Intramolecular Interaction between Hydroxyl Group and π-Electrons. VI[1]. Electronic Effect on the Interaction in ω-Arylalkanols

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In connection with the intramolecular interaction between hydroxyl group and π-electrons, the authors have measured the ν_{O-H} absorption of various substituted benzyl alcohols and concluded that the hydrogen atom of the hydroxyl group interacts with the π-electron on the carbon atom to which the hydroxymethyl group is attached. On the other hand, Goldman and Crisler[2] examined three phenethyl alcohol derivatives on the O–H stretching absorption and concluded that the hydrogen atom of the hydroxyl group interacts with the π-electron on the carbon atom to which the 2-hydroxyethyl group is attached. Meanwhile, the present authors predicted[3], by comparison of the two band intensities of the interacting forms in allyl alcohol and 3-buten-1-ol, that the interaction occurring in them might be different in nature, since allyl alcohol gives a larger band intensity of the interacting form than 3-buten-1-ol in spite of the fact that $\Delta\nu_{\max}$ is smaller in allyl alcohol than in 3-buten-1-ol. Moreover, it is reasonable to consider that allyl alcohol with benzyl alcohol and 3-buten-1-ol with phenethyl alcohol possess the same type of interaction. Therefore, it may be thought that there is a contradiction between the conclusion by Goldman and Crisler and that by the present authors. Since it is dangerous to draw a conclusion from a small number of examples, the ν_{O-H} absorptions of various ω-arylalkanols have been re-examined.

Experimental

Measurement.—It was performed similarly as described previously[3]. When a small peak was present (3-arylpropanols) or the presence of a peak was suspected (4-arylbutanol), the measurement was carried out with a quartz cell of 5 cm. length without alteration of concentration.

Calculation of Integrated Intensities.—It was carried out similarly as reported previously[3], when only two bands were present. However, the presence of three bands, two of which were derived from the presence of the rotational isomers and the third by the internal interaction, required modification to some extent. The two stronger bands were first obtained in the usual manner and the summation of the bands was subtracted from the apparent curve. This procedure usually gave rise to an unsymmetric band. The process was repeated through the trial-and-error method until the third band became symmetric.

Materials. — The compounds used for the measurement are known compounds, unless otherwise stated, and their physical constants well agree with those in the literature.

Preparation of ω-Arylalkanols by Lithium Aluminum Hydride Reduction of Esters.—To a slurry prepared from 2.5 g. (0.07 mol.) of lithium aluminum hydride and 100 ml. of ether, was added 0.1 mol. (0.05 mol. for amino-esters) of the corresponding ester[4]. After stirring for two hours at the room temperature, the excessive lithium aluminum hydride was decomposed by adding ethyl acetate in ether and then dilute sulfuric acid (aqueous sodium hydroxide in the case of aminoalcohols) was added. The aqueous layer was extracted with ether and ethereal extract was washed with aqueous sodium hydroxide. After drying over potassium carbonate followed by evaporation, the residue was either fractionally distilled or recrystallized from an appropriate solvent. Compounds with low melting points were once distilled and then recrystallized. The results are summarized in Table I.

Preparation of 2-(*m*-Aminophenyl)-ethanol.—2-(*m*-Aminophenyl)-ethanol (V) was prepared as illustrated in the following chart.

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[1] Part V of this series: This Bulletin, **32**, 955 (1959).

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

[3] M. Ōki and H. Iwamura, This Bulletin, **32**, 567 (1959).

[4] Amino-esters were conveniently prepared by hydrogenation of the corresponding nitro-esters or alkyl nitrocinnamates in the presence of U-Ni-A catalyst [Y. Urushibara, S. Nishimura and H. Uehara, This Bulletin, **28**, 466 (1955)]. Substituted cinnamic acids were also reduced with the same catalyst in excellent yields, when their sodium salts in water were used. The authors are grateful to Dr. S. Nishimura for hydrogenation.

[5] See; N. Carmack and M. A. Spielman, "*Organic Reactions*", John Wiley & Sons, Inc., New York, Vol. III, (1946), p. 83; E. Schwenk and E. Bloch, *J. Am. Chem. Soc.*, **64**, 3051 (1942).

[6] C. J. Collins, ibid., **73**, 1038 (1951).

[7] D. Sontag, *Compt. rend.*, **197**, 159 (1933).

