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Intramolecular Interaction between Hydroxyl Group and π-Electrons. XIX.[1] Steric Effects on the Interaction in *o*-(1-Alkenyl)phenols

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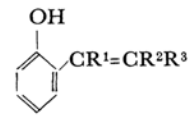
Nine *o*-(1-alkenyl)phenols, *o*-$HOC_6H_4CR^1{=}CR^2R^3$, have been prepared and their ultraviolet absorptions and the O–H stretching bands (ν_{O-H}) in the infrared absorption measured in an effort to explore the effect of the substituents, R^1—R^3, on the strength of the intramolecular interaction between the OH group and the π-electron system. The K-band of the styrene chromophore at 240—250 mμ is lost in the samples involving R^1, which is bulkier than methyl. As the size of R^1 increases from H, by way of Me, Et, and *i*-Pr, to *t*-Bu, the angle of the twist between the planes made by the benzene ring and the ethylenic group must increase; this trend is nearly parallel with the amount of the interacting ν_{O-H} in the infrared spectrum. The phenomenon is interpreted mainly by means of the favorable overlap between the O–H group and π-orbitals. *o*-Isobutenylphenol shows a ν_{O-H} triplet at 3610, 3576 and 3539 cm^{-1}. The latter two bands are assigned to the hydroxyl group interacting with π-electrons on the vinyl group intramolecularly. A tentative explanation has been developed which attributes the two interacting bands to the presence of two interacting conformations. The solvent effect on the ultraviolet absorptions is in accord with this explanation.

o-Vinylphenol shows a doublet O–H stretching vibration (ν_{O-H}) at 3611 and 3557 cm^{-1} in the infrared absorption spectra[2]; the latter band has been assigned to the hydroxyl group taking part in the intramolecular interaction with the π-electrons on the vinyl group. Although the interaction does not involve the lone pair of electrons as a proton acceptor, it has been found to be analogous to the ordinary hydrogen bonding in that the polarizable π-electrons play the role of the electron donor. Thus, in *o*-(*trans*-1-propenyl)-phenol, the electron-releasing methyl substituent on the vinyl group enhances the strength of the interaction, as is visualized by a greater shift of the ν_{O-H} to the lower frequency,[3,4] while in 2-hydroxy-*trans*-stilbene[2] and 2-hydroxy-ω-nitrostyrene,[5] the electron-attracting phenyl and nitro groups diminish and extinguish the interaction[6] respectively. These electronic effects have been fully discussed in a series of 2-hydroxybiphenyls,[7] which are aromatic analogs of *o*-vinylphenols.

Since the strength of the interaction must be sharply dependent on the overlap between the π-orbitals in the electron donor and the electron-accepting O–H orbital, the steric hindrance in the neighborhood of the interacting group may be expected to alter the interaction to a great extent. In the present paper, it will be shown that the substituents in the alkenyl group of *o*-(1-alkenyl)phenols (I—VIII) exert a conspicuous steric effect on the interaction in addition to the expected electronic effect. The steric environment of the phenols will be evaluated as a steric inhibition of the resonance between the benzene ring and the alkenyl group through the ultraviolet absorption spectra.



	R^1	R^2	R^3
I	H	H	H
II	Me	H	H
III	*t*-Bu	H	H
IV	H	Me	Me
IV′	H	Me	Et
V	Me	Me	Me
VI	*i*-Pr	Me	Me
VII	H	Me	H
VIII	Et	Me	H

Experimental

The Measurement of the Absorption Spectra.— The infrared measurements were carried out with a Perkin-Elmer 112 G grating infrared spectrometer, the spectral slit width under the 3 μ region being adjusted to 0.8 cm^{-1}. Samples were dissolved in carbon tetrachloride (redistilled over phosphorus pentoxide) with a

1) Part XVIII: M. Ōki and H. Iwamura, This Bulletin, **36**, 1 (1963).
2) M. Ōki and H. Iwamura, ibid., **33**, 681 (1960).
3) M. Ōki, H. Hosoya and and H. Iwamura, ibid., **34** 1391 (1961).
4) A. W. Baker and A. T. Shulgin, *Spectrochimica Acta*, **20**, 153 (1964).
5) The phenol shows a single symmetric band at 3597.5 cm^{-1} which, though shifted to a lower frequency, can be assigned to the free ν_{O-H}.
6) Undoubtedly the planarity of the molecule is unfavorable to the interaction in these compounds, as will be discussed later. However, the presence of the interaction in 2-hydroxy-*trans*-stilbene is an indication of a non-planar conformation, at least to a small extent, in comparison with the absence of the interaction in 1-naphthol.
7) M. Ōki and H. Iwamura, This Bulletin, **34**, 1395 (1961).

