Hydrogen Bonding Effect on the Electronic Absorption Spectrum of p-Hydroxyazobenzene

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When the effect of hydrogen bonding on the electronic absorption spectra of organic compounds came to be noticed, attention was drawn to the anomalies of the effects of the solvents on the spectra. It was then pointed out that the hydrogen bonding effect could serve as a new method for the study of the nature of hydrogen bonding itself[1]. Indeed some thermochemical quantities, such as free energy, entropy and enthalpy changes in hydrogen bonds, have been determined for a number of compounds, e. g. phenol[1-5], cresols[6,7], naphthols[7], pyridine *N*-oxide[8] etc. In all these studies the influence of hydrogen bonding on an electronic absorption was made clear by the use of a three-component system: an inert solvent, a solute of a chromophore, and a substance which forms hydrogen bond with the solute molecule. It may be added that this method of three-component system which was originally used in the study of the ultraviolet absorption of phenol[1,2] has recently been utilized by Brealey and Kasha in demonstrating the role of hydrogen bonding in the $n \to \pi^*$ blue shift phenomenon[9]. Further, it has been applied to the study of the fluorescence of some organic compounds[10].

The present article will suggest that there is another promising application of the studies concerning the hydrogen bonding effect, that is: a new clue to the nature of the absorption bands of a given molecule is to be provided from the spectral changes at the time of formation of a hydrogen bond. For this purpose, however, some additional information is required on the relation between the type of an electronic transition and the change in its corresponding spectrum accompanied by the hydrogen bonding.

With this point in mind, the hydrogen bonding effect on the absorption spectrum of *p*-hydroxyazobenzene has been newly investigated. This substance is provided with features fitted for the present purpose. It has a proton-donating hydroxyl group, and has several absorption bands of different types. Moreover, there is no ambiguity regarding its structure in solution. It is known that *p*-hydroxyazobenzene exists only in the azo-form in any common solvent, and further for this molecule one need not consider the formation of an intramolecular hydrogen bond such as occurs in *o*-hydroxyazobenzene[11].

Azobenzene and its derivatives, including *p*-hydroxyazobenzene, have three absorption bands in the visible and the near ultraviolet regions[12,13]. The band situated in the visible region has been assigned by McConnell[14] to an $n \to \pi^*$ transition, while the other two bands appearing in the ultraviolet region are considered to be due to $\pi \to \pi^*$ transitions[13]. In the following, it will be shown that the changes in $n \to \pi^*$ and $\pi \to \pi^*$ absorptions caused by the hydrogen bond between *p*-hydroxyazobenzene and ether or pyridine are of entirely different nature.

Experimental

Materials.—*p-Hydroxyazobenzene* (Kanto Chemical Co., Inc., guaranteed) was purified chromatographically through an alumina column by

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[1] H. Baba and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **72**, 3 (1951).

[2] S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, **74**, 5693 (1952).

[3] H. Tsubomura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **73**, 920 (1952).

[4] S. Nagakura, ibid., **74**, 153 (1953); *J. Am. Chem. Soc.*, **76**, 3070 (1954).

[5] S. Mizushima, M. Tsuboi, T. Shimanouchi and Y. Tsuda, *Spectrochim. Acta*, **7**, 100 (1955).

[6] H. Baba, *Monogr. Res. Inst. Appl. Elec.*, Hokkaido Univ., No. 4, 61 (1954).

[7] S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 734 (1954).

[8] T. Kubota, *J. Pharm. Soc. Japan*, **74**, 831 (1954); **75**, 1540 (1955).

[9] G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

[10] N. Mataga, Y. Kaifu and M. Koizumi, *Nature*, **175**, 731 (1955); This Bulletin, **29**, 115 (1956).

[11] See, for instance, H. Shingu, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **60**, 542 (1939).

[12] A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, **1952**, 3734.

[13] P. P. Birnbaum, J. H. Linford and D. W. G. Style, *Trans. Faraday Soc.*, **49**, 735 (1953).

[14] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

[15] W. R. Brode, *J. Phys. Chem.*, **30**, 56 (1926).

developing with benzene: m. p. 154°C (literature 152°C corrected[15], 155—156°C corrected[16]).

Iso-octane (2, 2, 4-trimethylpentane; Enjay Co., Inc., U. S. A.) was purified using the purification method for hexane[17]: b. p. 99°C, $n_D^{20}=1.3910$.

Ethyl ether (Kanto, guaranteed) was treated with mercury to eliminate peroxides and distilled: b. p. 34.5°C.

Pyridine was added to a solution of oxalic acid in acetone, and from the resulting precipitate of oxalate it was obtained in pure form[18]: b. p. 115—116°C, $n_D^{21}=1.5087$.

Method and Results. — Absorption spectra were obtained with a Beckman Quartz Spectrophotometer Model DU. A set of spectra were measured for the following solutions:

Solution 1, *p*-hydroxyazobenzene in *iso*-octane;
Solution 2, *p*-hydroxyazobenzene in *iso*-octane containing a small quantity of a proton-accepting substance;
Solution 3, *p*-hydroxyazobenzene in *iso*-octane containing a proton-accepting substance, the amount of which is about five times that in solution 2.

Ether and pyridine were used as the proton-accepting substance. The reference liquids adopted in measuring absorbances were *iso*-octane for solution 1, and *iso*-octane-ether or -pyridine mixtures for solutions 2 and 3 in which the concentrations of the latter substance were the same as in solutions 2 and 3, respectively. The concentrations of *p*-hydroxyazobenzene were about 5×10^{-5} mole/*l* in all cases. At such a low concentration one may expect that no association occurs among the *p*-hydroxyazobenzene molecules[19].

Measurements were made at room temperatures: 20°C for ether series, and 15°C for pyridine series. The observed spectra are given as curves 1, 2 and 3 in Figs. 1 and 2.

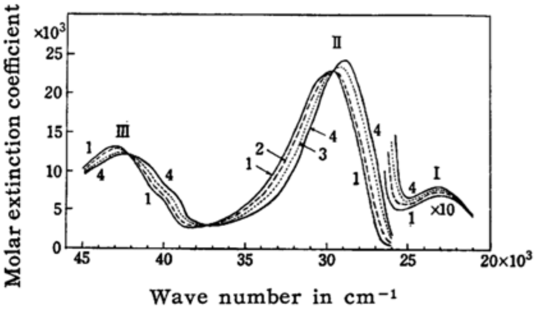


Fig. 1. The absorption spectrum of *p*-hydroxyazobenzene in *iso*-octane solution, and changes therein due to the addition of ether. The concentrations of ether: curve 1, zero; curve 2, 0.0152 mole/*l*; curve 3, 0.0797 mole/*l*. Curve 4 represents the absorption spectrum of the hydrogen bonded *p*-hydroxyazobenzene.

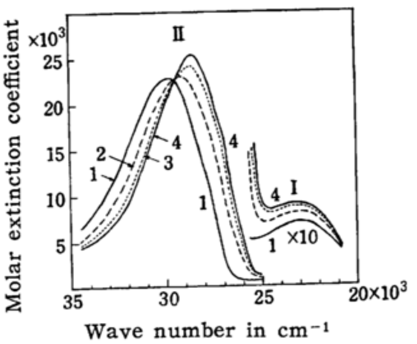
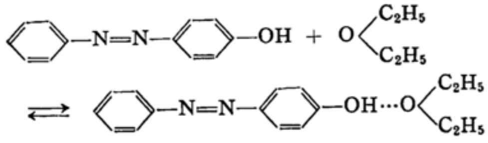
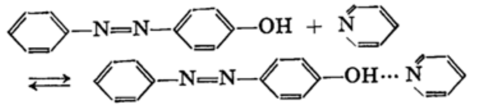


Fig. 2. The absorption spectrum of *p*-hydroxyazobenzene in *iso*-octane solution, and changes therein due to the addition of pyridine. The concentration of pyridine: curve 1, zero; curve 2, 0.00271 mole/*l*; curve 3, 0.0135 mole/*l*. Curve 4 represents the absorption spectrum of the hydrogen bonded *p*-hydroxyazobenzene.

The transitions are referred to as I, II and III in the order of increasing wave number. A remarkable spectral change occurs in the presence of a very small amount of ether or pyridine. Let it be assumed that the change is solely due to the formation of a hydrogen bond between *p*-hydroxyazobenzene and ether or pyridine.


(1)


(2)

Then the curves 2 and 3 will be interpreted as the superposition of two kinds of absorption; one is due to the free *p*-hydroxyazobenzene, and the other due to the hydrogen bonded *p*-hydroxyazobenzene. This view is substantiated by the existence of several isosbestic points in Figs. 1 and 2.

The equilibrium constant *K* for equilibriums (1) and (2) can be obtained according to the usual manner[4,6]. Let the total concentrations of the proton-accepting substance in solutions 2 and 3 be *C* and *C′*, respectively. Then it follows that

$$K=\frac{\varepsilon-\varepsilon_f}{\varepsilon'-\varepsilon}\frac{1}{C}-\frac{\varepsilon'-\varepsilon_f}{\varepsilon'-\varepsilon}\frac{1}{C'},\tag{3}$$

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[16] A. Pongratz, G. Markgraf and E. Mayer-Pitsch, *Ber.*, **71B**, 1287 (1938).

