Steric Effects on the O–H···π Interaction in 2-Hydroxybiphenyl[1]

Michinori Ōki and Hiizu Iwamura

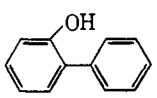
Contribution from the Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo, Japan. *Received July 18, 1966*

Abstract: The ultraviolet and the infrared spectra of 2-hydroxybiphenyls have been examined. From the K band maxima of these compounds in the ultraviolet region, the dihedral angle made by the two benzene rings is estimated. The strength of the "O–H···π hydrogen bonding" as indicated by the shift to the lower frequency of the O–H stretching vibration is found to increase with the increasing dihedral angle. The trend is interpreted in terms of the angular dependence of the overlap between the orbitals of the hydroxyl group and the π systems of the benzene ring *ortho* to the hydroxyl group. It is concluded that the π orbital of the 1′-carbon atom is mainly responsible for the interaction.

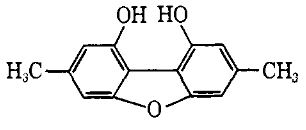
Since the observation by Wulf and his co-workers[2] on the doublet nature of the first overtone of the O–H stretching vibration (ν_{O-H}) in 2-hydroxybiphenyl (I), the appearance of the two bands has been observed and discussed by several authors,[3] and there seems to be some basis for assigning the lower frequency band at 3565 cm^{-1} to the fundamental ν_{O-H} of the hydroxyl group interacting with the π electrons on the phenyl group *ortho* to the hydroxyl.

In an explicit attempt to elucidate the true nature of the interaction, the structural requirement and the electronic effect have so far been extensively treated.[3g–i] Thus the strength of the interaction increases with the increasing electron-attracting power of the substituent on the phenolic benzene ring and decreases with the electron-donating ability of the substituent. On the other ring, electron-releasing ones are favorable, while electron-attracting ones are disfavorable for the interaction. The interaction seems to be analogous to ordinary hydrogen bonding in that polarizable π-electron systems, although the carbon atom is not highly electronegative, play the role of the proton acceptor. The difference is the rather small energy of interaction which has been shown to be around 1 kcal/mole, smaller than that of ordinary hydrogen bonding (a few kcal/mole).[4] Since the interaction is favored by substituents which lower the ionization potential of the π-electron systems and those which raise the electron affinity of the hydroxyl group, the energy of the interaction is regarded as originating from charge transfer between the antibonding orbital of the hydroxyl group as the electron acceptor and the occupied π orbitals as the electron donor. Thus the strength of the interaction must depend heavily on the overlap between the occupied π orbitals in the electron donor and the vacant O–H antibonding orbital, and the steric repulsion in the neighborhood of the interacting groups may favor or disfavor the interaction to a great extent.[5]

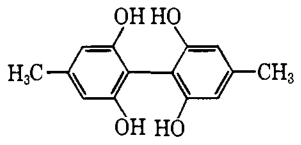
The angular dependence of the interaction in the 2-hydroxybiphenyl derivative has been pointed out before. For example, no interaction was observed in the infrared spectra of the oxygen-bridged biphenyl II, but O–H···O bonding was found to be particularly strong.[3f] This may be rationalized since II must be either planar or nearly so and there is only a slight possibility, if any, of overlap between the antibonding orbital of the OH group attached to one ring and the π orbitals of the other. The other extreme is afforded by 2,2′,6,6′-tetrahydroxybiphenyl derivative III, which, owing to a nearly perpendicular conformation, shows no O–H···O hydrogen bonding but only O–H···π interaction.[3f]



I



II



III

These examples are usually symmetrical biphenyls, and the O–H···π bands are accompanied by stronger O–H···O bands in the infrared spectra and are not the best examples for quantitative discussion. It is the purpose of the present paper to report the steric effects on the intramolecular interaction in the homologous series of the asymmetrical 2-hydroxybiphenyls (I, IV–VIII).

Results and Discussion

Ultraviolet Spectra and Dihedral Angles. The ultraviolet spectra of I and V–VIII are shown in Figure 1 and the spectral data from these curves are summarized

---

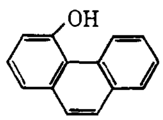
[1] Part XXI of the "Intramolecular Interaction between Hydroxyl Group and π Electrons." Part XX: M. Ōki, H. Iwamura, T. Onoda, and M. Nishida, *Bull. Chem. Soc. Japan*, **39**, 813 (1966).

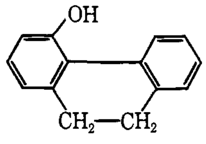
[2] O. R. Wulf, U. Liddel, and S. B. Hendricks, *J. Am. Chem. Soc.*, 58, 2287 (1936).

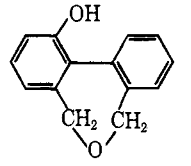
[3] (a) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1260 (1947); (b) W. Lüttke and R. Mecke, *Z. Elektrochem.*, **53**, 241 (1949); (c) W. Lüttke and R. Mecke, *Z. Physik. Chem.*, **196**, 56 (1950); (d) V. von Keussler and G. Rossmy, *Z. Elektrochem.*, **60**, 136 (1956); (e) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958); (f) H. Musso and S. von Grunelius, *Chem. Ber.*, **92**, 3101 (1959); (g) M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan*, **33**, 681 (1960); (h) M. Ōki and H. Iwamura, *ibid.*, **34**, 1395 (1961); (i) W. Beckering, *J. Phys. Chem.*, **65**, 206 (1961); (j) A. W. Baker and A. T. Shulgin, *Spectrochim. Acta*, **19**, 1611 (1963); (k) W. F. Baitinger, Jr., P. von R. Schleyer, and K. Mislow, *J. Am. Chem. Soc.*, **87**, 3168 (1965).

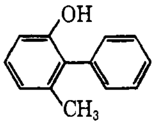
[4] M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan*, **33**, 717 (1960).

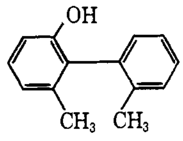
[5] M. Ōki and H. Iwamura, *ibid.*, **39**, 470 (1966).


IV


V


VI


VII


VIII

in Table I. Rather strong bands in the 240–270 mμ region of I, V, and VI are characteristic of the K band of the biphenyl chromophore, while the weaker ones in the 270–300 mμ are assigned to the phenolic B band. The former band weakens in its intensity in the ascending order of V, VI, I, VII, and VIII, and appears only as a shoulder in the last two compounds. It is well recognized that the simultaneous hypsochromic shift and decrease in intensity of the K band are the consequence of steric inhibition of conjugation between the two chromophoric systems, and many attempts have been made to relate semiquantitatively band parameters with interplanar angles.[6-8] According to these, the angles are estimated to increase in the order of decreasing λ_{max} in a series of otherwise electronically equivalent conjugated systems.

Table I. The Ultraviolet Spectral Data of the 2-Hydroxybiphenyls in Heptane[a]

	K band		B band		Dihedral
	λ_{max}, mμ	ϵ	λ_{max}, mμ	ϵ	angle θ, deg
	262		284		
V	269.0	14,100	291.0	7000	25
			302		
VI	252.0	10,700	297.0	5300	45
I	245.5	7,700	284.0	4100	50
VII	245.5	(sh)	274	(sh)	60
			280.5	1800	
VIII	240.0	(inf)	273.0	1300	70
			279.0	1300	

[a] Sh and inf stand for the shoulder and the inflection point, respectively.

