Intramolecular Interaction between Hydroxyl Group and π-Electrons. XIV[1]. *Electronic Effect of the Substituents on the Interaction in 2-Hydroxybiphenyls*

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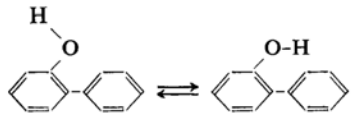
(Received March 27, 1961)

Since the observation by Wulf and his co-workers[2], it has been occasionally reported that 2-hydroxybiphenyl shows doublet O–H stretching band in the infrared absorption spectrum. The phenomenon was explained on the assumption that 2-hydroxybiphenyl would be composed of cis and trans isomers. Such an explanation had been adopted by Pauling[3] for the like phenomenon observed in the infrared spectrum of *o*-chlorophenol. As the cis isomer seems to be less stable because of



trans cis

the steric interference, there must exist a cause which makes the appearance of this form possible. Wulf and his co-workers attributed stabilizing force to the approach of the hydroxyl group to the first carbon atom of the benzene ring which is ortho to the hydroxyl group and to the consequent attraction between them, but failed to show the true nature. Later, Mecke[4] explained the phenomenon from the polarizable nature of the π-electrons in the benzene nucleus and assumed that a so-called π-complex was formed intramolecularly, without giving further details. Recently Musso and von Grunelius[5] reported some ν_{O-H} absorptions of 2,2′-dihydroxybiphenyl and their derivatives and discussed the competitive intramolecular hydrogen bond formation between O–H···O and O–H···π systems, with special reference to the geometrical consideration. The examples are, however, too complicated to help us to understand the nature of the latter interaction separately.

The present authors have preliminarily reported[6] that the energies of the intramolecular interaction between the hydroxyl group and the π-electrons in 2-hydroxy-4- and -4′-nitrobiphenyls are 2.5 and 0.9 kcal./mol., respectively. The present study was initiated on the expectation that the electronic effect of the substituents on the interaction will provide additional informatin in regard to the true nature of the interaction.

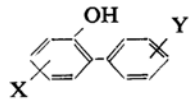
Experimental

Measurement and treatment of the infrared spectra were carried out as described previously[7]. The known samples were prepared according to the literature, and the new as described below. Their physical constants and analytical data are listed in Table I.

Materials. — *2-Hydroxyl-4-methoxybiphenyl.* — 2-Amino-4-methoxybiphenyl[13] (0.02 mol., 4.0 g.) was dissolved in aqueous sulfuric acid (4.5 ml. of concentrated sulfuric acid and 6 ml. of water) and diazotized with 1.5 g. of sodium nitrite in 3 ml. of water. The excess of nitrite was decomposed by a lump of urea and the solution was poured into 20 ml. of boilng 30% aqueous sulfuric acid. The separated dark oil was taken up in ether and the ether layer was extracted thrice with 20% aqueous sodium hydroxide solution. The alkaline extract was acidified and extracted with ether. The ether extract was treated with active charcoal, filtered and evaporated. The tarry residue was extracted with hot petroleum ether and the extract deposited prisms after cooling. The pure sample was obtained by recrystallization from petroleum ether.

1) Part XIII: M. Ōki, H. Hosoya and H. Iwamura, This Bulletin, 34, 1391 (1961).
2) O. R. Wulf, U. Liddel and S. B. Hendricks, *J. Am. Chem. Soc.*, 58, 2290 (1936).
3) L. Pauling, ibid., 58, 94 (1936).
4) W. Lüttke and R. Mecke, *Z. Elektrochem.*, 53, 241 (1949).
5) H. Musso and S. von Grunelius, *Ber.*, 92, 3101 (1959).
6) M. Ōki, H. Iwamura and Y. Urushibara, This Bulletin, 31, 770 (1958).
7) M. Ōki and H. Iwamura, ibid., 32, 567 (1959).

TABLE I. PHYSICAL CONSTANTS AND ANALYTICAL DATA OF THE SUBSTITUTED 2-HYDROXYBIPHENYLS



Substituent X	Substituent Y	M. p. or b. p. observed (lit.)	Analytical Data: Found C	Found H	Found N	Calcd. C	Calcd. H	Calcd. N
H	H	59°C (59°C[8])						
4-MeO	H	66~67°C	78.08	6.25		77.98	6.04	
4-Cl	H	38.5~39°C	70.46	4.43	(Cl=17.39)	70.42	4.43	(Cl=17.33)
4-NO_2	H	103~105°C (102°C[9])						
5-Et	H	122°C/2 mmHg (171~172°C/18 mmHg[10])	84.92	7.09		84.81	7.12	
5-PhN_2	H	95~96°C (94~95°C[11])						
5-CO_2Me	H	128~129.5°C	73.81	5.52		73.67	5.30	
5-NO_2	H	128°C (128°C[11])						
H	3'-MeO	90~91°C	78.13	6.09		77.98	6.04	
H	3'-CO_2Me	88~89°C	73.77	5.48		73.67	5.30	
H	3'-NO_2	99.5~100°C	66.78	4.22	6.44	66.97	4.22	6.51
H	4'-MeO	65~65.5°C	78.13	6.15		77.98	6.04	
H	4'-Cl	51~52°C (53°C[12])						
H	4'-Br	60°C (60~61°C[12])						
H	4'-I	74°C	48.79	3.15		48.67	3.06	
H	4'-CO_2Me	133~133.5°C	73.85	5.43		73.67	5.30	
H	4'-NO_2	123~124°C (122°C[12])						

4-Chloro-2-hydroxybiphenyl.—A half moles (86.3 g.) of 4-chloro-2-nitroaniline[14] was diazotized in 150 ml. of concentrated hydrochloric acid with 35 g. of sodium nitrite in 50 ml. of water, and decomposed in the presence of 2 l. of thiophene free benzene by adding an excess of sodium acetate. Stirring was continued over-night. The benzene layer was washed with aqueous sodium hydroxide and the solvent evaporated. 4-Chloro-2-nitrobiphenyl distilled at 160~166°C/2 mmHg, and solidified in the receiver. It was recrystallized from petroleum ether-benzene to give prisms melting at 53°C (lit.[15], 52~53°C). The nitro-compound (23 g., 0.1 mol.) was catalytically hydrogenated over platinized Raney nickel[16] in ethanol, 6.5 l. of hydrogen being absorbed in 2 hr. 2-Amino-4-chlorobiphenyl was, without further purification, diazotized in aqueous sulfuric acid with sodium nitrite and decomposed by pouring into 30% aqueous sulfuric acid. 4-Chloro-2-hydroxybiphenyl was recrystallized from carbon tetrachloride to form prisms.

5-Ethyl-2-hydroxybiphenyl.—To a solution of 5 g. of 5-acetyl-2-hydroxybiphenyl[10] in 100 ml. of acetic acid was added a few drops of 3 N hydrochloric acid and 100 mg. of platinum oxide. On shaking under hydrogen atmosphere, 1.1 l. of hydrogen was absorbed under the atmospheric pressure and at the room temperature. The solvent was evaporated under reduced pressure and the residue was distilled at 122°C/2 mmHg, giving the desired phenol, n_D^{15} 1.5893.

2-Hydroxy-5-methoxycarbonylbiphenyl.—5-Acetyl-2-hydroxybiphenyl[10] in pyridine was oxidized with iodine to the corresponding β-ketoalkylpyridinium iodide, which was cleft by aqueous alcoholic sodium hydroxide to 2-hydroxybiphenyl-5-carboxylic acid, as is specified by King[17]. The carboxylic acid was recrystallized from benzene to give plates melting at 148°C (lit.[18], 148~149°C). A suspension of 8 g. of the hydroxycarboxylic acid in 100 ml. of methanol was saturated with hydrogen chloride, refluxed on a water bath for two hours and then poured into 500 ml. of ice-water. The crystals were collected and recrystallized from benzene to give plates.

2-Hydroxy-3'-methoxybiphenyl.—To a mixture of 30 g. of *m*-bromoanisole and 50 g. of *o*-nitrochlorobenzene was added in five portions 50 g. of copper bronze at 200°C. The temperature was kept at 200~240°C for five hours longer. After cooling, the solid mass was extracted with acetone and the extract was fractionally distilled under diminished pressure, the fraction boiling at 150~175°C/1~2 mmHg being collected. On fractional recrystalliza-

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14) M. A. F. Holleman, *Rec. trav. chim. Pay-Bas*, **34**, 207 (1915).
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tion of the distillate from methanol, 10 g. of 3'-methoxy-2-nitrobiphenyl, melting at 83~84°C was obtained. Found: N, 6.28. Calcd. for $C_{13}H_{11}O_3N$: N, 6.11%. Catalytic reduction of the nitrocompound gave 2-amino-3'-methoxybiphenyl which was characterized as the acetyl derivative (m. p., 114°C) and analyzed. Found: C, 74.88; H, 6.48; N, 5.81. Calcd. for $C_{15}H_{15}O_2N$: C, 74.66; H, 6.27; N, 5.81%. Diazotization of the amine and the subsequent hydrolysis gave 2-hydroxy-3'-methoxybiphenyl.

2-Hydroxy-3'-methoxycarbonylbiphenyl.—2-Amino-3'-methoxycarbonylbiphenyl[19] was diazotized in aqueous sulfuric acid and decomposed at 80°C. The oily layer was extracted with ether and washed with aqueous sodium carbonate solution. The solvent was evaporated and the residue was recrystallized from carbon tetrachloride, to give prisms.

2-Hydroxy-3'-nitrobiphenyl.—To a solution of 3 g. of 2-methoxy-3'-nitrobiphenyl (m. p., 68.5~69°C)[20] in 50 ml. of acetic acid was added 20 ml. of 48% aqueous hydrobromic acid. The mixture was warmed on a water bath for five hours, when the oily layer disappeared. The solution was concentrated under reduced pressure and the residue was diluted with 50 ml. of water. Brown oil was extracted with benzene and the benzene layer was extracted with 20% aqueous sodium hydroxide. The aqueous layer was acidified and the product recrystallized from methanol to form needles.

2-Hydroxy-4'-methoxybiphenyl.—4'-Methoxy-2-nitrobiphenyl[21] (2.3 g., 0.01 mol.) was reduced with 13 g. of stannous chloride dihydrate and 15 ml. of concentrated hydrochloric acid in 20 ml. of alcohol by refluxing for two hours. The amine[22] in 30 ml. of water and 2 ml. of sulfuric acid was diazotized with 0.7 g. of sodium nitrite in 2 ml. of water and hydrolyzed as usual to the desired phenol. The phenol was recrystallized from a mixture of carbon tetrachloride and petroleum ether (1 : 1).

2-Hydroxy-4'-iodobiphenyl.—4'-Amino-2-hydroxybiphenyl[23] (3.7 g., 0.02 mol.) was diazotized in aqueous sulfuric acid (2.4 g. of concentrated sulfuric acid and 20 ml. of ice-water) with 1.5 g. of sodium nitrite in 3 ml. of water. The diazonium solution was added dropwise to the boiling aqueous potassium iodide solution (4 g. of potassium iodide in 5 ml. of water) and the separated brown oil was extracted with ether. On evaporation the ether extract gave heavy oil which was heated with hot petroleum ether and decanted. Repetition of the process gave thick prisms.

2-Hydroxy-4'-methoxycarbonylbiphenyl.—To a mixture of 50 g. (0.32 mol.) of *o*-nitrochlorobenzene and 26 g. (0.1 mol.) of methyl *p*-iodobenzoate, heated at 230~240°C, was added 80 g. of copper bronze for three hours. After cooling, the mass was extracted with acetone using a Soxlet extractor. The acetone extract deposited a large amount of 2,2'-dinitrobiphenyl, which was filtered off. The mother liquor was evaporated and the residue was refluxed with 500 ml. of ethanol and 160 ml. of 10% aqueous sodium hydroxide for three hours. The mixture was diluted with water to make up 1 l. and boiled for several minutes with active charcoal and then filtered. The filtrate was acidifed and the precipitate was collected. Recrystallization from acetic acid gave 6 g. of 2-nitrobiphenyl-4'-carboxylic acid, melting at 247°C (lit.[24], 250°C). It was catalytically hydrogenated over platinum oxide, as described in the literature[24]. The aminocarboxylic acid was diazotized and hydrolyzed as usual. The crude hydroxycarboxylic acid was used, without further purification, for the preparation of the corresponding ester. Esterification was carried out by saturating the methanolic suspension with hydrogen chloride nd refluxing the mixture for two hours. Recrystallization from carbon tetrachloride gave prisms.

Results and Discussion

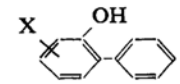
It must be confirmed in the first place that two bands which appear in the 3 μ region in the infrared are not derived from the intermoleculer hydrogen bonding but from the intramolecular origin. With 2-hydroxybiphenyl, the infrared spectra were measured over the concentration range from 0.5 to 0.001 mol./l. in carbon tetrachloride. At concentration of over 0.1 mol./l., a third band appears at 3460 cm^{-1}, which is assigned to the ν_{O-H} of the associated hydroxyl group, but, below 0.01 mol./l., this band disappears and the ratio of intensities of the remaining ones scarcely depend upon concentraion. All the following data were obtained in these conditions, usually 0.001 mol./l. solution being employed.

The absorption at the higher wave number of 2-hydroxybiphenyl is located at 3607 cm^{-1} and, referring to the free ν_{O-H} of phenol, 3610 cm^{-1} [25], is assigned to the trans form of the molecule having the free hydroxyl group (f). The other absorption at the lower wave number is tentatively assigned to the cis form having the intramolecular interaction with π-electrons of another benzene ring and having a less force constant of the O-H stretch (i). The intensities and the maxima of these two bands vary considerably with different substituents on each benzene ring. The apparent effect of the substituents on the infrared absorption spectra is shown in Figs. 1 and 2, and the numerical data are in Tables II and III. If the varied band properties can be explained reasonably in terms of the intramolecular interaction with π-electrons, the above assignment will be justified.

Substitution has been confined to the positions at 4, 5, 3' or 4' of the hydroxyl group

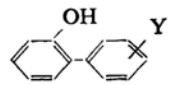
19) R. Adams and T. L. Cairns, *J. Am. Chem. Soc.*, **61**, 2179 (1939).
20) W. J. Dunstan and G. K. Hughes, *J. Proc. Roy. Soc. N. S. Wales*, **80**, 77 (1947); *Chem. Abstr.*, **42**, 4161a (1948).
21) B. Jones and F. Chapman, *J. Chem. Soc.*, **1952**, 1832.
22) I. G. M. Campbell and D. J. Morrill, ibid., **1955**, 1666.
23) W. G. Christiansen and S. E. Harris, *J. Am. Pharm. Assoc.*, **22**, 723 (1933); *Chem. Abstr.*, **29**, 4382 (1935).
24) I. G. M. Campbell, *J. Chem. Soc.*, **1950**, 3113.
25) P. J. Stone and H. W. Thompson, *Spectrochim. Acta*, **10**, 17 (1957).

Table II. ν_{O-H} absorptions of 2-hydroxybiphenyls substituted in A-ring



X	OH	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
H	f	3607.0	18.2	0.20	42.0	6.4
	i	3565.0	15.0	1.28		
4-MeO	f	3606.0	22.8	0.20	43.2	7.2
	i	3562.8	15.8	1.44		
4-Cl	f	3601.5	20.8	0.20	43.3	7.3
	i	3558.2	15.6	1.45		
4-NO_2	f	3597.8	19.6	0.23	44.0	7.4
	i	3553.8	19.4	1.70		
5-Et	f	3610.2	20.3	0.23	41.5	5.6
	i	3568.7	16.0	1.27		
5-PhN_2	f	3599.0	24.0	0.21	45.8	8.3
	i	3553.2	16.8	1.74		
5-CO_2Me	f	3596.7	18.6	0.18	46.1	8.8
	i	3550.6	15.8	1.59		
5-NO_2	f	3590.0	24.6	0.22	47.4	8.6
	i	3542.6	16.6	1.90		

Table III. ν_{O-H} absorptions of 2-hydroxybiphenyls subsituted in B-ring



Y	O-H	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
H	f	3607.0	18.2	0.20	42.0	6.4
	i	3565.0	15.0	1.28		
3′-MeO	f	3607.1	17.4	0.15	47.9	9.3
	i	3559.2	17.0	1.40		
3′-CO_2Me	f	3605.0	18.8	0.44	30.7	2.4
	i	3574.3	17.0	1.06		
3′-NO_2	f	3602.6	19.0	0.99	20.4	0.66
	i	3582.2	16.6	0.65		
4′-MeO	f	2607.1	18.0	0.15	47.6	9.7
	i	3559.5	17.6	1.45		
4′-Cl	f	3605.0	17.8	0.37	35.0	3.1
	i	3570.0	15.6	1.14		
4′-Br	f	3606.0	14.8	0.36	34.9	3.3
	i	3576.1	16.0	1.19		
4′-I	f	3605.3	13.4	0.32	35.1	4.1
	i	3570.2	16.0	1.32		
4′-CO_2Me	f	3304.4	17.2	0.34	33.0	3.6
	i	3571.4	16.2	1.21		
4′-NO_2	f	3602.1	17.2	0.79	22.5	0.97
	i	3579.6	17.6	0.77		

Added in proof: After this paper had been received, W. Beckering (*J. Phys. Chem.*, 65, 206 (1961)) reported O-H···π interaction in some of the examples included in the present study.

at 2-position in biphenyl skeleton in order to avoid either another intramolecular hydrogen bond[1] and/or steric influence[26], which make the consideration more complex. For the sake of convenience, the substituted 2-hydroxybiphenyls are calssified into two groups; one is those with the substituent on the benzene ring (A) which bears the hydroxyl group and the other those on the other ring (B).

The varied $\Delta\nu_{max}$ and A_i/A_f in Tables II and III may be considered to correspond to the strength of the interaction, since the former is known to be approximately proportional to the enthalpy (Eq. 1)[27] and the latter to the equilibrium constant (Eq. 2)[28] of the interaction. Therefore, neither value should be independent of the other and the relation between $\Delta\nu_{max}$ and $\log(A_i/A_f)$ must be linear (Eq. 3) if ΔS of the interaction, and the constants a and b are independent of the

26) Unpublished work. See also Ref. 5.

27) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, 5, 839 (1937).

28) M. Ōki and H. Iwamura, This Bulletin, 33, 1600 (1960).

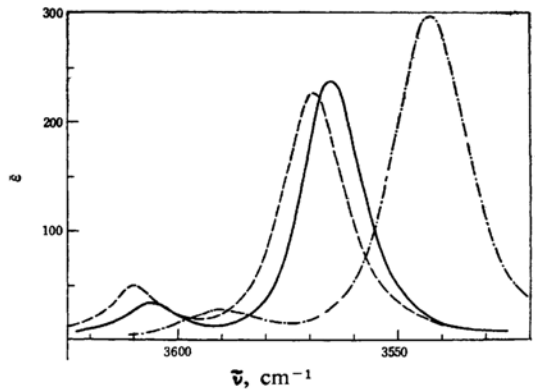


Fig. 1. The apparent ν_{O-H} absorptions of 2-hydroxybiphenyls (A).

——— 2-hydroxybiphenyl
——— 5-ethyl-2-hydroxybiphenyl
—·—· 2-hydroxy-5-nitrobiphenyl

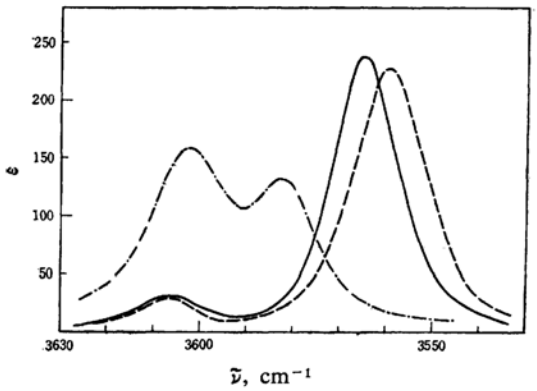


Fig. 2. The apparent ν_{O-H} absorptions of 2-hydroxybiphenyls (B).

——— 2-hydroxybiphenyl
——— 2-hydroxy-3′-methoxybiphenyl
—·—· 2-hydroxy-3′-nitrobiphenyl

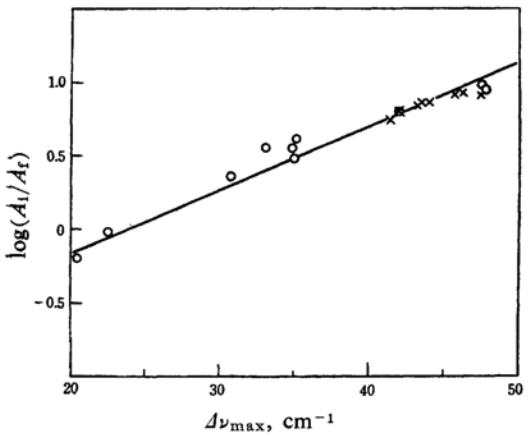


Fig. 3. Relation between $\log(A_1/A_f)$ and $\Delta\nu_{max}$, the cross and circle representing 2-hydroxybiphenyls substituted in the A and B ring, respectively.

substituents. The case is realized from Fig. 3. Strictly speaking, however, the line has a little convex curvature upwards, which may be attributed to the second order term neglected in

$$-\Delta H = a\Delta\nu_{max} \quad (1)$$

$$K = bA_1/A_f \quad (2)$$

$$RT\cdot\ln(A_1/A_f) = a\Delta\nu_{max} + (T\Delta S - RT\cdot\ln b) \quad (3)$$

the approximation, assuming the constancy of a, b and ΔS. From the gradient of the line, a constant a in the equation can be estimated to be 0.057 kcal.cm^{-1} at the measured temperature. It may be expressed otherwise by saying that the wave number shift of 18 cm^{-1} corresponds to the energy of the interaction of one kcal./mol. Compared with the ordinary hydrogen bonding, in which displacement of ν_{O-H} by 40 cm^{-1} corresponds to one kcal./mol. of the enthalpy change[27], these interactions seem to have the characteristic that a smaller $\Delta\nu_{max}$ corresponds to an appreciable enthalpy change. This is, however, overestimated, since the term $T\Delta S$ in Eq. 3 is some what dependent on $\Delta\nu_{max}$ and the greater $\Delta\nu_{max}$ makes the absolute value of ΔS, which is inherently negative, greater. It will tend to make its value less.

It is further shown in Fig. 3, that the points representing 2-hydroxybiphenyls substituted on the B-ring spread wider by about five times than those having the substituent on the A-ring; that is, the effect of the substituents on the phenomenon is more fully developed in the B-ring. As the first approximation, the strength of the intramolecular interaction between the hydroxyl group and π-elctrons is expected to be influenced by the substituent on the B-ring by directly affecting the π-electron density and the proton accepting character of the B-ring, while the substituent on the A-ring will not touch the π-electron density of the B-ring but affect the proton donating character of the hydroxyl group. The above observation means that the former effect is predominant.

As to the latter effect, it is well known that acid dissociation constant (pK_a) of phenols[29] and spectroscopically free ν_{O-H} of phenols in carbon tetrachloride solution[30], are in linear relationship with Hammett's sigma constants of the substituents. The free ν_{O-H} of 2-hydroxybiphenyls substituted in the A-ring have been examined in this connection and the results are presented in a Hammett sigma-rho plot in Fig. 4. A line with rho value of −13.8 is

29) H. C. Brown, D. H. McDaniel and O. Häfliger, "Determination of Organic Structures by Physical Methods", Ed. by E. A. Braude and F. C. Nachod, Academic Press Inc., New York (1955), p. 589.
30) L. L. Ingraham, J, Corse, G. F. Bailey and F. Stitt, *J. Am. Chem. Soc.*, **74**, 2297 (1952).

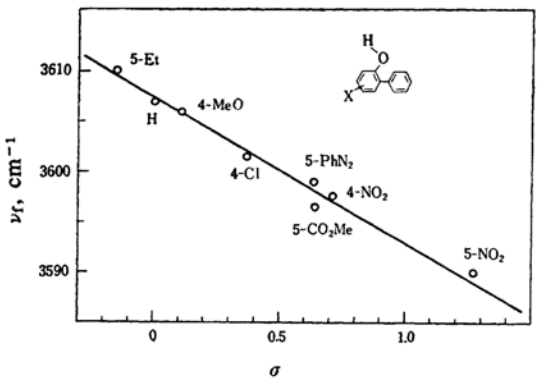


Fig. 4. ν_{O-H} frequencies of the free hydroxyl group in 2-hydroxybiphenyls substituted in the A ring versus the Hammett sigma constants.

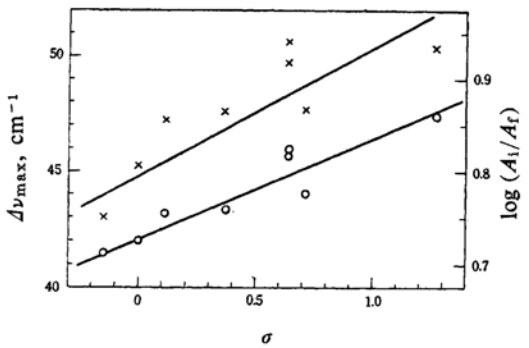


Fig. 5. Dependence of the two band properties, $\Delta\nu_{max}$ (the circles to the left ordinate) and $\log(A_1/A_f)$ (the crosses to the right ordinate) on the substituents in A-ring.

obtained, comparable to $\rho=-12.6$ in the substituted phenols[30]. This suggests that the substituents in the A-ring are really pertaining to the proton donating character of the hydroxyl group just as in phenols and thus must be affecting the strength of the intramolecular interaction. In Fig. 5, it is illustrated to what extent the strength of the interaction, i. e., $\Delta\nu_{max}$ and $\log(A_1/A_f)$ depends on the sigma constants of the substituents. It can be concluded from Figs. 4 and 5, that the intramolecular interaction between the hydroxyl group and π-electrons strengthens as the electron drawing power of the substituents or the acidity of the hydroxyl group enhances, and weakens with the electron-donating substituents.

As the substituents on the ring B govern the density and polarizability of π-electrons acting as the hydrogen accepter, it is natural that the variation in the B-ring substituent causes a salient change in the degree of the interaction in such a direction that the electron donating substituents (e. g., methoxyl) enhance the interaction, while the electron-attracting substituents (e. g., nitro) disfavor the interaction. Two kinds of band properties, $\Delta\nu_{max}$ and $\log(A_1/A_f)$ have again been tested for Hammett's sigma-rho relation, in the expectation that π-electron density and/or polarizability at the site of the interaction will be expressed in terms of sigma values, just as in the case of the electrophilic nuclear substitution reaction[31]. Although Wulf et al.[2] suggested that the hydroxyl group would approach the first carbon atom (1′-carbon), there is no a priori reason which of the 3′- or 4′- substituents may be regarded as *m*- or of *p*-position in respect of the site of the interaction. In the previous papers[32,33] the authors have succeeded in assigning the position of the hydroxylic proton in the interaction in benzyl and phenethyl alcohols by plotting $\log(A_1/A_f)$ against Hammett's sigma values considering the various possibilities, and by choosing the assignment of better linearity. The trial has again been applied to the present system but failed to obtain the precise linearity in either case. In Fig. 6 is shown the relation between $\log(A_1/A_f)$s' relative to that for 2-hydroxybiphenyl and the Hammett sigma constants, *m*- and *p*-values of which are allotted to 4′- and 3′-substituents, respectively. These are

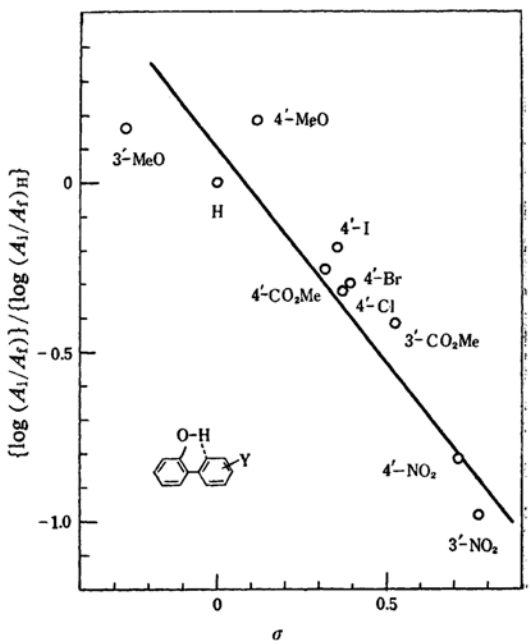


Fig. 6. Relation between $\{\log(A_1/A_f)\}/\{\log(A_1/A_f)_H\}$ and the Hammett sigma constants in 2-hydroxybiphenyl substituted in B-ring.

31) C. W. McGary, Jr., Y. Okamoto and H. C. Brown, ibid., 77, 3037 (1955).
32) M. Ōki and H. Iwamura, This Bulletin, 32, 955 (1959).
33) M. Ōki and H. Iwamura, ibid., 32, 1135 (1959).

in better linearity than the reverse assignment in so far as 3′-electrophilic substituents (e. g., nitro) disfavor the interaction more than the 4′-ones. Here it may be said that the hydroxylic proton is more concerned with π-electrons at 2′-carbon than at the 1′. Methoxyl group at 3′- and 4′-positions, however, favors the interaction equally, in spite of the fact that their sigma constants are of opposite sign and differ by 0.38. If the interaction is solely concerned with π-electrons at 2′-carbon, the methoxyl group at 4-position would not have favored the interaction. Putting the emphasis upon the last observation and regarding the difference in the electrophilic substituents minor, it may tentatively be concluded that the hydroxylic proton is concerned with π-electron density between 1′ and 2′ carbon atoms, like the structure of the complex formed between silver ion and benzene[34].

