60 spectrometer at various

concentrations. By using the method of sub-spectral analysis (6), estimated values of

the coupling constants and chemical shifts of the ABX system were obtained. These

estimates were used as input parameters for the modified computer programs NMREN and

NMRIT[*], which generated the coupling constants and chemical shifts given in table 1.

Table 1. Spectral parameters (in Hz) obtained for 3,3,3-trideutero-
-1-phenylpropanol-2 at different concentrations.

mole fraction in CCl_4	ν_X [a]	ν_A	ν_B	$\nu_A-\nu_B$	J_{AB}	J_{AX}	J_{BX}
.49	231.4	162.6	153.4	9.2	13.3	5.8	6.9
.42	230.9	162.2	153.5	8.7	13.5	5.6	7.0
.37	231.2	161.8	153.7	8.1	13.5	5.5	7.0
.32	231.1	161.2	154.0	7.3	13.6	5.3	7.2
.29	230.9	160.8	153.9	6.9	13.3	5.8	6.9
.27	230.4	160.1	153.9	6.1	13.4	5.6	7.3
.21	230.6	159.5	154.9	4.6	13.5	5.7	7.0

[a] All chemical shifts are relative to internal TMS.

The nonequivalence of the benzylic protons may be caused by a relatively slow interconversion of the various conformations by rotation round the $C_\alpha-C_\beta$ bond. The effect of the molecular asymmetry however, may be also observable at high interconversion rates (7). If the spectral changes were mainly due to a change in population of the molecular conformations, one would expect both the observed (average) coupling constants and the chemical shifts to change on dilution. The coupling constants however, do not vary, although $\nu_A-\nu_B$ differs by a factor of two over the same concentration range. Therefore, the nonequivalence of the benzylic protons will be mainly due to the molecular asymmetry. The variation of the magnitude of this effect is probably caused by the concentration dependence of the molecular association.

References.

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