In the present case of 2-hydroxybiphenyls, the hyperconjugative bathochromic effect of a methyl or a methylene group is not common for all. For a separate discussion of steric interference it is desirable that all compounds be compared at the common level of "dimethylhydroxybiphenyl" chromophore. Since a methyl or a methylene substitution produces an average bathochromic shift of *ca.* 3 mμ, λ_{max} of I and VII in Table I should be modified to 251 and 248 mμ, respectively. Then it follows that the decreasing order of the λ_{max} and, as a consequence, the increasing order of the interplanar angle are V, VI, I, VII, and VIII. The angles listed in the last column were estimated as follows. The angle in the oxepin derivative, VI, was assumed to be unaltered from that of the parent 5,7-dihydrodibenz[*c*,*e*]oxepin for the following reasons. The molecule of the latter is so constructed as to minimize the strain and the nonbonded repulsion in the oxepin ring and, at the angle of 45° so determined,[7] the distance between the hydroxyl oxygen and the *ortho*-prime hydrogen in VI is the same as the sum (2.6 A) of the van der Waals radii of the oxygen and hydrogen atoms, and so introduction of an *ortho*-hydroxyl group necessitates no more twist. For the same reasons, in the methyl and the dimethyl derivatives, VII and VIII, the interplanar angles of the parent hydrocarbons[7,8] were employed also. When the interplanar angles of the biphenyl skeleton is less than *ca.* 45°, introduction of an *ortho*-hydroxyl group brings the oxygen and hydrogen atoms within the van der Waals radii. The angle of I and V, therefore, cannot be substituted by those of the parent hydrocarbons, but must be widened somewhat. The expectation is supported by the hypsochromic shift of the K band by 5.5 mμ in I from biphenyl and by the unexpectedly small bathochromic shift (1.5 mμ) in V from 9,10-dihydrophenanthrene.[9] The angles were then calculated to be *ca.* 50 and 25° for I and V, respectively, by the method developed by Suzuki[7] which relates the angle to the excitation energy of the conjugation band by considering the angular dependence of the overlap integral of the orbitals of the carbon atoms pertaining to the pivot bond.[10] The dihedral angles thus derived may have considerable uncertainty, but it is only the order and the relative size that are of much concern in the following discussion.

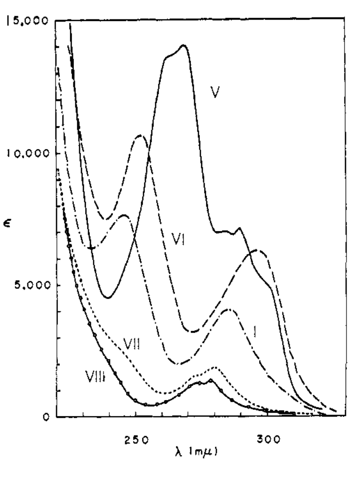


Figure 1. Ultraviolet absorption spectra of 2-hydroxybiphenyls in heptane.

Infrared Spectra and O–H···π Interaction. The ν_{O-H} absorptions of I and IV–VIII in the 3-μ region are presented in Figure 2, and in Table II are collected their absorption maxima (ν_{max}), half-band widths ($\Delta\nu_{1/2}^{a}$), integrated intensities (A), shifts of absorption

---

(6) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 3776 (1955).

(7) H. Suzuki, *Bull. Chem. Soc. Japan*, **32**, 1340, 1350, 1357 (1959); **33**, 109 (1960).

(8) K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, Jr., *J Am. Chem. Soc.*, **86**, 1710 (1964).

(9) The λ_{max} of 4-hydroxybiphenyl and 4-hydroxyfluorene lie at 256 and 267 mμ, respectively, longer wavelengths than those of the corresponding hydrocarbons by 5 mμ. Thus, without steric inhibition, the auxochromic effect of the hydroxyl group on the K band of the biphenyl chromophore can be regarded to be 5 mμ.

(10) As the longer wavelength side reference, 240 and 248 mμ of VII and VIII were adopted, for which θ's are 60 and 77°, respectively,[7] while the short wavelength side reference was λ_{max} 252 mμ of VI. θ's of I and V were derived by interpolating λ_{max} 251 mμ and extrapolating λ_{max} 265 mμ (center of gravity of the K band), respectively.

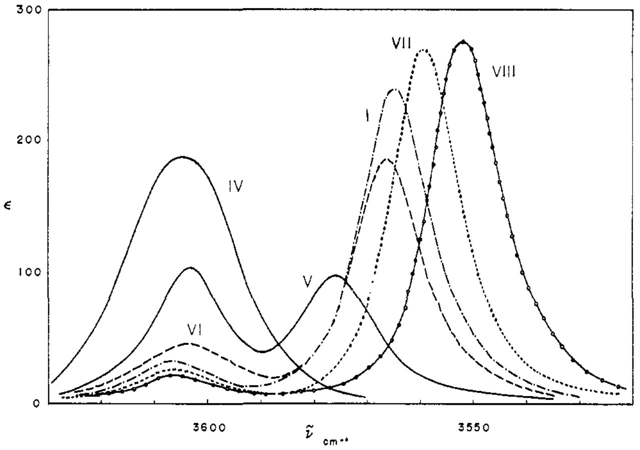


Figure 2. ν_{O-H} Absorptions of 2-hydroxybiphenyls.

