

*Intramolecular Interaction between Hydroxyl Group and π -Electrons. XIII¹⁾.
 ν_{O-H} Absorption of 2,6-Diphenylphenol and the Related Compounds*

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It has been clarified, by a series of reports²⁾ from this laboratory, that, if a hydroxyl group and the π -electrons are located at suitable positions, the intramolecular interaction takes place to the extent which is determined by the structure of the molecule, the strength of the proton-donor, and the strength of the proton-acceptor. Thus, in a usual case, two O-H stretching (ν_{O-H}) absorption bands corresponding to the free and the interacting hydroxyl groups appear in the 3μ region. The above consideration leads to the deduction that, if the steric factors force the hydroxyl group to approach the π -electrons, there would be no free hydroxyl group. Tribenzylcarbinol³⁾ will be one of the examples in this category.

Pauling suggested⁴⁾ that the hydrogen atom of the phenolic hydroxyl group is located in the plane of the aromatic nucleus because of the resonance stabilization. Later, the suggestion was found to be true when 2,6-dichlorophenol was found⁵⁾ to possess only an O-H...Cl bonded hydroxyl group from the O-H stretching absorption in the infrared region and the microwave data also⁶⁾ led to the same conclusion as Pauling's suggestion. Therefore, if a phenol carries two groups at both ortho-positions of the hydroxyl group, which contain π -electrons, the compound can be another example which has no free hydroxyl group. In this paper, 2,6-diphenylphenol and the related compounds are taken as examples and absence or presence of the free hydroxyl group will be discussed in terms of the steric factor.

Experimental

Measurement and Calculation.—The measurement of the absorption in the 3μ region was carried out with a Perkin Elmer 112G grating spectrometer and quartz cells of 2 and 5 cm. lengths as required.

1) Part XII: M. Ōki and H. Iwamura, *Tetrahedron*, in press.

2) See Part XII of this series and the preceding papers cited therein.

3) M. Ōki and H. Iwamura, *This Bulletin*, 33, 1632 (1960).

4) L. Pauling, *J. Am. Chem. Soc.*, 58, 94 (1936).

5) O. R. Wulf, U. Liddel and S. B. Hendricks, *ibid.*, 58, 2287 (1936).

6) Presented by T. Kojima before the 13th Annual Meeting of the Physical Society of Japan at Kyoto, October 1958. Also private communication from Prof. K. Shimoda, The University of Tokyo.

Carbon tetrachloride was used as a solvent. The concentration was $1\sim 2\times 10^{-3}$ mol./l. and the spectral slit width 1 cm^{-1} in this region. The calculation of the band intensities was performed as reported previously⁷⁾, the integrated intensities being the authors' choice. However, on some occasions, the assumption that the appearance of the two peaks or the asymmetric curve indicates the overlap of the two symmetric curves, each of which is expressed by the Lorentz function, is proved to be false, suggesting the presence of the third band. In such cases, the molecular extinction coefficients were taken instead of the integrated intensities for the convenience of the calculation.

Materials.—The compounds used for this work are known unless otherwise mentioned and their physical constants agreed with those reported in the literature.

4-Nitro-2,6-diphenylphenol.—This compound was prepared by condensation of nitromalonaldehyde and dibenzyl ketone according to the method described by Hill⁸⁾. The melting point of the compound was 115°C after four recrystallizations from ethanol. However, the melting point was suddenly raised up to 135°C when a large crystal was scratched, and the compound melting at 115°C has never been obtained thereafter. This phenomenon must be a type of polymorphism but the physical measurement was not carried out with the unstable form because of the lack of the sample. The melting point of the stable form was $135\sim 136^\circ\text{C}$ (lit.⁸⁾, $135\sim 136^\circ\text{C}$).

3,5-Dimethyl-2,6-dipropenylphenol.—A mixture of 20 g. (0.123 mol.) of 2-allyl-3,5-dimethylphenol, 15.7 g. (0.13 mol.) of allyl bromide, 18.0 g. (0.13 mol.) of potassium carbonate and 50 ml. of acetone was refluxed for ten hours. The filtrate from the reaction mixture was fractionated and gave 22 g. (87%) of allyl 2-allyl-3,5-dimethylphenyl ether, b. p., $148\sim 150^\circ\text{C}/15\text{ mmHg}$. The ether was refluxed with an equal amount of *N,N*-diethylaniline for three hours and, after cooling, the mixture was diluted with petroleum ether. The solution was shaken with dilute hydrochloric acid to remove *N,N*-diethylaniline and then extracted with Claisen's alkali. When the alkaline solution was diluted with water, an oil separated, which was distilled to give 83% 2,6-diallyl-3,5-dimethylphenol, b. p., $105\sim 106^\circ\text{C}/2\text{ mmHg}$, n_D^{20} 1.5410.

Found: C, 82.94; H, 9.05. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97%.

The phenol (10 g.) was dissolved in 30 ml. of

7) M. Ōki and H. Iwamura, *This Bulletin*, 32, 567 (1959).

8) H. B. Hill, *Am. Chem. J.*, 24, 1 (1900).

methanol containing 10 g. of potassium hydroxide and the solvent was evaporated until the temperature of the solution rose to 130°C. The mixture was refluxed for twenty hours at that temperature, cooled, diluted with water and extracted with ether. The ethereal extract was dried over potassium carbonate and fractionated to give 7.3 g. of 3,5-dimethyl-2,6-dipropenylphenol, b. p., 155°C/18 mmHg. The compound solidified and was recrystallized from petroleum ether. The melting point was 59~60°C.

Found: C, 83.04; H, 9.12. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

Results and Discussion

The ν_{O-H} absorptions of substituted 2,6-diphenylphenols and of 2-chloro-6-phenylphenol are summarized in Table I. As expected, these phenols did not possess absorption at the position (ca. 3600 cm^{-1}) where ordinary phenols do, but at the position which is too low a wave number to be assigned to the free hydroxyl group. Absorptions of 4-substituted 2,6-diphenylphenols are symmetric and appear at lower wave numbers as the substituent at 4 position is more electronegative, the phenomenon being common for the ordinary phenols⁹⁾ and 4-substituted 2,6-di-*tert*-butylphenols¹⁰⁾.

TABLE I. ν_{O-H} ABSORPTIONS OF PHENOLS
[2,4,6-XY(C_6H_5) C_6H_2OH]

Substituent X Y	ν_{max} cm^{-1}	ϵ_{max}	$A \times 10^{-4}$ $mol^{-1} l. cm^{-2}$
C_6H_5 NO_2	3531.2	366	2.54
C_6H_5 H	3553.3	305	1.93
C_6H_5 NH_2	3567.9	305	1.85
Cl H	3550.2	41	0.30
	3535.6	184	1.22

Since the hydroxyl group of the 4-substituted 2,6-diphenylphenols is considered to be all interacting with the π -electrons of the adjacent phenyl groups, it may be interesting to compare the absorptions of these compounds with those of the corresponding phenols in benzene. Thus the ν_{O-H} absorption of *p*-nitrophenol was measured in benzene solution, the absorption maximum being at 3527.4 cm^{-1} . The difference (3.8 cm^{-1}) from 4-nitro-2,6-diphenylphenol is rather small and supports the above mentioned idea. However, it must be considered that this difference is the combination of the solvent effect and the electronic effect of the substituent. 4-Nitro-2,6-diphenylphenol in benzene showed the ν_{O-H} absorption at 3523.3 cm^{-1} . Therefore, the difference between 3527.4 cm^{-1} and 3523.3 cm^{-1} may be attributed to the effect of two phenyl groups at *o*-positions. Phenol in ben-

zene is known to show its ν_{O-H} maximum at 3562 cm^{-1} ¹¹⁾. The deviation from 3553.3 cm^{-1} may be interpreted similarly.

2-Chloro-6-phenylphenol has its ν_{O-H} absorption maximum at 3535.6 cm^{-1} but the curve shows a shoulder at the higher wave number side. Therefore, the curve was divided into two, assuming that it was an overlap of two symmetric curves which could be expressed by the Lorentz function (Fig. 1). The authors

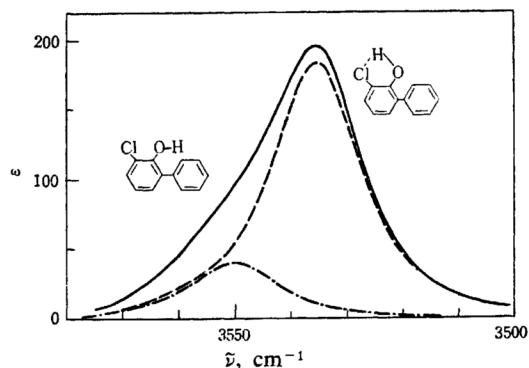


Fig. 1. ν_{O-H} absorption of 3-chloro-2-hydroxybiphenyl.

— the observed curve
--- O-H...Cl
- · - · O-H... π

have data, concerning the interacting form of 2-hydroxybiphenyl and the hydrogen-bonded form of *o*-chlorophenol, which reveal the fact that the former is located at 3565.0 cm^{-1} and the latter at 3547.0 cm^{-1} . Then it will be most probable to assign the band maximum at 3535.6 cm^{-1} to the hydrogen-bonded form of the hydroxyl group with ortho chlorine atom and that at 3550.2 cm^{-1} to the interacting form with π -electrons. The lowering of the wave number must be derived from the effect of the electron-drawing substituents. As to the integrated intensities of each component, the O-H...Cl bonded form is apparently large, but it may not necessarily mean that the molecule having the hydrogen bond between the hydroxyl group and the chlorine atom is greatly in the majority, since it is a well-known fact that the absorption intensity per molecule becomes stronger on O-H...Cl hydrogen bond formation.

As the source of the π -electrons, the propenyl group might be considered equally effective with the aromatic nucleus. Thus, various phenols containing propenyl groups are prepared and their ν_{O-H} absorptions examined. The results are summarized in Table II. As is clear from Table II, replacement of a phenyl

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

10) K. U. Ingold, *Can. J. Chem.*, **38**, 1092 (1960).

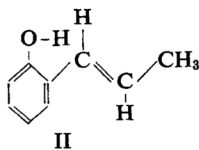
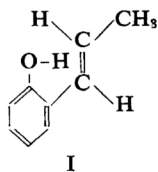
11) M. L. Josien, P. Dizabo and P. Saumagne, *Bull. soc. chim. France*, **1957**, 423.

TABLE II. ν_{O-H} ABSORPTION OF PHENOLS CONTAINING PROPENYL GROUP [2,6-X(CH₃CH=CH)C₆H₃OH]

X	O-H	ν_{max} cm ⁻¹	ϵ_{max}^a	$\Delta\nu_{max}$ cm ⁻¹
H	f*	3611.1	159.0	58.8
	i*	3552.2	34.0	
CH ₃ CH=CH-	f	3603.5	78.0	57.5
	i	3546.0	72.0	
C ₆ H ₅	f	3607.4	21.3	44.2
	i	3563.2	241.6	

* f and i denote the free and the interacting forms, respectively.

group by a propenyl group gives rise to the appearance of an absorption due to the free form of the hydroxyl group and this phenomenon is enhanced when two propenyl groups are introduced in place of the phenyl groups of 2,6-diphenylphenol. One of the possibilities which reasonably explains the phenomenon is the concept of the rotational isomerism. *o*-Propenylphenol is taken as an example for the explanation, because of its simplicity. In this case, the consideration of the *cis* form⁴⁾ will suffice to cover the possibilities, since 2,6-dipropenylphenol contains only this form whichever direction the O-H points.



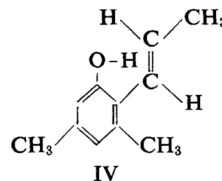
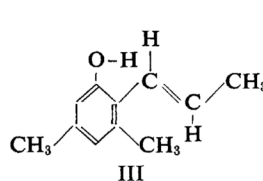
The authors are assured that *o*-propenylphenol assumes the *trans* form with respect of the ethylenic linkage¹²⁾. Then there will be two rotational isomers about the C_{Ph}-C_α axis, being represented by I and II. Structure II will possess a free hydroxyl group, if a pair of π -electrons are necessary for the interaction and/or if the hydrogen atom of the hydroxyl group must approach from the upper side to the π -electron cloud in order to establish the interaction. Thus, structure I may be the only form which possesses the interaction in *o*-propenylphenol. The availability of the π -electrons of 2,6-diphenylphenol, on the other hand, will not be altered no matter what rotational position is taken, because the structure corresponding to I is always involved in this compound. If the above assumption is correct, a compound which is forced to take structure I will have no free hydroxyl group. The enforcement may be given by the steric hindrance. 3,5-Dimethyl-2-propenylphenol and 3,5-dimethyl-2,6-dipropenylphenol were chosen

TABLE III. ν_{O-H} ABSORPTIONS OF 6-SUBSTITUTED 3,5-DIMETHYL-2-PROPENYLPHENOLS [6,3,5,2-X(CH₃)₂(CH₃CH=CH)C₆H-OH]

X	O-H	ν_{max} cm ⁻¹	ϵ_{max}^a	$\Delta\nu_{max}$ cm ⁻¹
H	f	3607.7	19.4	68.5
	i	3539.2	101.9	
CH ₃ CH=CH-	f	—	—	—
	i	3526.5	120.2	

as examples. The results are shown in Table III.

The steric effect of the methyl group may be too great to assume structure III and the structure IV becomes favorable. Therefore, the structure of 3,5-dimethyl-2-propenylphenol may be represented by IV. The structure IV is, at the same time, favorable for the internal interaction and these considerations predict that 3,5-dimethyl-2-propenylphenol contains more interacting molecules than 2-propenylphenol in spite of the fact that the methyl group is the electron-donating group which weakens the proton donating power of the phenols. Comparison of the data in Tables II

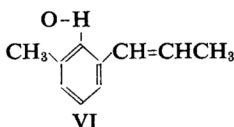
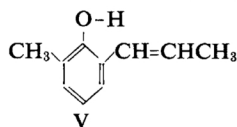


and III indicates that this is really the case. Since 2,6-dipropenyl-3,5-dimethylphenol has two propenyl groups which are sterically enforced to take the structure as IV, it is naturally expected that this compound will possess single ν_{O-H} absorption at a rather low frequency. Actually a perfectly symmetrical band is found at 3526.5 cm⁻¹. Hence, it is proved that the propenyl group can also be the source of the π -electrons which give the ν_{O-H} absorption at extraordinarily low frequency.

As to the steric effect on the interaction, it may also be interesting to examine the ν_{O-H} absorption of 2-methyl-6-propenylphenol. Since the hydroxylic hydrogen atom is located on the plane of the benzene nucleus, it is reasonably expected that, in *o*-cresol, the molecule will be more stable when the hydroxylic hydrogen is located on the opposite side of the methyl group. Therefore, in 2-methyl-6-propenylphenol, the contribution of structure V may be more than that of structure VI. This consideration suggests that there will be more molecules, which have the intramolecular interaction between the hydroxyl group and π -electrons, in 2-methyl-6-propenylphenol than in 2-propenylphenol. The former compound has one absorption maximum at 3617.0 cm⁻¹.

12) It is supported by the fact that *o*-propenylphenol possesses an absorption at 968.6 cm⁻¹ due to C-H out-of-plane deformation.

($\epsilon^a_{\max} = 83.8$) and another at 3548.3 cm^{-1} ($\epsilon^a_{\max} = 39.3$). Comparison of the results with these compounds indicates that the above consideration is correct, since both $\Delta\nu_{\max}$ and ϵ_i/ϵ_f are greater in 2-methyl-6-propenylphenol.



The $\nu_{\text{O-H}}$ absorptions of the precursors of the propenyl compounds, the phenols carrying allyl groups, are also examined in connection with the freedom of rotation and the basicity of the ethylenic linkage. The results are shown in Table IV. The diagrams of the $\nu_{\text{O-H}}$ absorptions of 2-allyl-3,5-dimethylphenol and 2,6-diallyl-3,5-dimethylphenol are also given in Fig. 2, because of the difficulty of understanding the matter from the mere numericals. The ϵ_i/ϵ_f of the phenols carrying allyl groups are always greater than those of the propenylphenol derivatives unless they carry methyl groups at 3 and 5 positions. This will mean that the effect of the basicity of the ethylenic