It has been assumed that the electronic effect of the substituents might be confined to the ring to which it is attached. Biphenyls are, however, characteristic of its conjugation between two phenyl rings, and a considerable conjugation has been demonstrated by the kinetic study[35] and the ultraviolet spectroscopy[36], even when it is substituted at one ortho-position by a rather small group[37]. Although there is no datum available for the 2-hydroxybiphenyl system, if the conjugation exists between two rings in this system, the free ν_{O-H} must also be dependent on the substituents on the B-ring. In Fig. 7 the wave number where the free ν_{O-H} appears is plotted to Hammett's sigma constants, *m*- and *p*-sigma values being alloted to the substituents at 3′- and 4′-positions, respectively. A line having an inclination of −3.9 is obtained and, compared with that of Fig. 4, −13.8, it can be

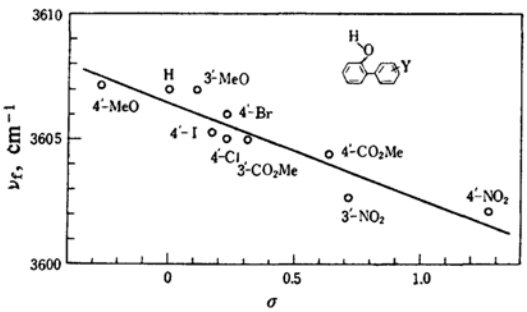


Fig. 7. ν_{O-H} frequencies of the free hydroxyl group in 2-hydroxybiphenyls substituted in the B-ring, versus the Hammett sigma constants.

34) R. E. Rundle and J. H. Goring, *J. Am. Chem. Soc.*, **72**, 5337 (1950).
35) E. Berliner and L. H. Liu, ibid., **75**, 2417 (1953).
36) V. P. Kreiter, W. A. Bonner and R. H. Eastmann, ibid., **76**, 5770 (1954).
37) G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, **1952**, 854.

stated that in 2-hydroxybiphenyls 28% of the electronic effect of the substituents can be transmitted across the pivot bond through mesomerism and/or induction. The degree of conjugation is rather great in spite of the ortho substitution when compared with biphenyls free from the substituent[35,36], because Berliner obtained, for example, $\rho=0.37$ from the dissociation constants of the substituted biphenyl-4-carboxylic acids, deducing 37% propagation of the substituent effect[38]. This may be reasonable, however, because the data obtained for 2-hydroxybiphenyls are for free ν_{O-H} of trans configration, which, unlike cis form, has only a little excessive steric hindrance compared with a hydrogen atom.

With these new informations of conjugative effect, the effect of the substituents at the A and the B-rings on the electron donating power of the B-ring and on the proton donating character of the hydroxyl group, respectively, must be reevaluated. Since the effect of the substituents is more strongly exerted by affecting the proton accepting power than the proton donating one, as shown in Fig. 3, the effect of the B-ring substituents on the apparent interaction by affecting the proton donating character of the hydroxyl group of the A-ring may be neglected. On the other hand, the effect of the A-ring substituents on the proton accepting character of the B-ring must be taken into account, since it amounts to 28% of that caused by the B-ring substituents and has as much influence on the interaction as the effect on the proton donatining power of the hydroxyl group. The electron attracting substituents (e. g., nitro), for example, influence the interaction as a result of two opposing effects. That is, they favor the interaction by strengthening the proton donating character of the hydroxyl group and disfavor it by lessening the proton accepting charactor of the B-ring. Although it is as yet impossible to separate the two competing effects quantitatively, it is clear that the pure effect of A-ring substituents on the proton donating character of the hydroxyl group is more pronounced than is estimated from Fig. 3.

The authors are indebted to Professor Yoshiyuki Urushibara for his encouragement and discussuion throughout this work. The authors' thanks are also due to the Ministry of Education for the Grant in Aid for Fundamental Scientific Research.

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38) E. Berliner and E. A. Blommers, *J. Am. Chem. Soc.*, **73**, 2479 (1951).