Intramolecular Interaction between Hydroxyl Group and π-Electrons. XVI.[1] ν_{O-H} *Absorption Spectra of Aryldimethylcarbinols and Related Compounds*

By Michinori Ōki and Hiizu Iwamura

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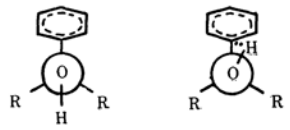
It has been shown in a previous paper[2] that the benzyl alcohols show doublet O–H stretching vibration spectra (ν_{O-H}) in the 3 μ region owing to the rotational isomerism about the C_α–O bond. The hydroxyl group in one (II) of the isomers takes part in the intramolecular interaction with π-electrons of the benzene nucleus and shows the lowered ν_{O-H} when compared with the normal one. Ring



I II

substitution at *p*- or *m*-position to the hydroxymethyl group has been found to alter considerably the apparent ν_{O-H} curve, that is, the relative amount of the two rotational isomers. Furthermore, the phenomenon has been ascribed solely to the change in the proton accepting power of the π-electrons on the benzene ring. In reference to the Hammett's sigma constants of the substituents, the π-electron density at the carbon atom to which the hydroxymethyl group is attached, has been found to have the greatest influence, and a "cis" structure is proposed for the isomer as expressed by model II.

Evans[3] has observed that in benzyl alcohol an unusual vibrational coupling takes place between the aromatic C–H in-plane deformation mode and a stretching mode of $-CH_2-O-$ group at 1020 cm^{-1}. According to the literature, this coupling should be permitted only when C_α–O bond lies in the plane perpendicular to that of the benzene ring. This configuration is in accordance with that of the "cis" structure proposed by the present authors.

There seems to be, however, another factor in the apparent substituent effects, that is, the proton donating character of the α-hydroxyl group might also be influenced by the ring substituent and the apparent substituent effects would be the result of a counteraction between the two effects just as is the case in 2-hydroxybiphenyls[4].

To clarify the ambiguity in the electronic effect, and to obtain further support on the configuration of the interacting form, aryldimethylcarbinols and the related tertiary carbinols in which the hyperconjugative electronic interaction between the hydroxyl group and the aromatic residue may be minimal, have been submitted to the ν_{O-H} spectral measurement.

Experimental

Spectral Measurement.—A Perkin Elmer 112 G grating infrared spectrometer was operated to measure ν_{O-H} absorption as described previously[5].

Materials.—They were prepared by action of an excess of methyl- or ethyl-magnesium halide on the corresponding ketones or carboxylic esters, unless otherwise stated. Decomposition of the reaction mixtures was always effected by an aqueous solution of ammonium chloride to avoid dehydration catalyzed by a trace of acid in the later process. Despite all the tests no *p*-dimethylamino derivative could be obtained, *p*-dimethylamino-α-methylstyrene, m. p., 75°C[6], being the sole product.

The two nitro derivatives were obtained by oxidation of the corresponding nitrocumenes as described for the *p*-isomer[7].

p-Methoxycarbonyl derivative was prepared by refluxing the silver salt of 2-(*p*-carboxyphenyl)-2-propanol[8] with methyl iodide in methanol.

Physical constants and analytical data, if necessary, of the samples are listed in Tables I and II.

Results and Discussion

In Fig. 1 are presented the apparent ν_{O-H} absorption curves of dimethylphenylcarbinol and the two extreme derivatives with respect to the Hammett's sigma constants of the substituents. All the numerical band properties are listed in Table III.

1) Part XV. M. Ōki and H. Iwamura, This Bulletin, **35**, 283 (1962).
2) M. Ōki and H. Iwamura, ibid., **32**, 955 (1959).
3) J. C. Evans, *Spectrochim. Acta*, **17**, 129 (1961).
4) M. Ōki and H. Iwamura, This Bulletin, **34**, 1395 (1961).
5) M. Ōki and H. Iwamura, ibid., **32**, 567 (1959).
6) Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 4978 (1958).
7) H. Kwart and P. S. Francis, ibid., **77**, 4907 (1955).
8) Y. Okamoto, T. Inukai and H. C. Brown, ibid., **80**, 4971 (1958).

