Intramolecular Interaction between Hydroxyl Group and π-Electrons. XVIII[1]. Proton Magnetic Resonance Spectra of Aryldimethylcarbinols and Related Compounds

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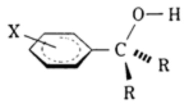
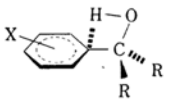
It has been recognized that aryldimethylcarbinols are the examples which have the intramolecular interaction between the hydroxyl group and the π-electrons (II). In a previous paper[2] the effect of the substituents on the equilibrium between I and II was investigated by infrared spectroscopy. In short, the ratios of the two absorption intensities, A_{II}/A_{I}, which may be regarded to express the equilibrium constant, K, are in linear relation with the Hammett's sigma constants with the negative inclination of $\rho = -0.358$ and the phenomenon has been attributed to the varied π-electron density on the benzene ring as a proton acceptor.



I



II

Recent exploitation of NMR spectroscopy as a tool of studying the hydrogen bonding[3] and of detecting the weaker interaction involving hydrogen atom prompted the present authors to study the above system by this newer method.

The chemical shifts of OH proton should differ greatly in I and II. Since the population of the molecular species depends remarkably on the ring substituents, the apparent chemical shifts of OH proton, which will appear singly at the average position between the signals characteristic of I and II, is expected to vary with the substituents.

Owing to the associative nature of the aryldimethylcarbinols, the data obtainable at the most dilute solution (ca. 10^{-2} mol./l.) with use of a nowadays available spectrometer have the contribution of the associated species and cannot reflect directly the status of the aforementioned equilibrium of monomeric nature. In these connections, measurement must be carried out over a range of finite concentration to describe the nature of the association and the data obtained was extrapolated to those at infinite dilution with which the discussion of the equilibrium, $\mathrm{I} \rightleftharpoons \mathrm{II}$, was attempted.

Experimental

Spectral Measurements.—NMR spectra were obtained by a Varian DP-60 high resolution NMR spectrometer at 60 Mc./sec. The samples were dissolved to a given concentration in carbon tetrachloride and sealed in glass tubes with outside diameter of 5 mm., the chemical shifts in p. p. m. being referred to cyclohexane as an internal standard. The side-band technique was employed to measure the precise chemical shifts[4].

Materials.—Preparation and purity of the compounds have been described in the previous paper[2].

Results and Discussion

The assignments of the NMR signals of the aryldimethylcarbinols which consist of a methyl signal with the intensity of six protons, an OH signal, multiplet signals due to the ring protons, and signals due to the ring substituents, if any, are straightforward. Out of these only the OH proton signal moves significantly with the varying concentration. In Figs. 1 and 2 are illustrated the displacement, due to the change in concentration, of the chemical shift of the OH proton of dimethylphenylcarbinol. It is well known that in a solution of associable solute, there is a definite composition at a given concentration between the several species possible, e. g., monomer, dimer, trimer, and the higher polymers. Although they have different kinds of the hydroxyl group and thus show different ν_{O-H}'s at the same time in the infrared absorption, NMR spectrum of the system shows usually a single OH proton signal, owing to the rapid exchange between, and consequent averaging of, the protons of various kinds. That is, the apparent chemical shift (δ^{a}) of the OH proton at a given concentration can be expressed as follows, where

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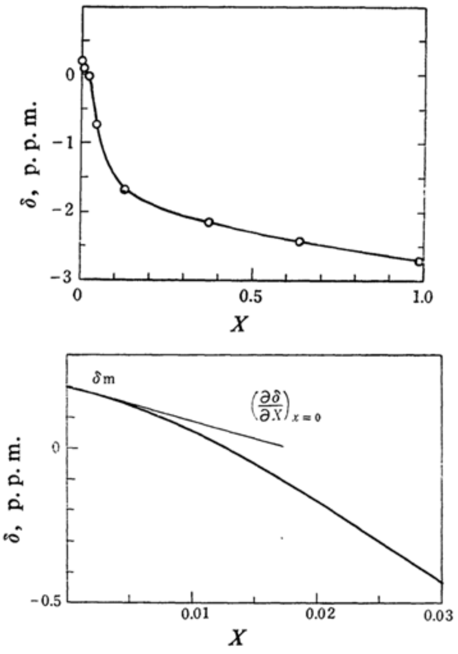
[1] Part XVII: M. Ōki and H. Iwamura, This Bulletin, 35, 1744 (1962).