Table I. Physical constants and analytical data of the *o*-(1-alkenyl)phenols

	Obs.		Lit.		Anal., %	
	B. p., °C/mmHg	n_D (°C)	B. p., °C/mmHg	n_D (°C)	Found	Calcd.
I	112/17	1.5775 (27)	93—94/12	1.577 (35.7)[9]		
II	92—93/16	1.5463 (20.5)	204/760[10]			
III	105—107/16	1.5171 (20.5)			C: 81.84 H: 9.25	81.77 9.15
IV	100—101/16	1.5606 (19.5)			C: 80.74 H: 8.32	81.04 8.16
IV′	84/4	1.5475 (24.2)			C: 81.41 H: 8.99	81.44 8.70
V	99—100/15.5	1.5390 (23.2)			C: 81.26 H: 8.99	81.44 8.70
VI	116—117/16	1.5170 (21)			C: 82.03 H: 9.35	82.06 9.54
VII	M. p., 36°C		M. p., 36.5—37°C[11]			
VIII	98—99/14	1.5320 (21.5)	112—113/19	1.53234 (17)[12]		

Table II. Physical constants and analytical data of the *o*-(1-alkenyl)anisoles
(*o*-MeO·C_6H_4·CR^1=CR^2R^3)

	Obs.		Lit.		Anal., %	
	B. p., °C/mmHg	n_D (°C)	B. p., °C/mmHg	n_D (°C)	Found	Calcd.
I	89—90/15	1.5552 (24)	73—75/10	1.5530 (20)[13]		
II	91—92/16	1.5304 (28)	56.5—57/2	1.5340 (20)[14]		
III	112/22	1.5111 (28)			C: 82.12 H: 9.52	82.06 9.53
IV	115/22	1.5460 (27)			C: 81.62 H: 8.79	81.44 8.70
IV′	102/15	1.5400 (26.8)			C: 81.70 H: 9.29	81.77 9.15
V	107/18	1.5183 (29)			C: 81.65 H: 9.02	81.77 9.15
VI	117—118/17	1.5178 (24.5)			C: 82.23 H: 9.64	82.30 9.87
VII	101/22	1.5562 (22)	104—105/13	1.5600 (30)[15]		
VIII	112—113/17	1.5188 (21)	113—115/19	1.52013 (17)[12]		

concentration of around 0.001 mol./l., unless otherwise stated. Quartz cells 2.0 and 5.0 cm. in optical length were employed in order to obtain the desired absorption intensity. The apparent absorptions were assumed to be expressed by means of the Lorentz curves and separated into the individual absorptions when they are overlapped. Each integrated intensity (A) was computed from the equation[8]:

$$A = K\frac{\pi}{2cl} \times \ln\left(\frac{I_0}{I}\right)_{max} \Delta\nu^a_{1/2}$$

where K was put at unity, $\Delta\nu^a_{1/2}$ being the apparent half band width.

The ultraviolet absorptions were measured with a Beckman DU spectrophotometer. The concentration of the samples in 95% aqueous ethanol or in *n*-heptane of a spectro-grade was nearly 10^{-5} mol./l. throughout.