TABLE I. ω-ARYLALKANOLS [x-$RC_6H_4(CH_2)_nOH$]

R	x	n	b. p. (°C) (3 mmHg)	m. p. (°C)	Crystal form	n_D	*Anal.* Calcd.	*Anal.* Found
Cl[a]	*m*	2	100.5	—	—	1.5475 (23°C)	C: 61.35 H: 5.73	61.59 6.00
CH_3[b]	*p*	3	97～98	23～25	plates	—	C: 79.95 H: 9.39	79.68 9.28
H_2N[c]	*p*	3	145～150	54～55	needles	—	C: 71.49 H: 8.67	71.26 8.70
Cl[d]	*p*	3	111～112	—	—	1.5428 (15.5°C)	C: 63.35 H: 6.49	63.87 6.59
H_2N[e]	*p*	4	—	71～72	needles	—	C: 72.69 H: 9.15	72.50 9.24

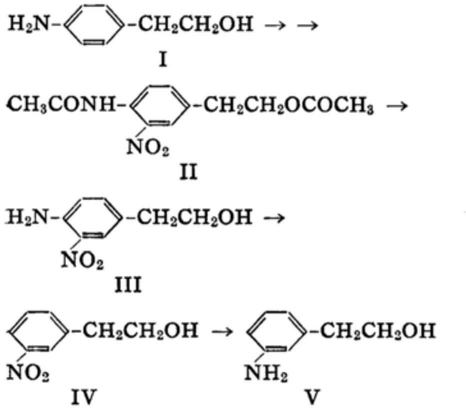
a) The starting material, methyl *m*-chlorophenylacetate, was conveniently prepared through the modified Wilgerodt reaction[5] using morpholine and *m*-chloroacetophenone followed by hydrolysis and then esterification. The over-all yield of the ester was 70%.

b) The melting point has not been reported[6].

c) Recrystallized from benzene containing a small amount of alcohol.

d) Refractive index was reported as 1.5424 (21°C) for substance obtained by the chlorination of 3-phenylpropanol[7].

e) This compound is rather unstable and discolors quickly in the air. Benzene was used as the recrystallization solvent.



2-(p-Acetamido-m-nitrophenyl)-ethyl acetate (II). To 102 g. (1 mol.) of acetic anhydride, 118 g. (0.86 mol.) of 2-(*p*-aminophenyl)-ethanol[8] was added and the mixture was heated on a water bath for thirty minutes. After cooling, 79 g. (1 mol.) of acetyl chloride was slowly added, and the mixture was heated under reflux on a water bath for one hour. Hydrogen chloride and the excessive reagents were removed in vacuo and the residue was dissolved in 400 ml. of acetic anhydride. The solution was cooled in an ice-salt bath and 106.5 ml. (1.7 mol.) of nitric acid (d=1.42) was carefully added at 10～20°C with good stirring. The mixture was stirred for further fifteen minutes at that temperature and then poured into 3 l. of ice-water. The crystals were collected and the major portion was submitted to the subsequent hydrolysis. The analytical sample was obtained by recrystallization from benzene-petroleum ether. It was obtained as yellow needles, m. p. 77°C.

Anal. Found: C, 53.95; H, 5.48. Calcd. for $C_{12}H_{14}N_2O_5$: C, 54.15; H, 5.25%.

2-(p-Amino-m-nitrophenyl)-ethanol (III). — The crude compound II was heated with 500 ml. of 6 N hydrochloric acid under reflux for three hours. The cooled reaction mixture was basified with aqueous sodium hydroxide and organic material was extracted with ether. The ethereal extract was dried over potassium carbonate and evaporated. The residue solidified on standing and was recrystallized from benzene. Orange flat needles, m. p. 85～87°C. Over-all yield, 88 g. (56%).

Anal. Found: C, 52.86; H, 5.63. Calcd. for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53%.

2-(m-Nitrophenyl)-ethanol (IV).—To a solution of 54.6 g. (0.2 mol.) of compound III in 80 ml. of concentrated hydrochloric acid and 20 ml. of water, was added 20.7 g. (0.3 mol.) of sodium nitrite in a minimal quantity of water at −5～−3°C. The mixture was stirred at 0°C for ten minutes and then 325 g. (1.5 mol.) of 30% hypophosphorus acid precooled to 0°C was added, the temperature being maintained at 0～3°C. The mixture was stirred for another hour and then allowed to stand in an ice-bath containing ca. 5 kg. of ice which melted in about twelve hours. After twenty-four hours, the mixture was extracted with ether and the ethereal extract was washed with aqueous sodium hydroxide. Drying with potassium carbonate followed by fractional distillation afforded 25.0 g. (50%) of an orange-yellow oil, b. p. 141～146°C/4 mm., which set to needles. The analytical sample was obtained through recrystallization from benzene-petroleum ether. It was obtained as faintly yellow needles, m. p. 50～51°C.

Anal. Found: C, 57.58; H, 5.55. Calcd. for $C_8H_9NO_3$: C, 57.38; H, 5.43%.