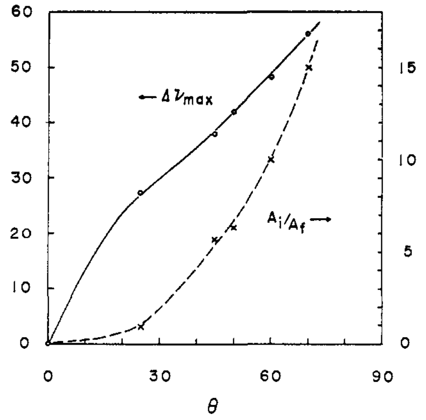


Figure 3. Dependence of A_i/A_f and $\Delta\nu_{max}$ on the dihedral angle θ in 2-hydroxybiphenyls.

Table II. ν_{O-H} Absorptions of the 2-Hydroxybiphenyls

	ν_{max}, cm^{-1}	$\Delta\nu_{1/2}{}^{a}$, cm^{-1}	$A \times 10^{-4}$, mole^{-1} l. cm^{-2}	$\Delta\nu_{max}$, cm^{-1}	A_i/A_f	θ, deg
IV	3604.5	25.1	1.69	0	0	0
V	3603.7	14.8	0.61	27.7	0.96	25
	3576.0	17.6	0.58			
VI	3604.2	20.1	0.18	38.0	5.75	45
	3566.2	15.7	1.04			
I	3607.0	18.2	0.20	42.0	6.4	50
	3565.0	15.0	1.28			
VII	3607.8	19.0	0.15	48.2	10.0	60
	3559.6	15.0	1.51			
VIII	3608.8	18.4	0.11	56.0	15.0	70
	3552.8	16.2	1.60			

peak ($\Delta\nu_{max}$), and the relative integrated intensities (A_i/A_f). The bands at *ca.* 3605 cm^{-1} are common for all, though their intensities are variable, and can be assigned to the ν_{O-H} of the free phenolic hydroxyl group.[3h] The second bands at the lower frequency are derived from the hydroxyl group interacting with the π electrons on the benzene ring *ortho* to the hydroxyl. Both A_i/A_f and $\Delta\nu_{max}$, which can indicate the strength of the interaction,[11] vary widely from compound to compound. It is clear that the variation is not due to the electronic effect. As shown in a previous paper,[3h] electron-releasing substituents have a definite influence on the strength of the interaction. Thus, when attached to the benzene ring *ortho* to the hydroxyl, an electron-releasing substituent strengthens, while, when attached to the benzene ring carrying the hydroxyl group, the same substituent weakens the O-H···π bonding.[12] The effect of the methylene and the methyl groups, however, is minor,[13] and can be neglected in the present discussion. Both A_i/A_f and $\Delta\nu_{max}$ increase continuously as the interplanar angle, θ, estimated in the preceding section increases (Figure 3). This conspicuous steric effect is rationalized since the interaction between the hydroxyl group and π electrons of the benzene ring depends critically on the orbital overlap. Owing to the directional nature of the orbitals concerned, the overlap depends not only on the distance but also on the angle made by them. In II and IV, the hydroxyl group is not so remote (1.62 A) from the 2′-carbon atom on the benzene ring *ortho* to the hydroxyl, but the OH proton points to the node of the π orbital, making the overlap least important, and O-H···π bonding in II and IV is absent. As the interplanar angle, θ, increases, the distance between the hydroxyl hydrogen and 2′-carbon atom increases while that between the hydroxyl hydrogen and 1′-carbon atom is kept constant. In these circumstances, the overlap between the two orbitals concerned becomes more favorable, since the hydroxyl group can gradually approach the π cloud from the upper side. This makes $\Delta\nu_{max}$ and A_i/A_f increase continuously with θ as shown in Figure 3.

It has long been a matter of controversy which of the π electrons of the two carbon atoms, 1′ and 2′, contributes more to the interaction with the 2-hydroxyl group. This must be determined by the symmetry of the π orbitals and by the amplitude of the coefficient of the atomic orbitals in the most contributing molecular orbitals. Examination of the electronic effect of the substituents on the strength of the interaction has allowed the tentative conclusion that the π electrons on the 1′- and 2′-carbon atoms are equally contributing.[3h]

Since the energy of the charge-transfer interaction is approximately proportional to the square of the overlap integral between the two orbitals concerned, the overlap integral S(1s,2pσ) between the hydroxyl hydrogen on the one hand and 1′-, 2′-, and 6′-carbon atoms on the other was read from the table of Mulliken and his co-workers.[14] The distance, R, between the atoms necessary for the computation was measured from the molecular geometry determined by using the conventional structural dimensions and angles. The overlap integral, $S(R, \phi)$, at a distance, R, and at an angle, ϕ, which is made by the axis of the π lobe and the line connecting the sp^2-carbon atom with the OH hydrogen

---

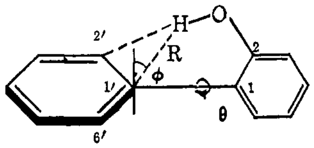
(11) G. C. Pimentel and A. L. McClellan, "Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp 82–102.

(12) In this meaning, I and VII lack the methyl group of the proton accepting benzene ring when compared with the rest of the 2-hydroxybiphenyls and the strength of the interaction may be underestimated. Also in I a methyl group is absent on the benzene ring to which the hydroxyl group is attached.

(13) For example, $\Delta\nu_{max}$ and A_i/A_f of the 5-ethyl derivative of I are 41.5 and 5.6, respectively.[3h] The electronic effect of the 2′-methyl group is estimated to increase the two band parameters only by 2.5 and 1.5 cm^{-1}, respectively.

(14) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 17, 1248 (1949).

(see IX)[15] was put to be equal to the product of cos ϕ and S at $\phi = 0$. The interplanar angular dependence is shown in Figure 4. Since a $\Delta\nu_{\max}$ *vs.* θ curve (Figure 3) is more similar to the curve 1′ in Figure 4 than the curve 2′ and 6′, as far as the relatively large dihedral angle is concerned, it is concluded that it is the π electrons at the 1′-carbon which contribute mainly to the interaction with the hydroxyl group. If the overlap with the 2′-carbon atom were significant, the strength of the interaction should have been maximum at a dihedral angle of about 40°. With a small dihedral angle, the convex nature of the $\Delta\nu$ *vs.* θ curve in Figure 3 is apparent, although the S^2 *vs.* θ curve with $C_{1'}$ is actually rather concave. This observation may be interpreted by considering the partial contribution of the overlap with $C_{2'}$ as is shown by the dotted curve in Figure 4.



IX

It must be mentioned that the conclusion is not the same with that derived from the study of the electronic effect (*loc. cit.*). The incompatibility may be ascribed to the perturbation given by the substituents. Those such as CH_3O and NO_2, which interact strongly with the benzene ring, have a considerable effect on the symmetry and the amplitude of the π orbitals, and the situation is quite different from the present 2-hydroxybiphenyls which are electronically less perturbed.

Experimental Section

Spectral Measurements. The infrared absorption was measured with a Perkin-Elmer Model 112-G grating infrared spectrometer, the spectral slit width being 1.0 cm^{-1}. Carbon tetrachloride distilled over phosphorus pentoxide was used as a solvent. A quartz cell of 2.0 cm in optical length was employed, and the concentration of the solution was *ca.* 1 mmole/l. at which dilution the association of the solute is negligible. 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 calculated according to the equation

$$A = K\frac{1}{2cl}\ln(I_0/I)_{\max}\,\Delta\nu_{1/2}{}^{a}$$

given by Ramsay,[16] where K is equal to unity.

The ultraviolet absorption was measured on a Hitachi EPS-2U automatic recording spectrophotometer. A quartz cell of 1.0 cm in length was employed and the concentration of the samples in heptane of a spectrograde was nearly 10^{-4} mole/l. throughout.

Materials. 1-Hydroxy-5,7-dihydrodibenz[*c*,*e*]ozepin. A solution of 4.8 g (0.02 mole) of 1-nitro-5,7-dihydrodibenz[*c*,*e*]oxepin[17] in 100 ml of ethanol was shaken with hydrogen over Raney nickel at room temperature under atmospheric pressure, 1.3 l. of hydrogen being absorbed in 40 min. After removing the catalyst by filtration and evaporating the solvent, the residue was recrystallized from benzene to give 4.0 g (yield, 95%) of the corresponding amine as needles, mp 129°. *Anal.* Calcd for $C_{14}H_{13}ON$: N, 6.63. Found: N, 6.68.

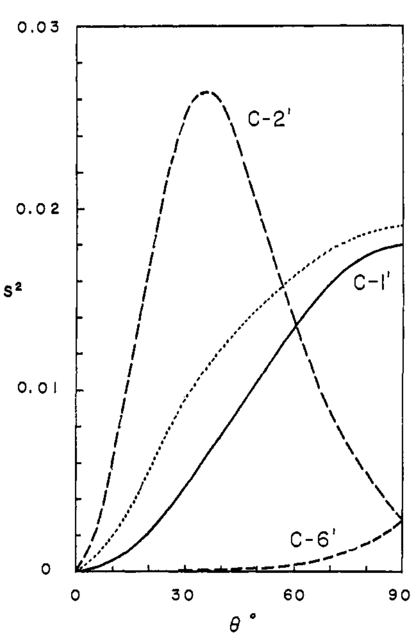


Figure 4. Angular dependence of the overlap integral between the hydroxyl hydrogen and 1′-, 2′-, and 6′-carbon atoms. The dotted curve represents C-1′ with partial (20%) contribution of C-2′.

The above amine was triturated with 50 ml of 3 *N* sulfuric acid and diazotized with sodium nitrite. The diazotized solution was hydrolyzed by pouring dropwise into a hot 30% aqueous sulfuric acid solution. After cooling, the solid was collected and crystallized from ethanol to give plates (2.8 g, 69% yield), mp 186–187°. *Anal.* Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.05; H, 5.81.

4-Hydroxy-9,10-dihydrophenanthrene. A mixture of 2.1 g (0.01 mole) of the above oxepin, 50 ml of 48% aqueous hydrobromic acid, and 5 ml of concentrated sulfuric acid was refluxed for 1 hr and diluted with 100 ml of water. The upper aqueous layer was decanted, the oily residue dissolved in ether, and the ether solution washed with aqueous sodium bicarbonate. The crude dibromide was used directly for the following reaction. The ethereal solution of phenyllithium prepared from 0.05 mole of bromobenzene was added dropwise to the ether solution of the above hydroxy dibromide, and the mixture was heated under reflux for 5 hr. The mixture was decomposed with 100 ml of 1 *N* sulfuric acid. The ether layer and the ether extract of the aqueous layer were combined, dried over anhydrous sodium sulfate, and distilled. A fraction boiling at *ca.* 130° (2 mm) solidified and recrystallized from petroleum ether-benzene (1:1 in volume) to give prisms, mp 73–73.5° (lit.[18] mp 72–74°).

2-Hydroxy-6-methylbiphenyl. 2-Methyl-6-nitrobiphenyl[19] (7 g, 0.033 mole) was hydrogenated over platinized Raney nickel in ethanol, 2.3 l. of hydrogen being absorbed. The amine obtained after removing the catalyst by filtration and evaporating the solvent was diazotized as usual, and the resulting solution was hydrolyzed by pouring into hot 30% aqueous sulfuric acid. The phenol was steam distilled. After 1 l. of the distillate was collected, the oil was extracted with ether and recrystallized from petroleum ether to give prisms (4.5 g), mp 55–56°. *Anal.* Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.80; H, 6.69.

2′,6-Dimethyl-2-hydroxybiphenyl. 2-Amino-2′,6-dimethylbiphenyl[20] was diazotized and hydrolyzed to give the phenol, as usual, in plates, mp 48.5–49°. *Anal.* Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.98; H, 7.05.

---

(15) This angle is taken as a paramter since only the s orbital is responsible for the hydrogen atom.

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

(17) M. Ōki, H. Iwamura, and N. Hayakawa, *Bull. Chem. Soc. Japan*, **37**, 1866 (1964).

(18) J. W. Krueger and E. Mosettig, *J. Org. Chem.*, **3**, 344 (1938).

(19) A. M. Sadler and G. Powell, *J. Am. Chem. Soc.*, **56**, 2650 (1934).

(20) P. M. Everitt, S. M. Loh, and E. E. Turner, *J. Chem. Soc.*, 4587 (1960).