The Preparation of the Samples.—*3, 3-Dimethyl-2-(2-hydroxyphenyl)-2-butanol.*—To a Grignard solution prepared from 41 g. (0.5 mol.) of *t*-butyl chloride, 12 g. (0.5 atom) of magnesium and 300 mol. of ether, was added 20.5 g. (0.15 mol.) of *o*-hydroxyacetophenone in 50 ml. of ether with efficient stirring and cooling. The mixture was heated under reflux for 2 hr., and then 600 ml. of anhydrous benzene added. The solvent was removed by distillation until the boiling point was attained (75°C). The remainder was heated for a further 6 hr. and, after cooling, decomposed with 500 ml. of 15% aqueous acetic acid. Stirring was continued throughout the process. The organic layer was separated, and the aqueous layer extracted with benzene. The combined benzene solution was washed with aqueous sodium bicarbonate, dried, and fractionally distilled to give 7.0 g. of recovered *o*-hydroxyacetophenone and 5.0 g. (17%) of the desired product as a highly viscous colorless oil, b. p. 118—120°C/4 mmHg. The oil later solidified and was recrystallized from petroleum ether to give colorless prisms, m. p. 75—77°C.

8) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

9) K. Fries and G. Fickewirth, *Ber.*, **41**, 367 (1908).
10) K. Fries, W. Gross-Selbeck and O. Wicke, *Ann.*, **402**, 305 (1914).
11) D. S. Tarbell, "Organic Reactions," Vol. II, John-Wiley & Sons, Inc., New York (1944), p. 27.
12) A. Mounié, *Bull. Soc. Chim. France*, [3] **29**, 350 (1903).
13) C. S. Marvell and D. W. Hein, *J. Am. Chem. Soc.*, **70**, 1895 (1948).
14) Y. Okamoto and H. C. Brown, ibid., **79**, 1912 (1957).
15) T. R. Govindachari and B. R. Pai, *J. Org. Chem.*, **18**, 1256 (1953).

Found: C, 74.20; H, 9.45. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

2, 4-Dimethyl-3-(2-hydroxyphenyl)-3-pentanol.—This was similarly prepared from methyl salicylate and isopropylmagnesium bromide; it was obtained as needles, m. p. 114—116°C, in a 40% yield.

Found: C, 75.36; H, 9.73. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

o-(1-t-Butylvinyl)phenol.—3, 3-Dimethyl-2-(2-hydroxyphenyl)-2-butanol (5 g.) and 10 mg. of iodine were heated in vacuo. The dehydration took place at ca. 100°C, and the product distilled at about 150°C (bath temperature). The distillate was taken up in ether, washed with aqueous sodium thiosulfate, and dried. Distillation gave 3 g. (60%) of a colorless oil.

Other *o*-(1-alkenyl)phenols were prepared similarly. The physical constants and the analytical data are collected in Table I.

The methyl ethers of the phenols were prepared by the methylation of the corresponding phenols with sodium hydroxide and dimethyl sulfate, or by the dehydration of dialkyl-*o*-methoxyphenylcarbinol. The physical constants and the analytical data are listed in Table II.

2, 4-Dimethyl-3-(2-methoxyphenyl)-3-pentanol.—This was an unknown compound and was prepared from methyl 2-methoxybenzoate and isopropylmagnesium bromide. It was a colorless oil boiling at 124—126°C/4 mmHg and was obtained in a 72% yield.

Found: C, 75.36; H, 9.73%. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98%.

Results and Discussion

The apparent ν_{O-H} absorption curves at around 3600 cm^{-1} are shown in Figs. 1, 2 and 3. In Table III are listed the ν_{O-H} maxima, the apparent half band widths ($\Delta\nu^a_{1/2}$), the integrated intensities, the shifts ($\Delta\nu_{max}$) of the interacting ν_{O-H} (ν_i) from the corresponding free ν_{O-H} (ν_f) and the ratios of A_i to A_f.

Although the phenols vary widely, there always appears an absorption of a certain intensity at about 3610 cm^{-1} in each phenol examined. Since phenol itself absorbs in this region in its monomeric state, it is reasonable to assign the absorption which appears here to the free ν_{O-H} band of the phenols.

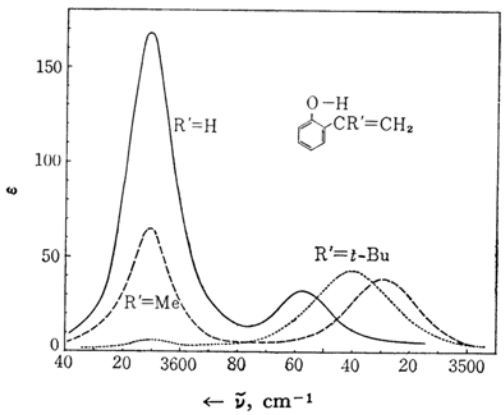


Fig. 1. ν_{O-H} absorptions of I, II and III.