2-(m-Aminophenyl)-ethanol (V)[9].—To a solution

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[8] H. M. Woodburn and C. F. Stuntz, *J. Am. Chem. Soc.*, **72**, 1362 (1950).

[9] This compound has been prepared by lithium aluminum hydride reduction of *m*-aminophenylacetic acid [J. B. Dickey and E. B. Towne, Brit. Pat., 722,367; *Chem. Abstr.*, **49**, 9935 (1955)]. They reported only the boiling point as 135～138°C/2 mm. but no melting point.

TABLE II. ν_{O-H} ABSORPTIONS OF 2-ARYLETHANOLS (x-$RC_6H_4CH_2CH_2OH$)

R	x	OH	ν_{max} (cm^{-1})	$\Delta\nu^a_{1/2}$ (cm^{-1})	$A\times10^{-3}$ (mol^{-1}·l.·cm^{-2})	$\Delta\nu_{III-I}$ (cm^{-1})	$A_I/(A_{II}+A_{III})$
H_2N	m	I	3598.0	25.6	3.62	37.5	1.50
		II	3625	18	0.60		
		III	3635.5	17.6	1.82		
	p	I	3597.8	24.4	3.14	37.2	1.14
		II	3623	18	0.53		
		III	3635.0	19.8	2.23		
CH_3O	m	I	3602.3	24.8	3.34	33.5	1.19
		II	3624	18	0.66		
		III	3635.8	17.9	2.14		
	p	I	3602.5	26.4	2.96	33.3	1.03
		II	3623	18	0.69		
		III	3635.8	18.0	2.19		
CH_3	m	I	3603.1	27.3	3.28	32.7	1.06
		II	3625	20	0.82		
		III	3635.8	18.1	2.27		
	p	I	3602.1	22.4	2.72	33.2	0.93
		II	3623	20	0.74		
		III	3635.5	17.0	2.19		
H		I	3606.4	24.4	2.62	29.6	0.86
		II	3626	17	0.68		
		III	3636.0	18.4	2.36		
Cl	m	I	3611.0	23.0	2.25	24.2	0.645
		II	3625	16	0.71		
		III	3635.2	15.8	2.78		
	p	I	3610.2	24.4	2.23	25.3	0.64
		II	3625	17	0.88		
		III	3635.5	15.2	2.61		
O_2N	m	I	3615.0	21.6	1.20	2.00	0.207
		II	3625	17	1.52		
		III	3635.0	15.4	4.29		
	p	I	3614.0	22.4	1.37	21.0	0.253
		II	3626	18	1.42		
		III	3635.0	14.6	3.99		

of 90 g. (0.36 mol.) of 90% stannous chloride in 80 ml. of concentrated hydrochloric acid, was added 20 g. (0.12 mol.) of compound IV and the mixture was stirred, when the spontaneous reaction set in. After the reaction subsided, the mixture was heated on a water bath for thirty minutes, cooled and decomposed with an excess of aqueous sodium hydroxide. When the mixture was chilled, the aminoalcohol solidified and was collected by filtration. It was recrystallized from benzene, m. p. 68~69°C. It sometimes forms needles and sometimes plates. Yield, 13 g. (80%).

Anal. Found: C, 70.00; H, 7.98. Calcd. for $C_8H_{11}NO$: C, 70.04; H, 8.08%.

Results and Discussion

2-Arylethanols. — The apparent O–H stretching absorption curves are divided into three, assuming that they are the overlap of the three symmetric bands which are expressed by Lorentz function. The apparent curves refuse to be divided into two to fit in, as was pointed out in the earlier paper[3]. The results are shown in Table II.

The actual features of division are shown in Fig. 1 and Fig. 2, 2-(p-aminophenyl)-ethanol and 2-(p-nitrophenyl)-ethanol being taken as the examples because of the extremity of Hammett's σ-values of the substituents.

Two (bands II and III) of the three ν_{O-H} absorption bands are derived from the rotational isomers of primary alcohols and their positions (3635 cm^{-1} and 3625 cm^{-1}) are in good agreement with the previous assignment[10]. The third band (band I) must be attributed to the presence of the intramolecular interation between the hydroxyl group and the π-electrons as

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[10] M. Ōki and H. Iwamura, This Bulletin, 32, 950 (1959).