[2] Part XVI: M. Ōki and H. Iwamura, ibid., 35, 1552 (1962).

[3] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., Inc., New York, N. Y. (1959), p. 400.

[4] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, 19, 1608 (1951).



Figs. 1 and 2. Dilution shifts of OH proton signal, δ (in p. p. m. from cyclohexane) versus mole fraction (X) of dimethylphenylcarbinol.

δ_i and x_i represent the chemical shift characteristic of, and the mole fraction of, the i'th

$$\delta^{a}=\sum_i \delta_i x_i \qquad \sum_i x_i=1 \tag{1}$$

species, respectively, and the summation is made over the whole species present. x_i's are related each other by the respective equilibrium constant, K_{ij}. Since the change in the total concentration (X) accompanies the redistribution between x_i's, δ^{a} becomes dependent on the concentration.

$$K_{ij}=\frac{(x_j)^n}{(x_i)^m} \tag{2}$$

Although it is almost impossible to analyze the formula 1 over a whole range of concentration, it may be possible to derive Eq. 3 as an approximation in the lower concentration region ($X \leqq 0.02$) where the contribution of only the first two terms, that is, monomer and dimer, may be regarded to be major. Here δ_m and δ_d represent the chemical shifts of the OH protons characteristic of monomer and dimer,

$$\delta^{a}=\delta_m x_m+\delta_d x_d \tag{3}$$ [5]

respectively. K stands for the equilibrium constant of dimerization (Eq. 4). Equation 5 is obtained by differentiating Eq. 3 and taking the limit. Since the left side of Eq. 5 is obtainable from the limiting slope of the δ

$$K=\frac{x_d}{x_m^{\,2}} \tag{4}$$

$$\left(\frac{\partial\delta^{a}}{\partial X}\right)_{x=0}=2K(\delta_d-\delta_m) \tag{5}$$

versus X curve in each carbinol (Fig. 2), it is now possible to derive either K or $\delta_d-\delta_m$, if the data of the other are available. It was the authors' choice to determine $\delta_m-\delta_d$ with use the value of K which is available independently from the infrared spectroscopy. To this purpose, the variation of ε at the absorption maximum of the monomeric ν_{O-H}, 3606 cm^{-1}, with concentration, was measured. Supposing that this ε_m represents the apparent absorption coefficient of the band due only to monomer, and that dimer is cyclic, the limiting slope of the ε_m versus concentration curve is found to be related to the equilibrium constant for dimer formation by Eq. 6;

$$\left(\frac{\partial\varepsilon_m}{\partial C}\right)_{c=0}=-2K_c\,\varepsilon_m{}^{0} \tag{6}$$ [6]

where $\varepsilon_m{}^0$ stands for ε_m at infinite dilution. The equilibrium constant expressed in terms of mole fraction (K_x) can be related to K_c by $K_x=K_c\times 10$ for the carbon tetrachloride solution.

In Table I are listed the OH proton chemical shift at infinite dilution, δ_m, the limiting slope of the δ versus X curve, $-\left(\frac{\partial\delta^{a}}{\partial X}\right)_{x=0}$, the equilibrium constant for dimer formation, K, and the difference in the chemical shift between monomer and dimer, $\delta_m-\delta_d$.

As shown in Fig. 3, K and $\delta_m-\delta_d$ are roughly in linear relation with the Hammett's sigma constants. They are also proportional to each other. Strictly speaking, the linearity with a positive slope which reign over the substituents of positive sigma value does not hold true for those of negative sigma constant. It is naturally expected that any ring substitution produces counteracting effect on dimerization. Those substituents which strengthen the proton donor ability of the hydroxyl group are weakening its proton accepting power at the same time. The above finding indicates that, while the electron-withdrawing substituents strengthen the dimerization in effect, the action is just balanced in the case of the electron-donating substituents. Since $\delta_m-\delta_d$ may be regarded to correspond to the strength ($-\Delta E$) of the association[7], the linearity between $\delta_m-\delta_d$ and

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[5] E. D. Becker, U. Liddel and J. N. Shoolery, *J. Mol. Spectroscopy*, **2**, 1 (1958).

[6] U. Liddel and E. D. Becker, *Spectrochim. Acta*, **10**, 70 (1957).

[7] L. W. Reeves, E. A. Allan and K. O. Strømme, *Can. J. Chem.*, **38**, 1249 (1960).

K is satisfying the relation, $-RT \ln K = \Delta E - T\Delta S$, where no anomaly in ΔS term is involved. This implies that the dimers of the aryldimethylcarbinols must have a similar structure.

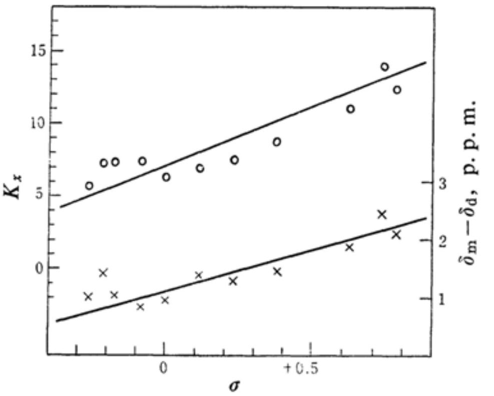


Fig. 3. The effect of the nuclear substitution on the dimer formation of aryldimethylcarbinols; the circle and the cross representing the equilibrium constant K_x and dimerization shift, $\delta_m - \delta_d$, respectively.

TABLE I. THE CHEMICAL SHIFTS OF OH PROTON AT INFINITE DILUTION IN CARBON TETRACHLORIDE AND THE DATA FOR THE DIMER FORMATION OF ARYLDIMETHYLCARBINOLS AND RELATED COMPOUNDS

$X\text{-}C_6H_4C(CH_3)_2OH$

X	δ_m p.p.m.	$-\left(\frac{\partial \delta^a}{\partial X}\right)_{x=0}$	K	$\delta_m - \delta_d$ p.p.m.
p-NO_2	0.26	54	12.5	2.17
m-NO_2	0.25	68	14.0	2.43
p-CO_2CH_3	0.24	45	11.2	2.01
m-Cl	0.28	25	8.7	1.44
p-Cl	0.23	20	7.4	1.35
m-MeO	0.26	19	6.9	1.38
H	0.20	12.7	6.5	0.98
m-CH_3	0.28	13	7.2	0.90
p-CH_3	0.29	14	7.2	0.98
m-Me_2N	0.23	20	7.3	1.38
p-MeO	0.33	12	5.6	1.09
p-$PhCH_2O$	0.29	15	6.2	1.21
Diethylphenylcarbinol	0.25	7	3.6	0.97
1-Methyl-1, 2, 3, 4-tetrahydro-1-naphthol	0.30	19	9.3	1.02
1-Phenylcyclohexanol	0.33	10	5.9	0.85

δ_m obtained by extrapolating δ versus X curve to the infinite dilution is only concerned with the monomeric hydroxyl proton. Since aryldimethylcarbinols have the equilibrium $I \rightleftharpoons II$ at this state, δ_m may be put as follows.

$$\delta_m = \delta_I x_I + \delta_{II} x_{II} \qquad (7)$$

The previous finding by infrared spectroscopy[2)] that x_{II}/x_I ranges from 0.85 (for p-nitrophenyldimethylcarbinol) to 4.0 (for 1-phenylcyclohexanol) may make one to expect that δ_m would vary considerably with different substituents according to Eq. 7. However, as shown in Fig. 4, it is not the case and δ_m's are almost independent of the substituents.