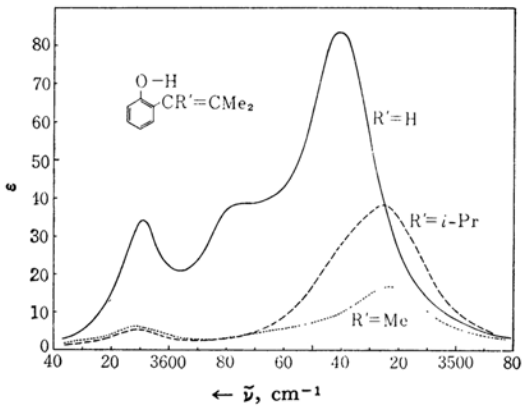


Fig. 2. ν_{O-H} absorptions of IV, V and VI.

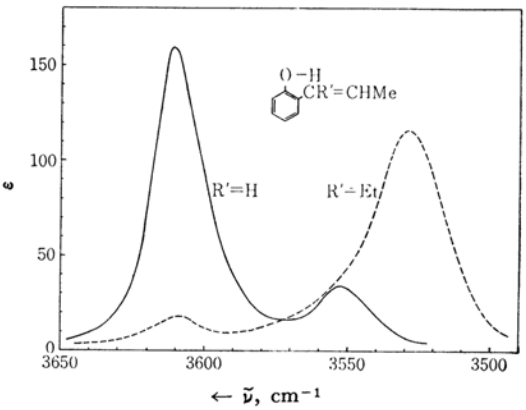


Fig. 3. ν_{O-H} absorptions of VII and VIII.

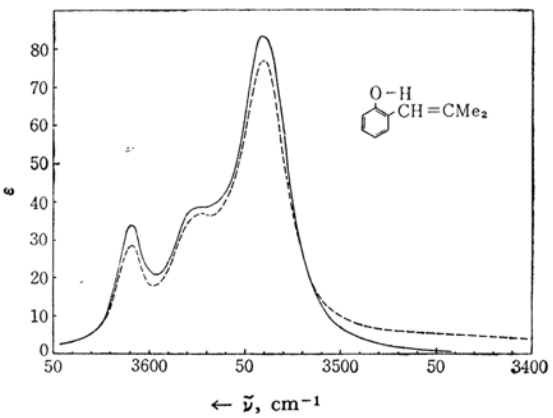


Fig. 4. Variation in ν_{O-H} absorption of *o*-isobutenylphenol (IV) with concentration.
—— 0.00154 mol./l. --- 0.113 mol./l.

Some of the ν_{O-H} curves are very unusual in shape; this complexity can be interpreted only when the curves are assumed to be overlaps of at least three symmetric curves, each expressed

in terms of the Lorentz function.[8] It has first been confirmed through dilution study that all these ν_{O-H} bands belong to the monomeric molecules of the phenols. Over a wide range of concentration, ν_{O-H} curves hardly change at all in any spectral properties, as is shown in Fig. 4. Secondly, the possibility of the incidental occurrence of the overtone or the combination bands in the midst of the ν_{O-H} region was discarded as a result of a deuterium-substitution experiment in the hydroxyl group. As is shown in Fig. 5, with the example of *o*-(2-methyl-1-propenyl)-phenol-*O*-d, the ν_{O-D} curve appears in the expected region of the lower frequency, with almost the same band shape as the original ν_{O-H} curve. Three absorptions in this case have the same ν_{O-H} to ν_{O-D} ratio of 1.35. It is quite natural that the anharmonicity of ν_{O-H} would not vary significantly after the O–H···π interaction, since it is suggested that ν_{O-H} is of normal anharmonicity or is possibly slightly more harmonic after the hydrogen bond formation.[16] Therefore, the lower ν_{O-H} bands appearing below 3600 cm^{-1} were all thought to result from the hydroxyl group interacting somehow with π-electrons in the vinyl group intramolecularly.