TABLE I. PHYSICAL CONSTANTS AND ANALYTICAL DATA OF THE ARYLDIMETHYLCARBINOLS, X-C_6H_4·CMe_2·OH

X	M. p. or b. p. observed (lit.)	Ref. index	Anal. Found C	Found H	Found N	Calcd. C	Calcd. H	Calcd. N
H	35°C (91°C/8 mmHg)[7]							
p-MeO	103°C/1 mmHg	n_D^{26} 1.5251	72.10	8.67		72.26	8.49	
m-MeO	34°C (34~35°C)[9]							
p-Me	78°C/1.5 mmHg (101°C/10 mmHg)[10]							
m-Me	100°C/7 mmHg (73°/3 mmHg)[10]							
m-Me_2N	73°C (73°C)[6]							
p-*tert*-Bu	79°C (79°C)[11]							
p-Cl	44°C (43.3°C)[12]							
m-Cl	87°C/3.5 mmHg, (88°C/2 mmHg)	n_D^{22} 1.5355 n_D^{20} 1.5370)[12]						
p-CO_2Me	122°C/3.5 mmHg		68.07	7.46		68.02	7.27	
p-NO_2	134°C/3.5 mmHg, (120.5~121°C/2 mmHg)	n_D^{24} 1.5520 n_D^{20} 1.5552)[7]						
m-NO_2	63~64°C		59.60	6.13	7.79	59.66	6.12	7.73

TABLE II. PHYSICAL CONSTANTS OF TERTIARY ALCOHOLS RELATED TO DIMETHYLPHENYLCARBINOL

	M. p. or b. p. (lit.)
Diethylphenylcarbinol	73°C/3.5 mmHg, n_D^{16} 1.5172 (79~82°C/3 mmHg, n_D^{20} 1.5178)[13]
1-Methyl-1, 2, 3, 4-tetrahydro-1-naphthol	88°C (88.5~88.7°C)[14]
1-Phenylcyclohexanol	62°C (60°C)[15]

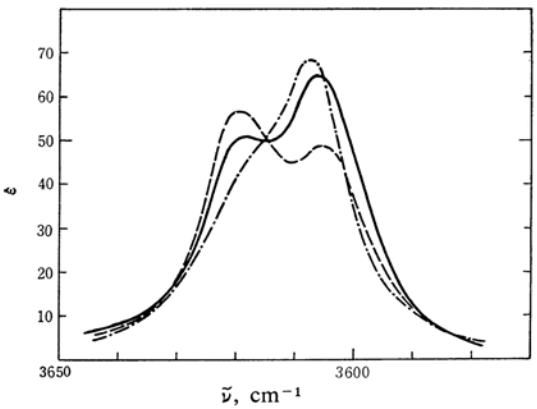


Fig. 1. ν_{O-H} Absorption of aryldimethylcarbinols.
Ph·CMe_2·OH ———
p-MeO·C_6H_4·CMe_2·OH —·—·—
p-NO_2·C_6H_4·CMe_2·OH — — —

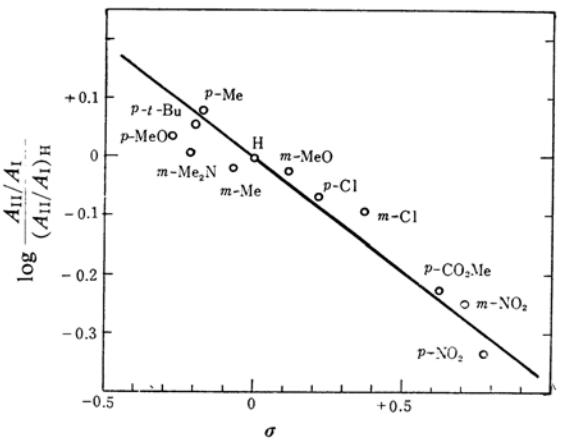


Fig. 2. Relation between $\log\frac{A_{II}/A_I}{(A_{II}/A_I)_H}$ and the Hammett's sigma constant.

In contrast with the benzyl alcohols[2] which have the ν_{O-H}'s at 3636 and 3617 cm^{-1}, all the present carbinols have doublet ν_{O-H}'s at 3620 and 3606 cm^{-1}. This is the due consequence of the tertiary nature of the hydroxyl group[16].

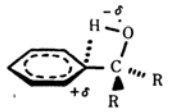
The relative intensity, A_{II}/A_I, which may be put approximately equal to the equilibrium constant, K, between I and II, varies considerably as the electron-releasing substituents in the benzene ring enhance the lower lying band, while the electron-withdrawing ones reduce it, relative to the higher absorption. In Fig. 2, it is illustrated quantitatively as the relation between log (A_{II}/A_I) and the Hammett's sigma constants. The inclination expressed as $\rho = -0.357$ is as large as that of the benzyl alcohols, $\rho = -0.475$[2], and suggests a similar mechanism

9) Y. Okamoto and H. C. Brown, ibid., **79**, 1912 (1957).
10) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, ibid., **79**, 1897 (1957).
11) H. Walther, *J. pharm. chim.*, **27**, 476 (1938).
12) H. C. Brown, Y. Okamoto and G. Ham, *J. Am. Chem. Soc.*, **79**, 1907 (1957).
13) A. Dierichs and E. Preu, *Chem. Ber.*, **90**, 1208 (1957).
14) T. Kusama and D. Koike, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 685 (1951).
15) C. D. Nenitzescu and I. Necsoni, *J. Am. Chem. Soc.*, **72**, 3483 (1950).
16) M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