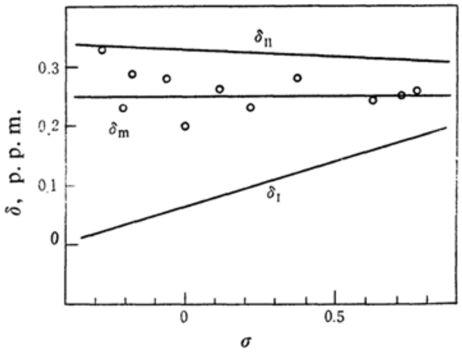
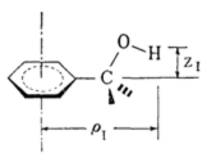
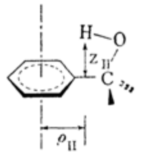


Fig. 4. The effect of the ring substituents on the monomeric OH proton shifts in aryldimethylcarbinols.

As regards the conformation of isomers, I and II, now assume that the plane made by C_α-O-H group will be situated perpendicularly to that of the benzene ring[8)] and that the bonds, Ar-C_α and O-H, will be disposed around the C_α-O bond to be "trans" and "cis", for I and II, respectively. Then through the diamagnetic anisotropy of the benzene ring with the π-current of $J = \frac{3e^2H_o}{2\pi mc}$ [9)], the hydroxyl proton in I will be deshielded by 0.234 p. p. m., while that of II will suffer from diamagnetic shift of 0.035 p. p. m., with respect to the hydroxyl proton indifferent to the ring current. A measure of $\delta_{II} - \delta_I = 0.27$ p. p. m. has now been obtained.



I′



II′

In order to see whether the above postulate on the conformations I and II be valid, δ_I and δ_{II} were actually determined, by solving Eq. 7 and $\delta_{II} - \delta_I = 0.27$ simultaneously, for the selected examples listed in Table II in which the π-electron density on the benzene ring may be considered to be equivalent. Fairly

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8) J. C. Evans, *Spectrochim. Acta*, **17**, 129 (1961).

9) E. C. Johnson, Jr. and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

good constancy of the calculated values of δ_I and δ_{II} obtained suggests the adequacy of the above conformations, I and II.

If δ_I and δ_{II} were constant over a whole range of the aryldimethylcarbinols, δ_m should have decreased with the increasing sigma value, because x_{II}/x_I has been shown to decrease in this order. The observed apparent indifference irrespective of the substituents must be ascribed to the change in the π-ring current. The reduced π-current density caused by the substitution with electron-withdrawing substituent will bring about the diminution of the ring current effect for both hydroxyl groups in I and II. However, the degree of this suffering may be seven times (derived from 0.234/0.035) greater in I than in II. That is, the absolute value of the positive slope of δ_I must be seven times greater than that of the negative inclination in δ_{II}, when they are plotted to the sigma constants, as illustrated in Fig. 4. Therefore, δ_m does not necessarily decrease proportionally to the decrease in x_{II}/x_I when the electron-withdrawing substituent is present.

TABLE II. THE COMPUTED OH PROTON SHIFTS IN THE CONFORMATION II

Carbinol	δ_m p. p. m.	x_I*	δ_{II}** p. p. m.
Dimethylphenylcarbinol	0.20	0.35	0.30
Dimethyl-*p*-methylphenylcarbinol	0.29	0.31	0.37
Dimethyl-*m*-methylphenylcarbinol	0.28	0.36	0.38
Diethylphenylcarbinol	0.25	0.56	0.40
1-Methyl-1, 2, 3, 4-tetrahydro-1-naphthol	0.30	0.41	0.41
1-Phenylcyclohexanol	0.33	0.21	0.39

* $x_I=\dfrac{A_I}{A_I+A_{II}}$, where A stands for the integrated intensity²⁾.

** $\delta_{II}=\delta_m+0.27\,x_I$

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