Table III. ν_{O-H} Absorptions of *o*-(1-alkenyl)-phenols

No.	ν_{max} cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol^{-1} l. cm^{-2}	$\Delta\nu_{max}$ cm^{-1}	A_i/A_f
I	3611.0	17.8	1.08	53.9	0.26
	3556.8	24.4	0.28		
II	3610.7	17.6	0.41	81.4	0.95
	3529.3	28.3	0.39		
III	3610.5	19.0	0.028	70.6	18.6
	3539.9	32.8	0.52		
IV	3609.8	14.6	0.12	33.7	10.1
	3576.1	37.0	0.40	70.5	
	3539.3	26.8	0.81		
IV′	3609.2	14.8	0.12	32.8	10.5
	3576.4	38.4	0.36	71.4	
	3537.8	29.6	0.90		
V	3612.2	27.2	0.051	52.9	4.6
	3559.3	39.0	0.043	87.8	
	3524.4	33.4	0.19		
VI	3611.1	20.2	0.026	69.6	18.8
	3541.5	23.4	0.086	86.4	
	3524.7	32.0	0.40		
VII	3611.1	16.8	0.84	9.9	0.67
	3601.2	19.2	0.29	58.9	
	3552.2	24.0	0.27		
VIII	3609.4	21.0	0.14	52.4	9.4
	3557.0	32.0	0.084	80.6	
	3528.8	29.6	1.23		

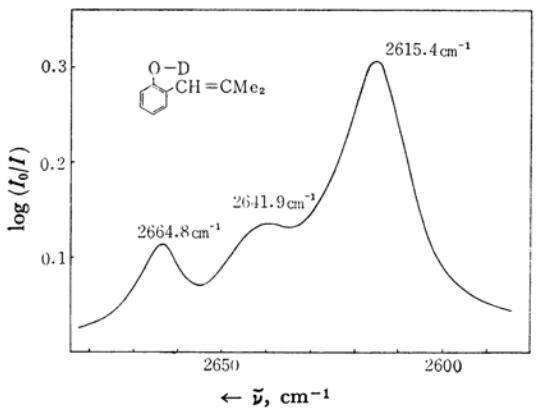


Fig. 5. ν_{O-D} absorption curve of *o*-isobutenyl-phenol-*O*-d.

By assigning in these ways, the remarkable effects of the substituents on the apparent absorption curves can be summarized as follows.

a) It is obvious from Figs. 1, 2 and 3, and also from the last column of Table III, that the degree of the interaction increases as the α-substituent on the vinyl group varies from methyl to ethyl, isopropyl and to *t*-butyl, because the intensity of the free ν_{O-H} band decreases, while the relative intensity of the interacting ν_{O-H} to the free one increases, in this descending order of substituents.

b) The phenols with a sterically-crowded alkenyl group show a rather less total intensity of the ν_{O-H} band.

c) In some instances, two or more kinds of ν_{O-H} bands appear interacting with π-electrons. This suggests the possible presence of more than one kind of interacting forms of a comparable stabilization.

d) The ν_{O-H} shifts following the interaction, which may be reagrded as corresponding to the

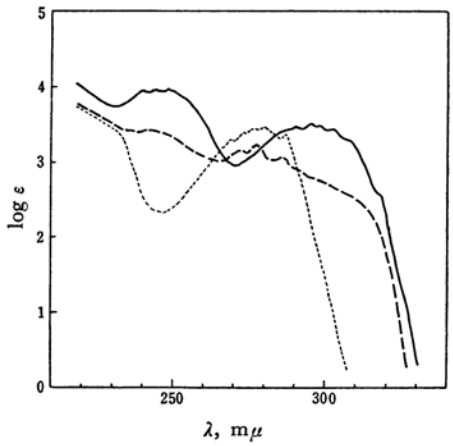


Fig. 6. The ultraviolet absorptions of I, II and III in *n*-heptane.

16) C. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco and London (1960), p. 114.

energy of the interaction, are not always in the order of the degree of the interaction, A_i/A_f.

