Intramolecular Interaction between Hydroxyl Group and π-Eelctrons. V⁽¹⁾. *Electronic Effect in Arylcarbinols and a Preliminary Note on the Interaction in Benzylaniline Derivatives*

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It has long been in question why absorption due to the O-H stretching vibration of benzyl alcohol or allyl alcohol appears at about 3620 cm^{-1}. However, from the standpoint of the rotational isomerism, the interaction between the hydroxyl group and the π-electrons will be a valuable explanation for the phenomenon, as suggested in the previous paper[1]. If the interaction is the real cause of the shift of the ν_{O-H} absorption, it is expected that the electron density of the carbon atom (C_1) to which the hydroxymethyl group is attached or the next (C_2) to it should have profound effect on the ν_{O-H} absorptions of arylcarbinols. Hence, fourteen meta- and para-substituted benzyl alcohols were prepared and their ν_{O-H} absorptions were determined with a grating spectrophotometer. Ortho-substituted benzyl alcohols are excluded because formation of the internal hydrogen bonding can not be avoided when an atom with a lone pair of electrons is involved.

Experimental

Measurement and Calculation.—They were carried out similarly as reported previously[2].

Materials.—The materials used for the measurement are known compounds, unless otherwise stated. Their physical constants agreed with those in the literature.

m-Cyanobenzyl alcohol.—It was prepared according to the procedure reported by Langguth[3]. Although he reported the compound as an oil, it boiled at 127∼127.5°C/3 mm. and solidified to form colorless needles on standing. The melting point is 28∼29°C.

m-Phenylbenzyl alcohol. — It was prepared by the lithium aluminum hydride reduction of *m*-phenylbenzoic acid. Although this compound has been reported[4] as syrup, it formed colorless needles, m. p. 55∼55.5°C, on recrystallization from carbon tetrachloride—petroleum ether.

Anal. Found: C, 84.70; H, 6.59. Calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.57%.

m-Benzyloxybenzaldehyde.—To a sodium ethoxide solution prepared from 5.5 g. (0.24 atom) of sodium and 150 ml. of alcohol was added 24.4 g. (0.2 mol.) of *m*-hydroxybenzaldehyde followed by 27.8 g. (0.22 mol.) of benzyl chloride. The mixture was heated under reflux for five hours, cooled and filtered to remove insoluble materials. Evaporation of the solvent gave crystals which were recrystallized to colorless small plates, m. p. 52∼53°C, from petroleum ether. Yield, 32.5 g. (82%).

Anal. Found: C, 79.29; H, 5.81. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

m-Benzyloxybenzyl alcohol. — To a slurry prepared from 1.5 g. (0.04 mol.) of lithium aluminum

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[1] Part IV: M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).
[2] M. Ōki and H. Iwamura, ibid., **32**, 567 (1959).
[3] St. Langguth, *Ber.*, **38**, 2062 (1905).
[4] M. P. Adam, *Ann. Chim. Phys.*, **15**, 245 (1888).

hydride and 50 ml. of ether was gradually added 19.6 g. (0.1 mol.) of *m*-benzyloxybenzaldehyde in 50 ml. of ether and the mixture was stirred at room temperature for two hours. The excessive lithium aluminum hydride was decomposed by adding ethyl acetate in ether and finally the mixture was treated with dilute sulfuric acid. The aqueous layer was extracted with ether and the ethereal extract was washed with aqueous sodium hydroxide and dried over potassium carbonate. Fractional distillation furnished a colorless oil boiling at 160°C/3 mm. which solidified. Recrystallization from benzene-petroleum ether (3 : 7) gave the substance in colorless needles, m. p. 44.5~45°C. Yield, 16.0 g. (81%).

Anal. Found: C, 78.54; H, 6.70. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%.

N-(p-Methoxybenzyl)-p-anisidine. — A mixture of 3.0 g. of *N*-(*p*-methoxybenzylidene)-*p*-anisidine, 1 g. of Raney nickel T-4 catalyst[5] and 100 ml. of alcohol was stirred in an autoclave at 80~100°C with 100 kg./cm^2 initial pressure. The heating was discontinued after two hours and, after cooling, the catalyst was removed by filtration. Evaporation of the solvent afforded a crystalline residue which was recrystallized from petroleum ether. Colorless plates, m. p. 94.5~95.5°C, were obtained in 1.5 g. (50%) yield. The rather low yield must be attributed to the hydrogenolysis of the *p*-methoxybenzyl group, since the oder of *p*-cresol methyl ether was distinct in the hydrogenation product.

Anal. Found: C, 74.22; H, 7.23. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04%.

N-p-Methoxybenzylaniline.—It was prepared in an analogous way. Though the melting point of this material was reported as 64.5°C[6], it melted at 46~47°C (colorless plates from petroleum ether). Since the micro-analyses agreed with the calculated values, it seems that this is one of the polymorphs.

Anal. Found: C, 78.99; H, 7.18. Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09%.

Results and Discussion

The apparent ν_{O-H} absorption curves of *p*-nitrobenzyl alcohol, *m*-cyanobenzyl alcohol, benzyl alcohol and *p*-benzyloxybenzyl alcohol are shown in Fig. 1. The selection was made because the para-nitro group is the most electron-attracting and the para-benzyloxyl group is the most electron-releasing group in respect of Hammett's σ values[7] among the compounds used in the present work and benzyl alcohol is an intermediate. *m*-Cyanobenzyl alcohol is also included because it gives two apparent maxima.

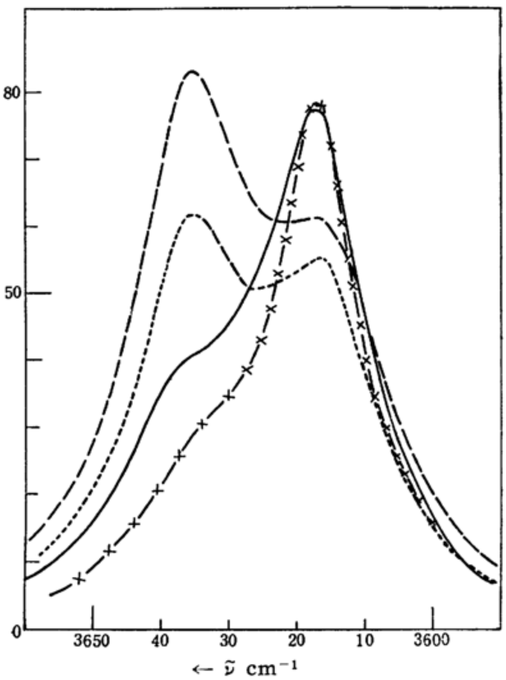

Fig. 1. ν_{O-H} absorption of *p*-nitrobenzyl alcohol (— — —), *m*-cyanobenzyl alcohol (---------), benzyl alcohol (-- -) and *p*-benzyloxybenzyl alcohol (—×—).

Introduction of an electron-releasing group such as a benzyloxyl group in the para position in respect of the hydroxymethyl group enhances the intensity of the band at 3617 cm^{-1} and an electron-attracting group such as nitro group in the para position enhances the band at 3636 cm^{-1}. Thus the main peak for the ν_{O-H} absorption of *p*-nitrobenzyl alcohol lies at ca. 3636 cm^{-1}. Splitting of the two bands into the two apparent maxima in *m*-cyanobenzyl alcohol will be a firm proof for the presence of the two ν_{O-H} absorption bands in benzyl alcohol derivatives. The results suggest that the number of molecules which possess internal interaction is greater in the benzyl alcohol with an electron-releasing group and this kind of electronic effect must be caused by the presence of the interaction between the hydroxyl group and the π-electrons, since such enhancement in the band intensities is naturally expected from the assignment suggested in the previous paper[1].

Now, when the internal interaction is taken into account, there are four possibilities in structure as shown in Fig. 2. The figures are presented both as sketches

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[5] S. Nishimura. This Bulletin, **32**, 61 (1959). The authors are indebted to Dr. Nishimura for preparation of this catalyst.

[6] O. F. Steinhart, *Ann.*, **241**, 332 (1887).

[7] L. P. Hammentt, "Physical Organic Chemistry", McGraw-Hill Book Co., New York (1940), p. 184. Also see: H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[8] D. S. Trifan, J. L. Weinmann and L. P. Kuhn, *J. Am. Chem. Soc.*, **79**, 6566 (1957).

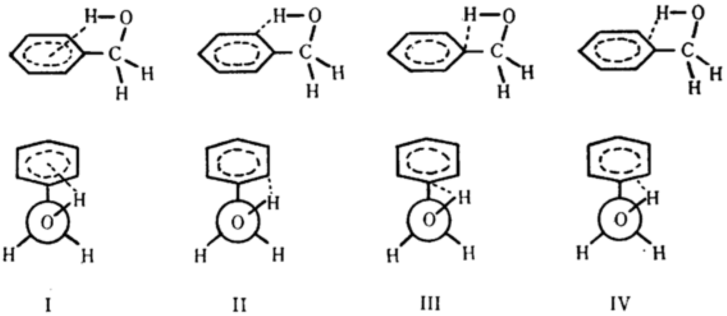

Fig. 2.

and as projections through the O–C axis. The first (I) is the interaction between the hydroxyl group and the aromatic nucleus as a whole and this type of interaction was empirically quoted by Trifan and his co-workers[8] for α-hydroxyethylferrocene. In the second case (II), the direction of the hydrogen atom of the hydroxyl group points to the carbon atom (C_2) or the π-electron on C_2. This type of interaction has not been suggested, but the suggestion by Lüttke and Mecke[9] for 2-hydroxybiphenyl may fall into this category. In the third (III), the hydrogen atom of the hydroxyl group points to C_1 of the benzene nucleus or the π-electron on C_1. This type of interaction was implied by Goldman and Crisler[10] for phenethyl alcohol derivatives. The fourth case (IV) is the interaction in which the hydrogen atom turns toward the midst of C_1 and C_2, and the overlapping π-electrons on C_1 and C_2, take part in the interaction. The last case was suggested by Baker and Shulgin[11] for *o*-allylphenol and *o*-propenylphenol. Structures I and IV are considered as sorts of π-complexes and structures II and III σ-complexes.

Since the above assignments of the structures are all empirical, it is necessary to assign the structure on the basis of the experimental results. Now it can be hoped that the nature of the interaction may be clarified by changing the substituent on the benzene nucleus, because it is known, as mentioned above, that the interaction is markedly affected by the introduction of certain kinds of substituents. The same substituent was introduced into meta and para positions in respect of the hydroxymethyl group, because electron density on C_2 caused by a substituent in the para position should be roughly reproduced[12] on C_2 by introducing the same substituent into the meta position to the hydroxymethyl group.

If the π-complex (I or IV) is the real case, there should not be much difference between the two arylcarbinols which possess the same substituent, since the electron density of the aromatic ring as a whole must be the same and that in the middle of the two carbon atoms (C_1 and C_2) is considered to be nearly the same, although the effect of the substituent may be seen because of the different electron densities. If II is the case and an electron-releasing group is introduced, the meta-substituted benzyl alcohol would have a stronger absorption band at 3617 cm^{-1} than the para-substituted isomer, because the electron density on C_2 is higher in the meta-substituted compound than in the para-substituted one. And if III is the case, the situation must be opposite to that stated in case II and a compound with an electron-releasing group in the para-position to the hydroxymethyl group must have stronger absorption at 3617 cm^{-1} than the meta-substituted one.

The actual absorption curves are divided into two, assuming that the curves are the overlap of two symmetric bands which are expressed by the Lorentz function and the half widths and the integrated intensities are shown together with absorption maxima in Table I.

As is seen from Table I, an electron-releasing group in the para-position to the

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[9] W. Lüttke and R. Mecke, *Z. Elektrochem.*, **53**, 241 (1949); *Z. physik. Chem.*, **196**, 56 (1950).

[10] I. M. Goldman and R. O. Crisler, *J. Org. Chem.*, **23**, 751 (1958).

[11] A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958).

[12] In addition to the effect given by σ_p, we must consider σ_o because the ortho positions to the hydroxymethyl group correspond to ortho and para positions to a new substituent for meta-substituted benzyl alcohol. Therefore, the electron density on C_1 or C_2 is different, even if the effect of the hydroxymethyl group is neglected.

TABLE I. ν_{O-H} ABSORPTION OF ARYLCARBINOLS (x-$RC_6H_4CH_2OH$)

R	x	OH	ν_{max} (cm^{-1})	$\Delta\nu_{max}$ (cm^{-1})	$\Delta\nu^a_{1/2}$ (cm^{-1})	$A\times10^{-3}$ ($mol^{-1}\cdot l.\cdot cm^{-2}$)	A_i/A_f
NO_2	m	i *	3616.3	18.9	20.4	3.70	0.84
		f **	3635.2		18.8	4.41	
	p	i	3616.0	19.5	23.6	3.98	0.77
		f	3635.5		20.0	5.15	
CN	m	i	3616.2	19.2	19.0	2.98	0.75
		f	3635.4		20.8	3.98	
	p	i	3616.4	19.0	19.8	3.49	0.71
		f	3635.4		20.8	4.93	
Cl	m	i	3617.0	19.4	18.6	3.74	1.30
		f	3636.4		21.4	2.88	
	p	i	3617.1	18.2	17.6	3.56	1.38
		f	3635.3		21.2	2.58	
C_6H_5	m	i	3616.6	19.6	16.6	4.17	1.92
		f	3636.2		21.6	2.18	
	p	i	3617.0	19.4	15.4	3.92	1.88
		f	3636.4		20.4	2.08	
H***		i	3617.1	19.2	17.0	4.26	1.69
		f	3636.3		24.0	2.59	
CH_3	m	i	3616.7	20.1	16.6	4.18	1.85
		f	3636.8		22.6	2.26	
	p	i	3617.4	18.4	15.6	3.67	2.02
		f	3635.8		24.2	1.82	
CH_3O	m	i	3616.9	19.3	16.6	4.04	1.69
		f	3636.2		25.6	2.40	
	p	i	3617.1	18.9	16.4	4.33	2.48
		f	3636.0		27.8	1.75	
$C_6H_5CH_2O$	m	i	3616.1	20.4	16.6	4.32	2.11
		f	3636.5		20.0	2.05	
	p	i	3617.0	18.2	15.0	3.89	2.70
		f	3635.2		20.0	1.44	

* i: denotes interacted form of the hydroxyl group.

** f: denotes free form of the hydroxyl group.

*** Taken from reference 1.

hydroxymethyl group enhances the intensity of the band at 3617 cm^{-1} more than one in the meta position and the tendency is opposite when an electron-attracting group is introduced. This fact excludes the possibility of structure I, II or IV. Hence it is concluded that the interaction between the hydroxyl group and the π-electrons of the aromatic nucleus in benzyl alcohol is of the type expressed by structure III.

The consistency of the wave number ($3615.9\sim3617.4\,cm^{-1}$ and $3635.2\sim3636.8\,cm^{-1}$) at which two absorption maxima exist is another proof that the origin of the bands is the rotational isomers, because in phenethyl alcohol derivatives the shift of the wave number, where an absorption of the interacted form appears, is observed[13].

The sum of the integrated intensities of the two bands is not always constant and there is a tendency that a more electron-attracting group gives rise to greater integrated intensity, as has been observed in substituted phenols[14]. However, when $\log\frac{A_i/A_f}{(A_i/A_f)_0}$, where A_i is the integrated intensity of the absorption band due to the interacted form, A_f that of free form and $(A_i/A_f)_0$ is the ratio given by benzyl alcohol, is taken into consideration, this value would represent the equilibrium constant and is in linear relation with

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[13] See the following paper.

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

TABLE II. ν_{N-H} ABSORPTION OF *N*-ARYLMETHYLARYLAMINES (p-$XC_6H_4CH_2NHC_6H_4$-Y-p)

X	Y	N-H	ν_{max} (cm^{-1})	$\Delta\nu^a_{1/2}$ (cm^{-1})	A$\times 10^{-3}$ (mol$^{-1}\cdot$l.$\cdot$cm^{-2})	$\Delta\nu_{max}$ (cm^{-1})
H	H	I	3417.4	28.0	2.24	32.8
		II	3450.2	25.6	2.11	
CH_3O	H	I	3418.0	26.8	2.63	32.1
		II	3450.1	23.7	1.73	
H	CH_3O	I	3405.6	35.8	1.93	37.1
		II	3442.7	30.2	1.74	
CH_3O	CH_3O	I	3406.6	35.3	2.03	36.2
		II	3442.8	29.6	1.30	

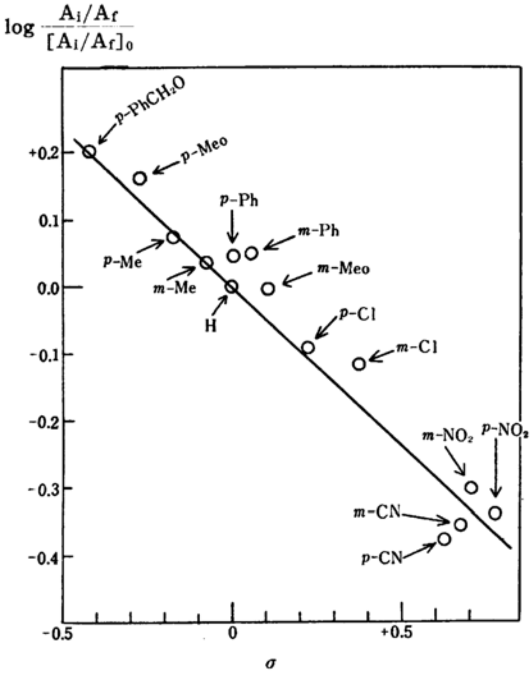

Fig. 3.

Hammett's σ values (Fig. 3). This linear relationship result is again a strong support to the idea of the existence of structure III. Although σ value for the *m*-benzyloxyl group has been unknown, it is now estimated from Fig. 2, by pointing 2.11 on the straight line and projecting to the σ axis, as -0.204.

A similar situation is expected for benzylaniline derivatives, which showed two distinct maxima for N–H stretching 30~40 cm^{-1} apart. The data are given in Table II.

It is understood from Table II, 1) that higher electron density on the benzene nucleus enhances the N–H stretching band at lower wave number, 2) that ν_{N-H} absorption shifts to lower wave number as Colichman & Liu[15] and also Krueger & Thompson[16] have pointed out for the arylamines, and 3) that $\Delta\nu_{max}$ is greater when the basicity of the arylamine increases. The full discussion will be presented in the near future.

Summary

Absorption due to the O–H stretching vibration in the fundamental region was measured with fourteen benzyl alcohol derivatives to see the electronic effect of the substituent on the interaction between the hydroxyl group and the π-electrons and the following conclusions are deduced.

1) The nature of the interaction or the structure of the molecule which gives rise to the ν_{O-H} absorption at 3617 cm^{-1} is discussed and the interaction between the hydroxyl group and the π-electron on the carbon atom to which hydroxymethyl group is attached (structure III) is favored.

2) The consistency of the wave numbers at which two ν_{O-H} absorptions appear, gives further support to the idea that these absorptions originate in the existence of the two rotational isomers.

3) Log $\frac{A_i/A_f}{(A_i/A_f)_0}$ is in linear relation with Hammett's σ values and the σ value of the *m*-benzyloxyl group is estimated as -0.204.

A similar phenomenon is also observed in the substituted benzylanilines.

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[15] E. L. Colichman and S. K. Liu, *J. Am. Chem. Soc.*, **76**, 913 (1954).

[16] P. J. Krueger and H. W. Thompson, *Proc. Roy. Soc.*, **A243**, 143 (1957).