[17] T. Kuwada, "Solvents", p. 117, Maruzen, Tokyo (1953).

[18] E. L. Whitford, *J. Am. Chem. Soc.*, **47**, 2934 (1925).

[19] M. Tsuboi, *Kagaku-no-Ryoiki*, **7**, 611 (1953).

where ε_f is the molar extinction coefficient of free *p*-hydroxyazobenzene (see curve 1), and ε and ε' are apparent coefficients of *p*-hydroxyazobenzene in solutions 2 and 3, respectively (see curves 2 and 3). All these coefficients refer to a given wave number. Using the above K value, the molar extinction coefficient ε_b of the hydrogen-bonded *p*-hydroxyazobenzene is calculated as

$$\varepsilon_b = \varepsilon' + \frac{\varepsilon' - \varepsilon_f}{KC'}. \qquad (4)$$

The values of K obtained from the spectral data are 25 and 450, respectively, for equilibriums (1) and (2). By the relation $\Delta F = -\boldsymbol{RT} \ln K$, these K values lead to the free energy changes of -1.9 kcal./mole and -3.5 kcal./mole, respectively. The calculated molar extinction coefficients of the hydrogen-bonded complexes are indicated as curves 4 in Figs. 1 and 2.

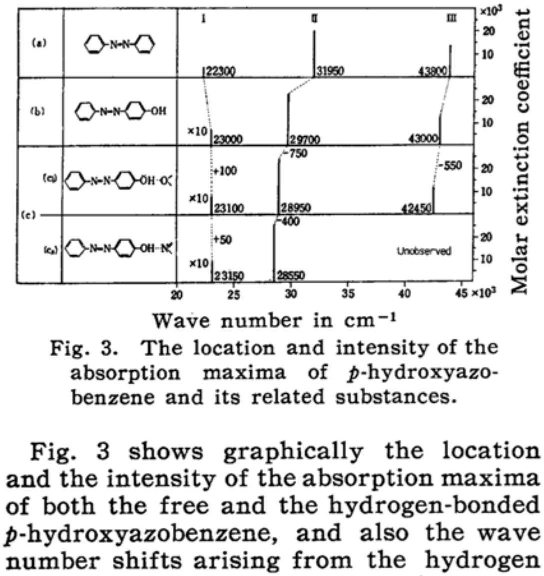

Fig. 3. The location and intensity of the absorption maxima of *p*-hydroxyazobenzene and its related substances.

Fig. 3 shows graphically the location and the intensity of the absorption maxima of both the free and the hydrogen-bonded *p*-hydroxyazobenzene, and also the wave number shifts arising from the hydrogen bond formation. The data for the parent compound, azobenzene[13,20], are given for the sake of comparison.

Discussion

Solvent effects in electronic spectra depend upon a number of factors, among which the dispersion and the polarity of solvents have been regarded as two important factors. The measure of the former is the refractive indices for the visible light and that of the latter is the dipole moments or sometimes the dielectric constants of the solvents. It is generally accepted that when the solvent has no dipole moment, the effect is largely determined by its refractive index, irrespective of whether the solute is polar or non-polar. On the other hand, when both the solvent and the solute are polar the solvent effect is determined by the magnitude of the dipole moment as well as the refractive index of the solvent[21,22].

In the present experiments the solute, *p*-hydroxyazobenzene, is polar and the solvent, *iso*-octane, is non-polar. In the case of solutions 2 or 3 there is an additional polar substance, ether or pyridine. Since the concentration of the last substance amounts to only 1% or less in mole ratio of the main solvent, *iso*-octane, one may expect that both the refractive index and the dielectric constant of the solvent remain almost unchanged with the addition of the polar substance. Therefore it may be reasonable to ascribe the spectral changes, which are observed when passing from *iso*-octane to *iso*-octane-ether or -pyridine mixture, to specific interaction of hydrogen bonding.

The spectral changes due to the hydrogen bonding are not independent of the type of the transition concerned. As is seen from Fig. 3, $n \rightarrow \pi^*$ transition I slightly shifts to the shorter wavelengths in the sequence (a) to (c), while $\pi \rightarrow \pi^*$ transitions II and III shift to the longer wavelengths in the same order. For the interpretation of the above phenomena it will be useful to refer to the fact pointed out by several authors[23] that introduction of an electron-repelling substituent such as OR or NR_2 into a chromophore often results in a red-shift of a $\pi \rightarrow \pi^*$ transition and a blue-shift of an $n \rightarrow \pi^*$ transition.

Let us consider $n \rightarrow \pi^*$ transition I. This transition corresponds to the jump of an electron from the non-bonding orbital of nitrogen atoms of the azo group to the lowest vacant π-orbital. The effect of substitution with an electron-repelling group upon an $n \rightarrow \pi^*$ transition was discussed by the present writer[24,25], and the following conclusions were drawn: (i) The

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[20] A. Burawoy, *J. Chem. Soc.*, **1937**, 1865.

[21] N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950); N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

[22] Y. Ooshika, *Bull. Kobayashi Inst. Phys. Research*, **2**, 99 (1952); *J. Phys. Soc. Japan*, **9**, 594 (1954).

[23] See, for instance, A. E. Gillam, E. S. Stern and E. R. H. Jones, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Chap. 8, Edward Arnold (1954).

[24] H. Baba, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 74 (1951).

[25] H. Baba, ibid., **72**, 341 (1951).

rate of the electron migration, hence the stabilization energy due to the electron migration, is smaller in the excited state than in the ground state of a substituted molecule. (ii) As a result, the $n \rightarrow \pi^*$ transition energy increases in comparison with that of the parent molecule. (iii) Such an effect will become larger with decreasing ionization potential of the non-bonding electron belonging to the substituent.

From (ii) the increase of the $n \rightarrow \pi^*$ absorption frequency from (a) to (b) may be understood. If the hydrogen bonds expressed in equilibriums (1) and (2) are formed, the ionization potential of the non-bonding electron of the hydroxyl group will decrease. Then from (iii) it follows that the absorption frequency is increased by the formation of the hydrogen bonds (see (b) and (c) of Fig. 3).

According to (i) the electronegativity of the oxygen atom of the hydroxyl group is expected to be lowered as a result of the $n \rightarrow \pi^*$ transition. Therefore the $\mathrm{O{-}H\cdots O}\!<$ or $\mathrm{O{-}H\cdots N}\!<$ hydrogen bonding energy will be smaller in the excited state than in the ground state. This fact will also contribute to the increase of the $n \rightarrow \pi^*$ absorption frequency[†].

The situation is entirely different for the $\pi \rightarrow \pi^*$ transitions. In the excited state for a $\pi \rightarrow \pi^*$ transition of a substituted molecule the rate of electron migration is in general larger than in the ground state[24,26]. This illustrates the reduction of the absorption frequency in the order (a) to (c) as contrasted with the case of the $n \rightarrow \pi^*$ transition. This behavior of the $\pi \rightarrow \pi^*$ absorption bands of the *p*-hydroxyazobenzene is quite similar to that of $\pi \rightarrow \pi^*$ bands of other molecules reported in the literature[1-7].

Lastly let consideration be given to the difference between the effects of $\mathrm{O{-}H\cdots O}\!<$ and $\mathrm{O{-}H\cdots N}\!<$ hydrogen bonds. The present experiments have revealed that both the equilibrium constant and the frequency shift for the $\mathrm{O{-}H\cdots N}\!<$ bond are larger than those for the $\mathrm{O{-}H\cdots O}\!<$ bond (see (c_1) and (c_2) of Fig. 3). It is then suggested that the proton-accepting power of the nitrogen atom is stronger than that of the oxygen atom. This is in accord with Tsuboi's conclusion derived from infrared spectroscopy[19].

Summary

The electronic absorption spectra of *p*-hydroxyazobenzene in *iso*-octane and also in the mixtures of *iso*-octane-ether and *iso*-octane-pyridine were measured. The spectral change observed when addition was made of a small amount of ether or pyridine to a solution of *p*-hydroxyazobenzene in pure *iso*-octane was satisfactorily interpreted as due to the formation of a hydrogen bond between the solute molecule and ether or pyridine. The equilibrium constants for the hydrogen bonds and the absorption curves of the hydrogen-bonded complexes were determined from the spectral data.

It is made clear that the effects of hydrogen bonding on the absorption bands are dependent upon the type of the electronic transitions from which the bands originate. The $\pi \rightarrow \pi^*$ bands situated in the ultraviolet region are markedly displaced to the red, while the $n \rightarrow \pi^*$ band in the visible region slightly to the blue. A theoretical explanation for the above phenomena is offered.

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26) K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).

[†] As is seen from Figs. 1 and 2, $n \rightarrow \pi^*$ absorption band I is superposed on the tail of $\pi \rightarrow \pi^*$ band II which is of high intensity and is displaced to the red by the hydrogen bonds. This fact may be responsible to some extent for the observed blue-shift of the $n \rightarrow \pi^*$ band.