Intramolecular Interaction between Hydroxyl Group and π-Electrons. XI[1]. *High Resolution Proton Magnetic Resonance Spectra of Tertiary Alcohols Having π-Electrons*

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It has been shown through infrared studies[1] that the intramolecular interaction between hydroxyl groups and π-electrons shifts the O–H stretching vibration (ν_{O-H}) to lower frequencies in comparison with an ordinary hydrogn bonding. In connection with recent high resolution nuclear magnetic resonance spectroscopy which has successfully been applied to the study of hydrogen bonding[2], variation of the proton resonance of some alcohols with concentration changes in carbon tetrachloride was studied in order to detect any effect of the aforementioned interaction to the NMR spectra, which must give rise to a different magnetic shielding of hydroxylic proton of the interacting form from that of the free one.

A Varian model V-4300 high resolution NMR spectrometer was operated at 56.4 Mc/sec. Samples include *tert*-amyl alcohol, allyldimethylcarbinol, benzyldimethylcarbinol and tribenzylcarbinol. Preparations and purities of the samples are specified in the preceding paper[1]. Measurements were carried out at 20°C, the samples being dissolved in a given amount of carbon tetrachloride and sealed in glass tubes with the outer diameter of 5 mm. The magnetic field was swept twice in both decreasing and increasing directions and the average of the records of both directions of the sweep taken. The calibration of the sweep rate was made by recording the spectrum of toluene and by reading the separation of the two peaks as 4.90 ppm[3]. The chemical shift (δ) was referred to water as an external standard and corrected for bulk diamagnetic susceptibilities of *tert*-amyl alcohol, allyldimethylcarbinol and benzyldimethylcarbinol, $-\chi_v \times 10^6$ being 0.644, 0.585 and 0.696[4], respectively.

While the absorption lines assigned to hydrogen attached to carbon atom shifted less than 0.5 ppm from thet pure liquid to the sample at infinite dilution, that of hydroxyl proton showed a marked concentration dependence as shown in Figs. 1 and 2. On dilution, the chemical shifts gradually moved to higher magnetic field and at about 0.02 mol. fraction a reversal of the curvature was observed with three carbinols. This phenomenon is understood to be characteristic of a system consisting of monomer, dimer and high polymer[2a]. Tribenzylcarbinol showed, unlike these, no association pattern within the measured concentration range. The curves were extrapolated to infinite dilution and the chemical shifts of pure monomers obtained. Under these conditions, *tert*-amyl alcohol is quite free from association and tribenzylcarbinol possesses only

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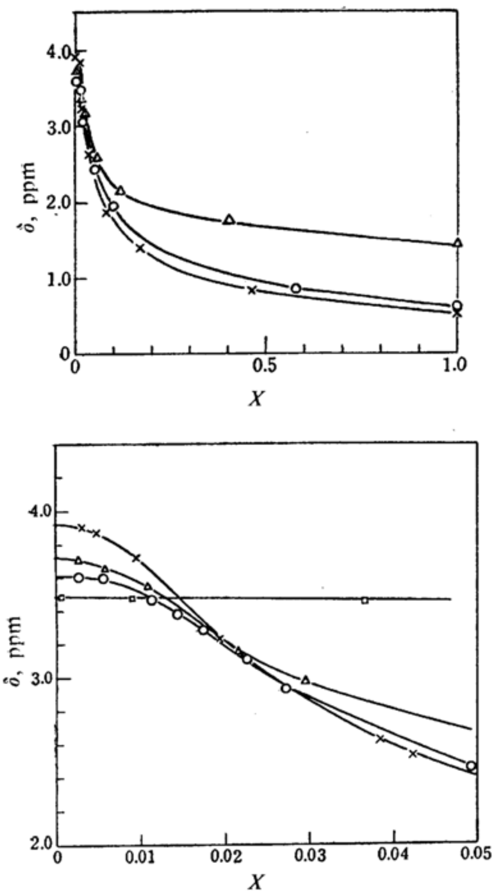
[1] Part X: M. Ōki and H. Iwamura, This Bulletin, 33, 1600 (1600); see also the foregoing papers.

[2] a) E. D. Becker and U. Liddel, *J. Mol. Spectroscopy*, 2, 1 (1958), and others cited in the literature. b) The NMR study of the interaction pertaining to the π-electron system was presented by N. Nakagawa at the Symposium on Structural Chemistry, the Chemical Society of Japan, Tokyo, September, 1959, phenylacetylene being the example.

[3] N. F. Chamberlain, *Anal. Chem.*, 31, 56 (1959).

[4] Measurements were kindly made by Mr. Minoru Kinoshita, to whom the authors, thanks are due.



Figs. 1 and 2. Chemical shifts of the OH proton resonance, δ in ppm, vs. mole fraction of alcohols, X.

I. *tert*-Amyl alcohol -×-×-
II. Allyldimethylcarbinol -○-○-
III. Benzyldimethylcarbinol -△-△-
IV. Tribenzylcarbinol -□-□-

the hydroxyl group which is intramolecularly interacting with π-electrons of the benzene nucleus, while allyldimethylcarbinol and benzyldimethylcarbinol are in equilibrium mixtures of free and interacting hydroxyl groups. The composition of the equilibrium estimated from the integrated intensities of infrared absorption is added to the last column in Table I.

TABLE I. CHEMICAL SHIFTS AND THE COMPOSITION AT INFINITE DILUTION IN CARBON TETRACHLORIDE

	$\delta_{X=0}$ ppm	$\Delta\delta$ ppm	Mole fraction of the interacting form
tert-Amyl alcohol	3.92	0	0
Allyldimethylcarbinol	3.61	0.31	0.37
Benzyldimethylcarbinol	3.72	0.20	0.43
Tribenzylcarbinol	3.49	0.43	1

In contrast with the infrared spectra which show separate ν_{O-H} bands, the NMR spectra of hydroxyl proton are absolutely single. This must be attributed to the short lifetime and rapid exchange of free and interacting forms of these carbinols. The single proton resonance is therefore observed at the field corresponding to the average shielding of the two forms. When δ value of *tert*-amyl alcohol is taken as the chemical shift of purely free tertiary alcohols and that of tribenzylcarbinol as that interacting form, the composition of the equilibrium of benzyldimethylcarbinol may be computed from its δ value. The $\Delta\delta$ (0.20) of benzyldimethylcarbinol is divided by 0.43 and the quotient (0.47 mole fraction) is found to be in good agreement with the infrared datum (0.43). Unfortunately, the true chemical shift of hydroxyl proton taking part in the interaction with π-electrons of ethylenic linkage can not be determined because of lack of the sample which possesses only the interacting form. Assuming that the observed $\delta_{X=0}$ value of allyldimethylcarbinol is a weighted mean between free and interacting forms, the δ value of the interacting form can be estimated with use of composition datum (0.37 mole fraction) obtained from the infrared spectra. Thus $\Delta\delta$ is 0.31/0.37 or 0.838 ppm, δ being 3.08 ppm. Therefore, it may be said that, with the intramolecular interaction of the hydroxyl group with π-electrons of ethylenic linkage, the magnetic shielding of tertiary hydroxyl proton becomes less and δ value shifts to the lower magnetic field by less than one ppm. The chemical shift of the hydroxyl proton having interaction with π-electrons of the benzene nucleus is 0.41 ppm higher than this value. The ring current diamagnetic effect must be operative in the latter case. More precise evaluation is in progress in the hope of obtaining the knowledge about the geometry of the interacting form.

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