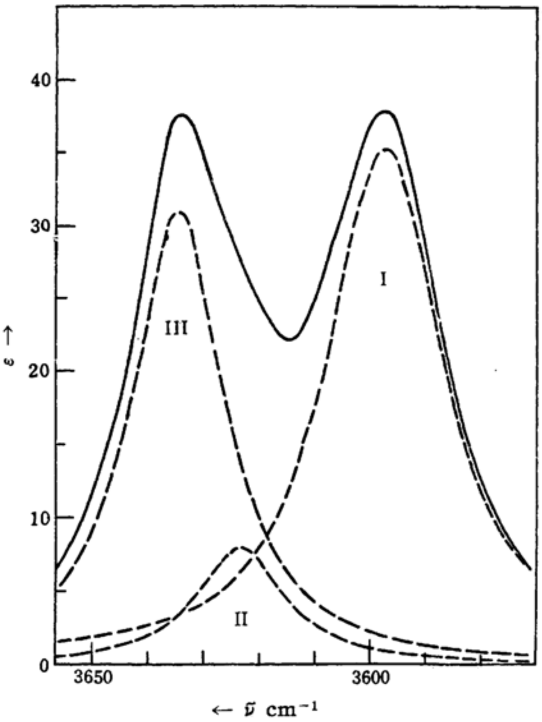

Fig. 1. ν_{O-H} absorption of 2-(*p*-aminophenyl)-ethanol.

Trifan and his coworkers[11,12], Anet and Bavin[13] and Goldman and Crisler[2] have assigned. Since the error involved in dividing the original band into three is rather great, especially for band II, it is not allowable to use the integrated intensity of band II for discussion, although molecular scale models tell that band II is derived from the only rotational form that makes the interaction possible. Hence, the difference of the wave numbers is shown by $\nu_{III}-\nu_I$ rather than by $\nu_{II}-\nu_I$ and the ratio of the integrated intensities is also exemplified by $A_I/(A_{II}+A_{III})$ rather than by A_I/A_{II}.

As clearly understood from Table II, the electronic effect from the substituent is observed. The wave number of the ν_{O-H} absorption maximum (band I) of the interacting form shifts to a lower wave number as the substituent becomes more electron-releasing, and the electron-attracting substituent causes the wave number of band I to shift and approach to the absorption of normal primary alcohols, this phenomenon having not been observed in benzyl alcohol derivatives. The integrated intensity of band I also increases as the electron-releasing group is introduced.

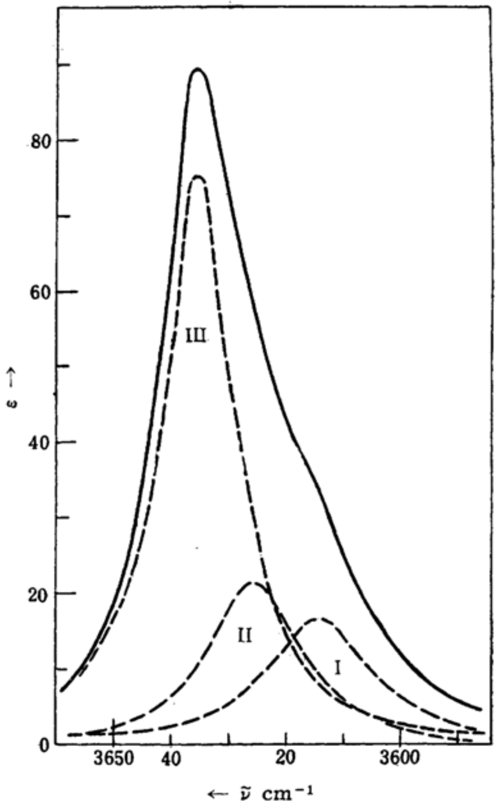

Fig. 2. ν_{O-H} absorption of 2-(*p*-nitrophenyl)-ethanol.

As to the molecular structure of the internally interacting form, the authors pointed out four possibilities as shown in Fig. 3[1]. Structure VI indicates the interaction between the hydroxyl group and the benzene nucleus as a whole, the case having been suggested by Trifan and his coworkers[11]. Structure VII, representing the interaction which includes C_1 of the benzene nucleus, was deduced by Goldman and Crisler[2] by comparison of three ν_{O-H} curves of 2-phenylethanol, 2-(*p*-methoxyphenyl)-ethanol and 2-(*p*-nitrophenyl)-ethanol. Structure VIII with the participation of C_2 of the benzene nucleus was suggested by Lüttke and Mecke[14], and structure IX, in which C_1 and C_2 take part, by Baker and Shulgin[15].

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[11] D. S. Trifan, J. L. Weinmann and L. P. Kuhn, *J. Am. Chem. Soc.*, **76**, 6566 (1957).

[12] P. von Schleyer, D. S. Trifan and R. Bacskai, ibid., **80**, 6691 (1958).

[13] F. A. L. Anet and P. M. G. Bavin, *Can. J. Chem.*, **34**, 1756 (1956).

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

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

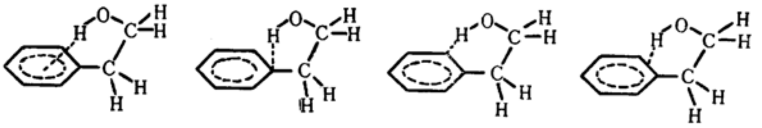
VI VII VIII IX

Fig. 3.

Structure VII is first excluded on the basis of the experimental results given in Table II, because compounds with the same substituent in the meta and in the para positions to the 2-hydroxyethyl group give similar curves. Structure VII expects a favored interaction in the 2-phenylethanol with a strongly electron-donating group in the para position over the compound possessing the same substituent in the meta.

Structure VI is rather improbable because it has no orbital which would couple with that of the hydrogen atom. If such interaction took place, further lengthening of the O–H bond should be expected, which would give rise to further lowering of the wave number of band I because of a weaker force constant. Structure VI is made improbable also by the theoretical treatment of the complex of benzene with hydrogen ion or silver ion as discussed below. The structure should not be hexagonally symmetrical, nor should the positive ion be on the plane of the benzene nucleus[16].

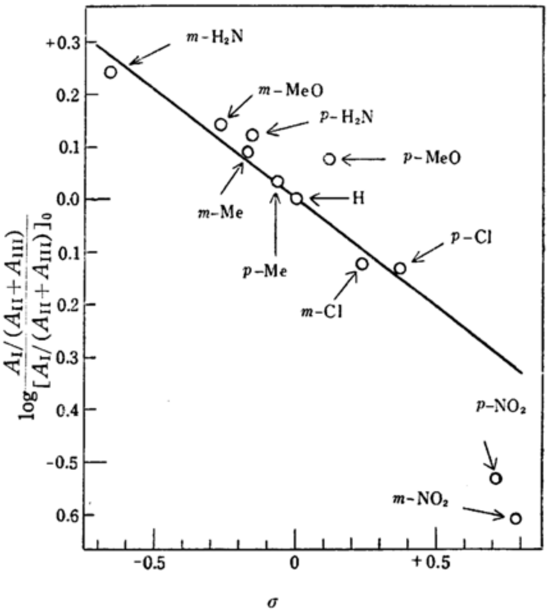

Fig. 4. Relation between $\log\frac{A_{\rm I}/(A_{\rm II}+A_{\rm III})}{[A_{\rm I}/(A_{\rm II}+A_{\rm III})]_0}$ in 2-arylethanol and σ constants for structure VIII.

Thus, there are two possibilities left for the structure. It seems that structure VIII is more convincing when Hammett's σ values[17] of the ortho position in respect of 2-hydroxyethyl group is taken for the ordinate and $\log\frac{A_{\rm I}/(A_{\rm II}+A_{\rm III})}{[A_{\rm I}/(A_{\rm II}+A_{\rm III})]_0}$, where $[A_{\rm I}/(A_{\rm II}+A_{\rm III})]_0$ is the ratio obtained with 2-phenylethanol, for the abscissa (Fig. 4), because they are nearly in linear relation. However, the defect of this structure can be pointed out immediately because of the far deviation of 2-(p-methoxyphenyl)-ethanol from a straight line, or, in other words, because 2-(p-methoxyphenyl)-ethanol and 2-(m-methoxyphenyl)-ethanol show almost the same internal interaction in spite of the great distance between σ constants ($\sigma_m=+0.115$, $\sigma_p=-0.268$). Even the correction which will be discussed in the following paragraph modifies only σ_m but does not affect σ_p. The deviation of 2-(nitrophenyl)-ethanols can be attributed to the error in dividing the apparent curves into three, since the bands I of these compounds are the smallest comprising no maxima nor distinct shoulders.

The relation between the σ constants and $\log\frac{A_{\rm I}/(A_{\rm II}+A_{\rm III})}{[A_{\rm I}/(A_{\rm II}+A_{\rm III})]_0}$ for structure IX is shown in Fig. 5. The σ constants for the para-substituted compounds should be the mean values of those for meta and for para and those for the meta-substituted compounds should be expressed by $\left(\frac{\sigma_o+\sigma_p}{2}+\sigma_m\right)\Big/2$. Unfortunately, however, few σ values for ortho-substitution have been known, the only example having been provided by Shulgin and Baker[18]

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[16] R. S. Mulliken, *J. Chem. Phys.*, **19**, 514 (1951); *J. Am. Chem. Soc.*, **74**, 811 (1952).

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

[18] A. T. Shulgin and A. W. Baker, *Nature*, **182**, 1299 (1958).

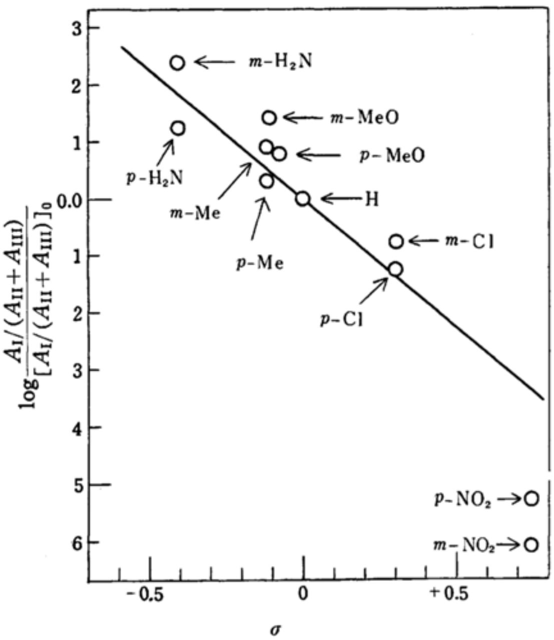

Fig. 5. Relation between $\log\frac{A_I/(A_{II}+A_{III})}{[A_I/(A_{II}+A_{III})]_0}$ in 2-arylethanol and σ constants for structure IX.

who found the same values for ortho-chloro and para-chloro within the experimental error and a slightly more negative value for ortho-methoxyl than for para-methoxyl. Electron densities computed by the molecular orbital method have been reported in some instances and slight differences between ortho- and para-position have been reported, although they do not cover all the substituents used in the present work. Hence, $(\sigma_m+\sigma_p)/2$ is used as an approximation for the substituents in the meta-position except the methoxyl group for which respective values for ortho and for para are available.

There are deviations from a straight line, even though the results are better than those considered from structure VIII. In other words, the meta-substituted 2-phenylethanol is always favored in the internal interaction over the para-substituted, or the former always gives a greater integrated intensity of band I, when an electron-releasing group is introduced. The deviations may be caused by neglecting the electron density of the ortho-position and/or by the contribution of structure VIII to some extent, which favors 2-phenylethanols with an electron-donating group in the meta-position for the interaction. The deviation may be also caused by using $A_{II}+A_{III}$ instead of A_{II} as the integrated intensity of the free form, since the scale model indicates that the free form capable of producing such an interaction is only one, of which integrated intensity is given by A_{II}.

If the intramolecular interaction between the hydroxyl group and the π-electrons is considered as a complex formation between a cation and an aromatic nucleus, structure IX can be supported. Namely, Rundle and Goring[19] observed on the basis of diffraction data that the silver ion in the complex with benzene is bonded equally with the two carbon atoms of the benzene nucleus and is located above the surface. Judged from the present results shown in Table II, the wave number of the ν_{O-H} absorption of the interacting form can be said just the same for a given substituent irrespective of its position. This fact strongly supports structure IX as the internally interacting form of 2-phenylethanol.

Strictly speaking, however, structure VIII can not be totally rejected, because it is one of the possibilities that favor the meta-substituted compounds in the internal interaction more than the para-substituted. Doering et al.[20] studied the structure of the heptamethylbenzenonium compound and postulated the 1, 1, 2, 3, 4, 5, 6-heptamethylbenzenonium ion with C_1 of the tetrahedral structure, without totally rejecting another with the methyl ion located between the two carbon atoms of the benzene nucleus and out of the plane. On the contrary, the present conclusion is that structure IX is the main contribution[21].

3-Arylpropanols.—As the representatives of 3-arylpropanols the ν_{O-H} absorption curves of 3-(*p*-aminophenyl)-propanol and 3-(*p*-chlorophenyl)-propanol and the corresponding divided values are shown in Figs. 6 and 7, respectively. The results are summarized in Table III.

It may be suspected that the lowest

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[19] R. E. Rundle and J. H. Goring, *J. Am. Chem. Soc.*, **72**, 5337 (1950).

[20] W. von Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards and G. Laber, *Tetrahedron*, **4**, 178 (1958).

[21] It may be pointed out that another possibility exists in which either structure VII or VIII contributes. Namely, the direction of the hydroxyl group points to either C_1 or C_2 depending on the favorable electron density on the carbon atom. This is improbable, however, since interacting forms of both meta- and para-substituted compounds absorb at nearly the same wave number, while, in O-H…O hydrogen bonding, ν_{O-H} absorption generally appears at lower wave numer in the formation of a six-membered ring than of a five-membered ring.