TABLE III. ν_{O-H} ABSORPTIONS OF ARYLDIMETHYLCARBINOLS, X-C_6H_4·CMe_2·OH

X	ν_{O-H}	ν_{max} cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	A 10^3 mol^{-1} l. cm^{-2}	$\Delta\nu_{max}$ cm^{-1}	$\log(A_{II}/A_I)$
p-MeO	I	3620.1	16.4	1.50	13.4	0.310
	II	3606.7	15.0	3.06		
m-Me_2N	I	3619.8	19.4	1.66	13.6	0.280
	II	3606.2	14.0	3.16		
p-*tert*-Bu	I	3620.7	19.0	1.55	13.7	0.336
	II	3607.0	16.0	3.36		
p-Me	I	3620.3	16.2	1.53	12.7	0.353
	II	3607.6	15.6	3.45		
m-Me	I	3620.2	18.8	1.74	13.0	0.255
	II	3607.2	15.0	3.13		
H	I	3620.4	15.2	1.72	13.5	0.276
	II	3606.9	14.4	3.25		
m-MeO	I	3620.7	17.2	1.85	14.0	0.251
	II	3606.7	15.0	3.30		
p-Cl	I	3620.2	15.0	2.01	14.2	0.203
	II	3606.0	15.8	3.21		
m-Cl	I	3620.7	15.0	2.13	15.2	0.184
	II	3605.5	15.8	3.25		
p-CO_2Me	I	3621.2	13.4	2.64	14.6	0.050
	II	3606.6	17.0	2.96		
m-NO_2	I	3620.2	15.0	2.69	15.3	0.024
	II	3604.9	16.0	2.84		
p-NO_2	I	3619.5	14.6	3.17	14.6	−0.067
	II	3604.9	15.8	2.72		

of interaction. If the interaction bore a fairly polarized mechanism with considerable contribution of the intramolecularly charge-transferred structure, III, the electronic interaction between the substituent and the site of the interaction would be pronounced and the σ^+



III

proposed by Brown and Okamoto[9], rather than the original σ constants would have given the better linearity. Since this is not the case, the interaction may be considered to include but little contribution by such a structure. A slight diminution in the absolute value may be due to the weakened ability of the tertiary carbinols as proton donors rather than the primary ones.

There is no doubt about assigning the isomer II, having the intramolecular interaction with the π-electrons, to the band at lower frequency, 3606 cm^{-1}. Then the apparent variation in A_{II}/A_I may be, as a first approximation, attributed to the change in the proton attracting power of the π-electron on the benzene ring. Since the doublet ν_{O-H} maxima vary only within the experimental error, the ring substituents might be regarded to be indifferent to the force constant of the hydroxyl group. ν_f which appears at 3620 cm^{-1} can validly be said to be indifferent to the ring substituent in contrast to the substituted phenols[17] in which ν_f's are in linear relation with the sigma constants of the ring substituents. It is, however, rather dangerous to conclude from the apparent constancy in the wave number that the hydroxyl groups having the intramolecular interaction with the π-electrons are also independent of the substituents.

With the intention of making it clear that the ring substituents might not be concerned with the donor ability of the hydroxyl group,

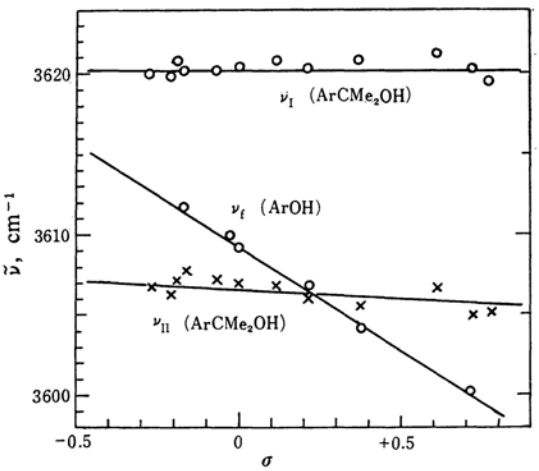


Fig. 3. The effect of the nuclear substitution on the ν_{O-H} maxima of aryldimethylcarbinols and phenols.

17) P. J. Stone and H. W. Thompson, *Spectrochim. Acta*, **10**, 17 (1957).