Before ascribing these effects mainly to the steric factors and discussing them further, it would be more instructive to inspect here the configuration of the molecules with reference to the ultraviolet absorption spectra, together with the corresponding anisoles which lack the O–H···π interaction. Figure 6 illustrates the ultraviolet absorption curves of the selected examples in the region from 215 to 350 mμ, the numerical data of these, together with other phenols, being tabulated in Tables IV and V.

The absorption bands may be classified into two groups. The first, appearing in the 240—250 mμ region with a greater intensity, can only include the samples without a rather bulky group in the α-position of the vinyl group; the K-band of styrene chromophore[17] is characteristic. Styrene has been shown to be planar and, according to the thermochemical data,[18] to be stabilized through conjugation between the benzene ring and the vinyl group by 1.5 kcal./mol. Though no direct data is available for *o*-vinylphenol, it is not unreasonable to regard the molecule as planar, since the K-band is actually observed and there is no benefit in the non-planar structure with a loss of the resonance energy. The α-methyl substituent is not enough to make this conjugation band vanish and so retains it as a shoulder. The second bands appear in the 270—300 mμ region, with the maximum molar absorptivity in the neighborhood of $2—3\times10^3$. This is assigned to the B-band of the benzene derivatives with an oxygen function, such as phenol and anisole.[19]

Those homologs with a rather bulky α-substituent have only the latter absorption; it is, in addition, very akin to that of phenol itself in its shape and in the location of the absorption peak. There is no conjugation between the vinyl group and the benzene ring in these cases. It is most probable that the loss of the conjugation is due to the non-bonded repulsion between the group(s) on the vinyl group on the one hand and the hydroxyl group (the methoxyl group, in the case of anisoles) and the hydrogen atom of the benzene ring ortho to the alkenyl group on the other, and that it arises from the rotation of the alkenyl group around the bond through which it is connected to the benzene ring and from the consequent non-coplanarity between the two planar systems concerned. As the angle between them increases by way of a change in the α-substituents from methyl to ethyl, isopropyl, and to *t*-butyl, the non-bonded repulsive energy is relieved at the expense of the resonance energy. The compromise is attained at a certain angle of twist; thus, the conformation of the *o*-(1-alkenyl)phenols is determined. Since their

Table IV. The ultraviolet absorptions of *o*-(1-alkenyl)phenols in *n*-heptane (H) and 95% aqueous ethanol (A)

No.	Solv.	K-band		B-band	
		λ_{max}	log ε_{max}	λ_{max}	log ε_{max}
I	H	245.5	3.96	296.5	3.49
				310.0	3.21
	A	246.5	4.04	302.5	3.63
II	H	243.0	3.41	271.5	3.15
				278.0	3.22
				283.5	3.09
	A	245.0	3.46	277.5	3.21
III	H			280.0	3.47
				286.0	3.34
	A			278.0	3.44
IV	H	235.0	3.79	282.0	3.41
	A	242.0	3.96	287.5	3.57
IV′	H	235.0	3.75	281.5	3.47
	A	242.0	3.98	287.0	3.56
V	H			281.5	3.48
				288.5	3.42
	A			278.0	3.45
				280.5	3.48
VI	H			281.0	3.48
				288.5	3.36
	A			280.0	3.47
VII	H	243.0	3.94	291.0	3.57
		247.0	3.97	300.0	3.55
		251.5	3.97	312.5	3.21
	A	245.0	3.99	298.0	3.67
		254.5	4.04	305.0	3.68
VIII	H			274.5	3.33
				279.5	3.37
	A			279.0	3.39

Table V. The ultraviolet absorptions of *o*-(1-alkenyl)anisoles (*o*-MeO·C_6H_4·CR^1=CR^2R^3) in *n*-heptane

No.	K-band		B-band	
	λ_{max}	log ε_{max}	λ_{max}	log ε_{max}
I	247.0	4.03	301.0	3.58
			312.5	3.32
II	237.0	3.84	273.5	3.30
			279.5	3.36
III			280.0	3.49
			287.0	3.36
IV	245.0	4.05	286.0	3.58
IV′	247.5	4.03	285.0	3.57
V			274.5	3.36
			280.0	3.38
VI			281.0	3.52
			289.0	3.45
VII	248.0	4.05	293.0	3.60
	253.0	4.06	300.0	3.61
VIII			275.0	3.37
			280.0	3.38

17) R. Y. Mixer, R. F. Hech, S. Winstein and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953).
18) H. Grasshof, *Chem. Ber.*, **84**, 916 (1951).
19) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, New York (1951).

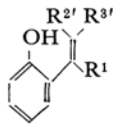
ultraviolet absorptions are, with one exception to be discussed later, very similar to the corresponding anisoles, it may be concluded that a third effect, that of the intramolecular interaction between the hydroxyl group and π-electrons on the conformation of the molecule, is a minor one and that the interaction takes place in a steric environment determined mainly by the resonance and the steric hindrance of the alkenyl group.

The trend mentioned in a) can now be explained. As the angle between the planes made by the benzene ring and the vinyl group increases, the localization of the π-electrons on the vinyl group commences to reduce their ionization potential, and so the strength as the electron donor of the π-electron system increases. This tendency is in the same direction as the inductive electron-donating ability of the alkyl groups, and it must be a factor in the observed substituent effect. In addition, the increased rotation of the plane of the vinyl group from that of the benzene ring is sure to produce a more favorable overlap between the π- and O–H orbitals, because the directional O–H anti-bonding orbital can approach the highest-occupied π-orbital in the vinyl group from the upper side of the electron cloud. Thus, the following order of the $\Delta\nu_{max}$ values is reasonable: II>I; III>I; V>IV; VIII>VII. It must be a reflection of the electronic effect that V and VII have greater $\Delta\nu_{max}$ than II and I, respectively. Nevertheless, the orders, II>III and V>VI, which are obtained by assuming that the $\Delta\nu_{max}$ values are direct measures of the strength of the interaction, can not be explained satisfactorily by the above interpretation. An inspection of the molecular models suggests that, when the α-substituents are greater than the methyl group, the dihedral angle made by the planes of the vinyl group and the benzene ring becomes great enough to make the hydroxyl and the vinyl groups overlap in the desired direction, but that the distance between the two groups increases a little, thus resulting in a reduction of their overlap. Thus, if the energy of the interaction is expressed by $\Delta\nu_{max}$, then methyl group as an α-substituent seems to afford the optimum among the two opposing steric effects, in addition to the favorable electronic effect.

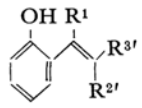
The steric effect may be an attractive means of interpreting of the decrease in the total intensity of the phenols with a rather sterically-crowded alkenyl group, since the bulky alkenyl group may dislocate the hydrogen atom of the hydroxyl group out of the benzene ring, thus giving a lower absorption intensity, from the analogy of comparison of the intensities of phenols and alcohols. However, this is not the case for sterically-hindered phenols. Ingold and Taylor[20] have reported that, among the homologous series of alkyl- or alkenyl-substituted phenols, the molar absorptivity did not change significantly. The present authors are tentatively inclined to attribute this phenomenon to the electronic effect of the substituent. That is, the vinyl group withdraws the electron, thus increasing the molar absorptivity of the ν_{O-H}, unless the steric effect is operating. When the steric effect forces the vinyl group to rotate out of the plane of the benzene ring, the vinyl group which is carrying some alkyl groups now acts as an electron-releasing group to lessen the molar absorptivity. We have to await further investigations to confirm this hypothesis, but the authors are postulating this on the basis that the compound V gives the least total intensity, whereas the second least is that of the compound VI, and the third least, that of the compound III.

As has been discussed above, the ultraviolet spectra indicate that I and VII are planar. If the molecule is perfectly planar, however, even the conformation IX cannot show the O–H···π interaction, because the hydroxyl group is pointing to the node of the π-orbitals on the vinyl group. A slight rotation around the bond which connects the vinyl group with the benzene ring will not lose the resonance energy materially, while the overlap between the O–H and π-orbitals may become possible; this must be the case in I.

The free ν_{O-H} in I is practically symmetric under the resolution of the present spectrometer. In VII, on the contrary, the band at the higher frequency is asymmetric. The tailing on the lower frequency side is reminiscent of the second absorption at 3601 cm^{-1}. Since it is shifted only 10 cm^{-1} from the free ν_{O-H}, the band is in its nature free. In this latter case, the basicity of the



IX



X

π-electron system as the proton acceptor is enriched by the β-alkyl substitution, and the hydroxyl group in the conformation X may be perturbed a little. Since the energy gained by the O–H···π interaction is not enough to compensate for the loss in the resonance energy in X, X cannot be a form which has a strongly interacting ν_{O-H}; it shows only a perturbed free ν_{O-H}.

When $R^{2'}$ is methyl, the vinyl group must be buttressed out of the plane of the benzene ring by the hydrogen at the 3-position with respect to the hydroxyl group, and some overlap between the hydroxyl group and the π-orbital becomes possible in X, giving an interacting ν_{O-H} curve different from that in IX. This must be the reason for the doublet interacting ν_{O-H} bands

20) K. U. Ingold and D. R. Taylor, *Can. J. Chem.*, **39**, 471 (1961).

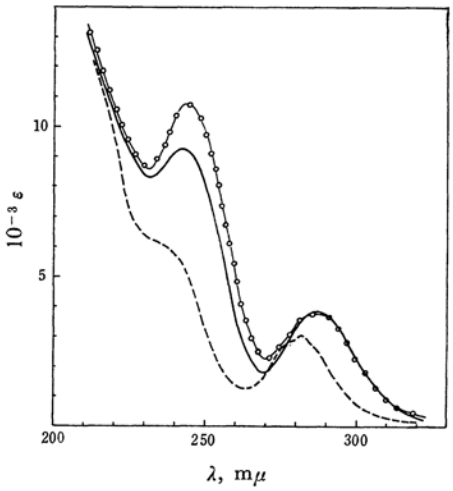


Fig. 7. The effect of solvents on the ultraviolet absorptions of *o*-isobutenylphenol (IV) and its methyl ether.

——— IV in 95% ethanol (A)
----- IV in *n*-heptane (H)
—○— IV methyl ether in A and H

in IV and IV′. This explanation has already been adopted by Baker and Shulgin[4] for the ν_{O-H} curves of IV and *o*-(*cis*-1-propenyl)phenol.

In this connection, it should be mentioned that the solvents and *O*-methylation have marked effects on the ultraviolet spectra of IV. Figure 7 shows the ultraviolet absorptions of IV in 95% aqueous ethanol and in *n*-heptane. The corresponding methyl ether has, in both solvents, the same absorption pattern as that of IV in ethanol, the data of which can be seen in Tables IV and V. Since the ether exhibits the K-band characteristic of the styrene chromophore, the molecule can be assumed to have a fairly planar structure. This must hold true in IV in ethanol. It is only in IV in *n*-heptane that the intramolecular interaction between the hydroxyl group and the π-electrons of the vinyl group takes place in this system. From the fact that it is only under these conditions that the K-band is weakened, it may be concluded that, when the interaction is possible, the angle made by the planes of the isobutenyl group and the benzene ring increases, thus producing better overlap of the orbitals of the hydroxyl group and the π-cloud on the isobutenyl group. This is the first observation of the effect of the intramolecular O–H$\cdots\pi$ interaction on the ultraviolet absorption spectra.

As regards the remaining assignment, concerning which of the two bands, at 3576 and 3539 cm^{-1}, should correspond to the conformations represented by IX and X, it is effective to compare the $\Delta\nu_{max}$ value of IV with those of I and VII. Since the $\Delta\nu_{max}$ values of 53.9 and 58.9 cm^{-1} of I and VII respectively, can be regarded as originating from the conformation IX, this form of IV must have a greater $\Delta\nu_{max}$ value because the basicity of the π-electrons is increased by one more methyl substitution. It is the band at 3539 cm^{-1} which conforms to this requirement; therefore, it may rather safely be concluded that the bands at 3576 and 3539 cm^{-1} should be assigned to the interacting hydroxyl groups in X and IX respectively.

A confirmative support of this assignment is now being investigated; it will be presented in a forthcoming paper.

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