TABLE III. ν_{O-H} ABSORPTIONS OF 3-ARYLPROPANOLS (x-$RC_6H_4CH_2CH_2CH_2OH$)

R	x	OH	ν_{max} (cm^{-1})	$\Delta\nu^a_{1/2}$ (cm^{-1})	$A\times10^{-3}$ (mol^{-1}·l.·cm^{-2})	$\Delta\nu_{III-I}$ (cm^{-})	$\Delta\nu_{III-II}$ (cm^{-1})
H_2N	m	I	3587.0	33.0	1.11	52.9	12.7
		II	3627.2	24.0	2.15		
		III	3639.9	17.6	3.33		
	p	I	3590.0	29.0	0.98	49.9	14.1
		II	3625.8	20.0	1.92		
		III	3639.9	16.7	3.32		
CH_3O	m	I	3593.0	35.0	0.50	47.2	15.0
		II	3625.2	24.0	2.28		
		III	3640.2	16.6	3.62		
	p	I	3595.0	27.0	0.39	45.0	13.4
		II	3626.8	21.2	2.05		
		III	3640.2	14.6	2.92		
CH_3	m	I	3593.2	30.6	0.43	46.8	13.0
		II	3627.0	23.0	1.97		
		III	3640.0	15.8	2.99		
	p	I	3598.0	31.4	0.51	42.6	12.1
		II	3628.5	22.6	2.23		
		III	3640.6	15.6	3.01		
H		II	3623.0	21.6	1.93		16.7
		III	3639.9	16.0	3.57		
Cl	p	II	3627.8	24.8	2.53		12.6
		III	3640.4	16.6	3.40		

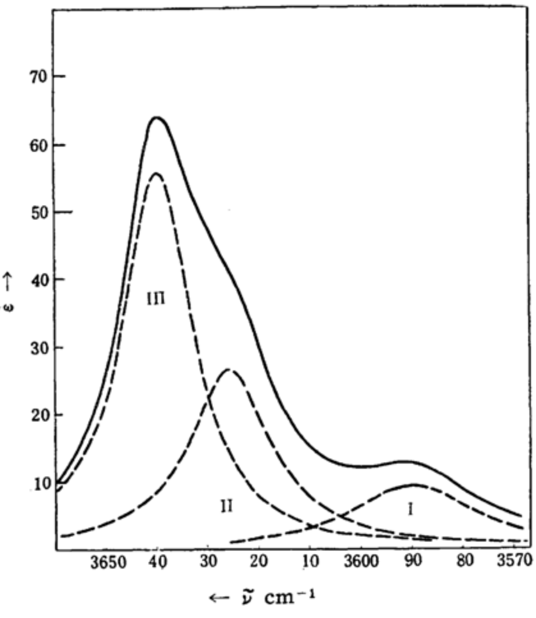

Fig. 6. ν_{O-H} absorption of 3-(p-aminophenyl)-propanol.

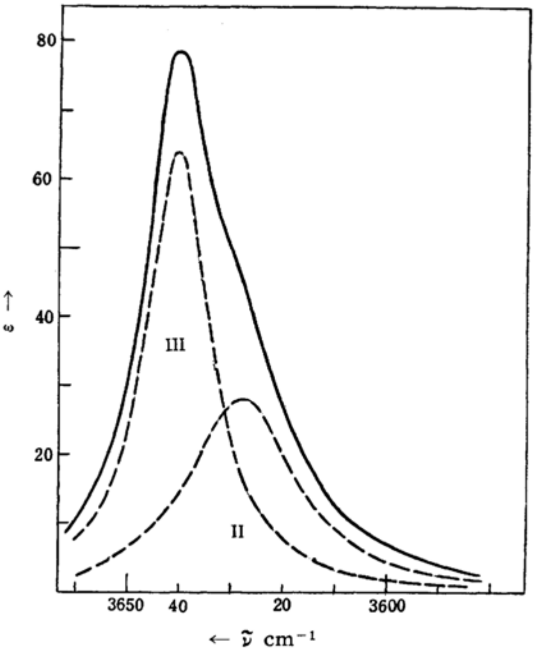

Fig. 7. ν_{O-H} absorption of 3-(p-chlorophenyl)-propanol.

ν_{O-H} absorption (band I) of 3-(aminophenyl)-propanols might be the ν_{N-H} absorption, but actually ν_{N-H} absorptions are found at 3479 cm^{-1} and 3393 cm^{-1} for 3-(m-aminophenyl)-propanol. The shift in the wave numbers of the ν_{O-H} absorption of the interacting form is consistent with the results obtained with 2-arylethanols. Namely, the methoxyl and the methyl groups give bands I at nearly the same wave number and the amino group further lowers the wave number. The difference between the meta- and the para-substituted compounds can not be taken as an

TABLE IV. ν_{O-H} ABSORPTIONS OF 4-ARYLBUTANOLS (p-$RC_6H_4CH_2CH_2CH_2CH_2OH$)

R	OH	ν_{max} (cm^{-1})	$\Delta\nu^a_{1/2}$ (cm^{-1})	$A\times10^{-3}$ (mol^{-1}·l.·cm^{-2})	$\Delta\nu_{max}$ (cm^{-1})
H_2N	II	3626.1	19.8	2.21	13.0
	III	3639.1	17.4	3.26	
H	II	3626.6	23.2	2.36	13.3
	III	3639.9	17.6	3.43	

important indication, because bands I constitute the smallest peaks and errors involved in dividing the apparent absorption do not allow to discuss such a small difference.