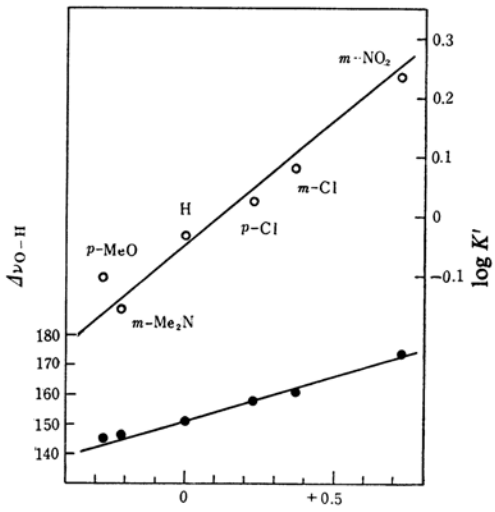


Fig. 4. The association between aryldimethylcarbinols and diethyl ether in carbon tetrachloride.
● Shift of ν_{O-H} maxima.
○ Equilibrium constant defined by
$$K' = \frac{[Ar \cdot CMe_2 \cdot OH \cdots OEt_2]}{[Ar \cdot CMe_2 \cdot OH]}$$
the denominator being estimated from the intensity of the remaining free ν_{O-H}.

but solely with the π-electron system as the proton acceptors, the intermolecular association of these carbinols with diethyl ether as a common proton acceptor in carbon tetrachloride was investigated. Unexpectedly, the association IV was found to be dependent on the substituents as is seen from the ν_{O-H} of the hydroxyl group taking part in the association, and from the association constants (K'), in Fig. 4. The electron-withdrawing group such as nitro

$$Ar \cdot CMe_2 \cdot \overset{-\delta}{O}\text{-}H \cdots \overset{+\delta}{O}Et_2$$
IV

tends to strengthen, while the electron-releasing one weakens, the association between the aryldimethylcarbinols and diethyl ether. Compared with the free ν_{O-H}'s which are quite independent of the ring substitution, it has become reasonable to conclude here that the effect of the ring substituents on the hydroxyl group becomes the more conspicuous, when the hydroxyl group is more polarized by the formation of hydrogen bonding or the like interactions. The electronic structure of the hydroxyl group should be expressed as a resonance hybrid between V, VI and VII. The increased contribution of the structures VI and VII by any mechanism will lower the force constant of O–H which in turn makes sharper response to the electronic changes in the rest of the

R-O-H	R-$\bar{O}$-$\overset{+}{H}$	R-$\overset{+}{O}$-$\bar{H}$
V	VI	VII

molecule, R. This finding bears a resemblance to the substituent effects on the reaction kinetics and the ultraviolet spectra, in which the excited state rather than the ground state suffers from more distinguished electronic effect of the substituents.

Since the strength of, and the polarization in the hydroxyl group by, the O–H$\cdots\pi$ interaction, as realized in aryldimethylcarbinols, may be regarded to lie between the two extremes, the effect of the substituent on the proton donor character of the hydroxyl group will be medium and can not be evaluated quantitatively. The effect of the substituent in this sense will make ν_i's lower by way of strengthening the proton donor character, as the electron-withdrawing power of the substituent increases, and may be opposite to the direct substituent effect on the proton accepting ability of the π-electrons. Thus, it is rather practical to assume that the apparent constancy of ν_i's over a wide range of aryldimethylcarbinols would be the result of the counterbalance between a favorable effect on the proton donor and an unfavorable influence on the proton acceptor in the case of the electron attracting substituent. The same interpretation will also be operative of the electron releasing groups.

In Table IV are listed ν_{O-H} data of diethylphenylcarbinol, 1-phenylcyclohexanol and 1-methyl-1, 2, 3, 4-tetrahydro-1-naphthol. Though the hydroxyl groups in these compounds are in the same structural position as those of the aryldimethylcarbinols with respect to the benzene ring, and the π-electron density as a proton acceptor is common, they have the

Table IV. ν_{O-H} Absorptions of tertiary alcohols

	ν_{O-H}	ν_{max} cm^{-1}	$\Delta\nu^{a}_{1/2}$ cm^{-1}	A 10^3 mol^{-1} l. cm^{-2}	$\Delta\nu_{max}$ cm^{-1}	log (A_{II}/A_I)
Diethylphenylcarbinol	I	3618.2	17.8	2.71	10.0	−0.10
	II	3608.2	19.0	2.16		
1-Phenylcyclohexanol	I	3620.5	17.7	1.10	15.3	0.57
	II	3605.2	12.8	4.10		
1-Methyl-1, 2, 3, 4-tetrahydro-1-naphthol	I	3616.0	10.2	1.85	12.2	0.16
	II	3603.8	13.6	2.65		

varied value of log (A_{II}/A_I). The phenomenon can not be attributed to the electronic effect, but rather to the steric effect. Taking 1-phenylcyclohexanol as an example, the hydroxyl

Ia IIa

hydrogen in Ia has a steric interference with the axial hydrogens at 3- and 5-positions of the cyclohexane ring. Thus the stability of isomer Ia relative to IIa will be diminished considerably, and the value of log (A_{II}/A_I) is the largest ever examined for a compound of this type.

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Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo