Intramolecular Interaction between Hydroxyl Group and Aromatic Nucleus in 2-Hydroxy-4- or 4'-nitrobiphenyl

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(Received June 3, 1958)

In the course of a study on the ultraviolet spectra of biphenyl derivatives, the authors observed a phenomenon¹⁾ possibly interpretable from the intermolecular

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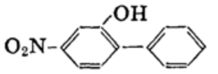
1) For example, 2-methyl-4-nitrobiphenyl shows an ultraviolet absorption maximum at a shorter wave length than 2-methyl-4'-nitrobiphenyl does. A paper on this phenomenon was presented at the Eleventh Annual Meeting of this Society, April, 1958, in Tokyo, but no full explanation has been obtained so far.

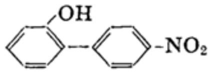
TABLE I

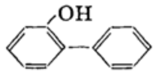
INFRARED SPECTRA OF 2-HYDROXY-4-NITROBIPHENYL (I) AND 2-HYDROXY-4'-NITROBIPHENYL (II)

Compound	Temp. (°C)	Hydroxyl	ν_{max} (cm^{-1})	$\Delta\nu^{a}_{1/2}$ (cm^{-1})	$A\times10^{-4}$ $mole^{-1}\cdot liter\cdot cm^{-2}$	$\Delta\nu_{max}$ (cm^{-1})
I	26.5	interacted	3553.8	19.4	1.703	44.0
		free	3597.8	19.6	0.233	
II	23.5	interacted	3579.6	17.6	0.765	21.4
		free	3601.0	17.2	0.787	

interaction involving a participation of the aromatic nucleus, which led the authors to study the absorption spectra of 2-hydroxy-4-nitrobiphenyl (I)[2], m.p. 103~105°C, and 4'-nitro-isomer (II)[3], m. p. 123~124°C.


I


II


III

Wulf[4] observed two O–H stretching bands in the first overtone region in 2-hydroxybiphenyl (III), attributing them to *cis* and *trans* isomerism. Barnard et al.[5] also observed two bands in 3μ region in cumene α-hydroperoxide. In view of recent studies on the intermolecular interaction between the hydroxyl group and the aromatic nucleus, these phenomena are undoubtedly caused by the intramolecular interaction between the hydroxyl group and the π-electrons of the aromatic nucleus. While the present study was in progress, Trifan and his coworkers[6] reported that they also observed two O–H stretching bands in α-hydroxyethylferrocene and β-phenethyl alcohol.

It can naturally be expected that introduction of a nitro group into compound III will either enhance or suppress the interaction by the electron drawing power of the nitro group and compounds I and II will be the two extremes as far as the positions 4 and 4' concern on the basis of Hammett's σ values.

The infrared absorption was measured with a Perkin Elmer Model 112–G Double Pass High Precision Grating Infrared Spectrometer, the spectral slit width being 0.82 cm^{-1} in this region. Eastman-Kodak spectro grade carbon tetrachloride was used as a solvent without further treatment. A quartz absorption cell of 2 cm. length was used with a ca. 0.001 mol./l. solution. The temperature varied from 25° to 65°C. The integrated intensity was calculated from the equation given by Ramsay[7], four parameters a_1, b_1, c_2 and b_2 being used for the two bands. Examples of the results are shown in Table I.

Energy differences between free and interacted hydroxyl groups calculated from the values at various temperatures are 2.5±0.2 and 0.93±0.03 kcal./mol. for compounds I and II, respectively, and are in good agreement with the expectation. There may exist a relation between ΔE and $\Delta\nu$ or the integrated intensities of free and interacted forms, but we can not comment about this until further examples are studied.

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