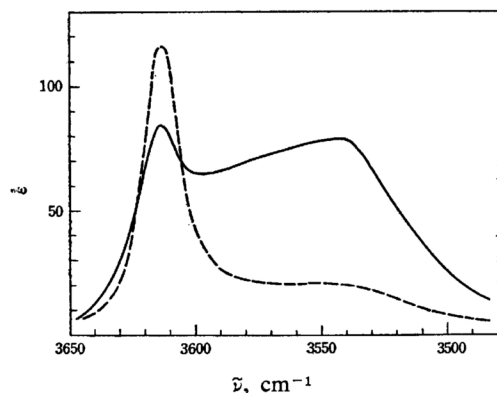


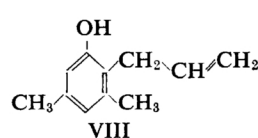
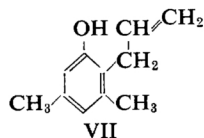
Fig. 2. The apparent $\nu_{\text{O-H}}$ absorption of 2,6-diallyl-3,5-dimethylphenol (—) and 2-allyl-3,5-dimethylphenol (---).

TABLE IV. $\nu_{\text{O-H}}$ ABSORPTIONS OF PHENOLS CARRYING ALLYL GROUPS

Phenol	O-H	ν_{\max} cm^{-1}	ϵ^a_{\max}	$\Delta\nu_{\max}$ cm^{-1}
3-Allyl-2-hydroxy-biphenyl	f	3609.2	13.9	46.0
	i	3563.2	259.5	
2,6-Diallylphenol	f	3616.0	45.5	71.7
	i	3544.3	88.3	
2-Allyl-3,5-dimethylphenol	f	3614.0	116.0	66.8
	i	3547.2	20.6	
2,6-Diallyl-3,5-dimethylphenol	f	3614.0	84.5	72
	i	3542*	79	
2-Allyl-6-methylphenol	f	3619.0	77.8	71.0
	i	3548.0	52.3	

* Four place number is given because of the uncertainty due to the broadness of the band (see Fig. 2).

bond plays the major role and the rotation about $\text{C}_{\text{Ph}}-\text{C}_\alpha$ axis the minor role, for the interaction. This is because the basicity of the ethylenic linkage in the propenylphenols is rather low due to the conjugation with the benzene nucleus. In contrast with the above situation, when methyl groups are present at 3 and 5 positions, the allylphenols show smaller ϵ_i/ϵ_f value than those of the corresponding propenylphenols. This is without doubt caused by the freedom of rotation. That is, it is possible for "cis" 2-allyl-3,5-dimethylphenol to take the conformations illustrated, for example, by VII and VIII, which are unfavorable for the intramolecular interaction. The possibilities of taking these unfavorable structures are owing to the rotation about $\text{C}_{\text{Ph}}-\text{C}_\alpha$ and $\text{C}_\alpha-\text{C}_\beta$ axes, while, in 3,5-dimethyl-2-propenylphenol, the rotation about the $\text{C}_{\text{Ph}}-\text{C}_\alpha$ is at least partially restricted due to the resonance stabilization and the steric interference of the methyl group, possibly causing all the cis forms to be the interacting. Baker and Shulgin¹³⁾ have mentioned that the steric effect of the methyl group in 2-allyl-3,5-dimethylphenol is favorable for the interaction, when compared with 2-allylphenol, probably because the contribution of structures such as VIII is less. Nevertheless, the conclusion is not contradictory, since it may be possible for



structure VIII to be present to a small extent and it is out of the question at the present time which structure is the main contribution for the free cis form.

When an asymmetrical band is assumed to be an overlap of the symmetrical bands, the compounds which contain one or two propenyl groups at ortho positions of the hydroxyl group usually possess three $\nu_{\text{O-H}}$ bands unless the absorption corresponding to the interacting form is very strong. In the case of 2-phenyl-6-propenylphenol, the three bands may be reasonably assigned to the free, the interacting with the phenyl group, and the interacting with the propenyl group. However, the situation must be further studied with other compounds before obtaining a general conclusion.

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