It is apparent that the interaction is less favored in 3-arylpropanols than in 2-arylethanols, because even 3-(aminophenyl)-propanols give the smaller integrated intensities of band I. 3-Phenylpropanol itself does not show any absorption corresponding to band I of the other compounds with an electron-releasing group. However, the close examination of band II reveals that band II of 3-phenylpropanol is located at a rather low wave number, $\Delta\nu_{III-II}$ being as large as 16.7 cm^{-1}, in comparison with 12~15 cm^{-1} of others. It may be attributed to the fact that the peak corresponding to band I of 3-phenylpropanol is too small to be separated from others by the present technique. The above assumption seems verifiable because 3-(p-chlorophenyl)-propanol gives bands II and III in the normal positions for primary alcohols, $\Delta\nu_{III-II}$ being 12.6 cm^{-1}. In this case, the electron-attracting power of the chlorine atom seems to prohibit the interaction from taking place.

It is rather strange that 3-arylpropanols possess smaller numbers of internally interacting molecules even though the interacting form seems to be more stabilized than that in 2-arylethanol, because the wave numbers of bands I of 3-arylpropanols are lower than those of 2-arylethanols[22]. It must be attributed either to the unfavorable change in entropy and energy or to the difference in nature, as the authors pointed out for allyl alcohol and 3-buten-1-ol[3]. In this case, however, the present authors will choose the former for the following reasons. Firstly, the electronic effect in 3-arylpropanols shows the same trend as that in 2-arylethanol, and, secondly, the interacting form in 3-arylpropanol requires the all-*gauche* form including two carbon and one oxygen atoms, while that in 2-arylethanol requires the *gauche* form including one each of carbon and oxygen atoms. Hence, even though the interacting form of 3-arylpropanols will be more stabilized, if once formed, the unfavorable change in entropy and energy will limit the number of the molecules.

As to the nature of the interaction, 3-arylpropanols do not provide further information. The authors again come to a difficulty because of the weakness of bands I, but would like to assign tentatively the same structure as 2-arylethanols, because the meta- and the para-substituted compounds give nearly the same ν_{O-H} absorptions.

4-Arylbutanols.—The results of 4-arylbutanols are shown in Table IV.

From Table IV, it is obvious that 4-phenylbutanol does not possess any intramolecular interaction between the hydroxyl group and the π-electrons, since its ν_{O-H} absorption is normal for primary alcohols. Even 4-(p-aminophenyl)-butanol shows the normal absorption for primary alcohols in spite of the favorable electron density on the aromatic nucleus due to the presence of the strongly electron-releasing amino group. And again, this fact must be attributed to the unfavorable change in both entropy and energy.

Thus, it can be concluded that the internal interaction between the hydroxyl group and the π-electrons of the benzene nucleus occurs, when the hydroxyl group is an alcoholic O-H and the carbon chain is not fixed, up to 3-phenylpropanol in the series of ω-arylalkanols.

Summary

The electronic effect on the intramolecular interaction between the hydroxyl group and the π-electrons of the benzene nucleus was studied with various ω-arylalkanols. In 2-arylethanols, introduction of an electron-releasing group into the benzene nucleus gives rise to the shift of the ν_{O-H} absorption maxima to a lower wave number and to greater integrated

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[22] For example, see R. M. Badger and S. H Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

intensities of the band due to the interacting form, and introduction of an electron-attracting group to a higher wave number and smaller integrated intensities. However, the wave number of the band due to the interacting form is not affected by the position of the substituent, as far as the substituent is the same. Thus, the structure represented by IX is favored. On the other hand, a compound with an electron-releasing group in the meta position always shows greater integrated intensities of the band due to the interacting form than the para-substituted isomer and this fact saves structure VIII from entire rejection. Hence, the authors tentatively assign structure IX as the most favorable with participation of structure VIII to some extent.

In 3-arylpropanols the interaction is observed only in the compounds with an electron-releasing group and 3-(*p*-chlorophenyl)-propanol shows the normal ν_{O-H} absorption for primary alcohols. The phenomenon that 3-arylpropanols show smaller interaction in spite of the appearance of the band due to the interacting form at a lower wave number is attributed to the unfavorable change in both energy and entropy.

In 4-arylbutanol no interaction is observed, even though a strongly electron-donating group is introduced.

Thus, as the authors predicted, it has been proved that the intramolecular interaction occurring in 2-phenylethanol is different in nature from that in benzyl alcohol.

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