Benzylideneaniline. II. Iodine Complexes of Benzylideneaniline and its Derivatives

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In the preceding paper the author proposed for benzylideneaniline a structure with the benzene ring of N side nearly perpendicular to the rest of the molecule. Then the non-bonding electron will migrate into the benzene ring to a large extent, and the ionization potential of the lone-pair electron will increase and its donor ability will decrease compared with the case where there is no interaction. To examine the validity of this assumption, the nature of the lone-pair electron is now investigated by means of the measurement of the equilibrium constant of iodine complex.

Iodine Complex.—The interaction between iodine molecule and aromatic compounds was firstly suggested by Benesi and Hildebrand(1) to be the acid-base type interaction, where the iodine molecule behaves as an acid and the aromatic molecule as a base. It has been shown by Mulliken(2) that this type of interaction is based upon charge-transfer resonance stablilization, and the new absorption band in the ultraviolet region, which was absent in both component molecules but now comes into appearence in the complex, can be interpreted as the charge-transfar band, for which this resonance interaction is responsible. This band was also explained by Kuboyama and Nagakura(3) from the LCMO treatment to be due to the electron transition from the perturbed higest filled orbital of the donor component to the lowest vacant σ_u MO of iodine component. Also the absorption band of I_2 shifts toward shorter wavelengths when a complex is formed, which again can be interpreted from the consideration that the σ_u MO of I_2 is raised while the π_g MO is not so much affected(4). This phenomenon has been investigated extensively by many authors(2-7) for a large variety of compounds including as bases those with lone pair electrons or π-electrons, and the equilibrium constants, as well as heats and entropies of formation of these complexes have been measured(8-10).

Hastings, Franklin, Schiller and Matsen(11) and McConnell, Ham and Platt(12) correlated the positions of charge-transfer absorption maxima with the ionization potentials of the donor molecules and found an excellent agreement between theory and experiments.

When benzylideneaniline is used as the base, the donor orbital may be non-bonding orbital, π-orbital or both, and the position of the charge-transfer band will be the fingerpost for assuming the ionization potential of the donor orbital, and the equilibrium constant will serve as a criterion of the geometry of this molecule.

Results and Discussion

The spectra of the mixtures of iodine and benzylideneaniline in various concentrations in

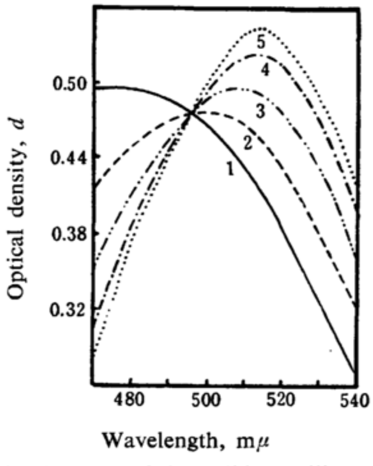

Fig. 1. Spectra of benzylideneaniline$+I_2$ in CCl_4; Base concentration: 1, —— 1.10; 2, ---- 0.55; 3, -·-·- 0.275; 4, -·-· 0.138; 5, ······ 0.069 mol./l. I_2 concentration 1.74×10^{-4} mol./l.

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(1) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **70**, 2832 (1948).

(2) R. S. Mulliken, ibid., **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(3) A. Kuboyama anb S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 1082 (1954).

(4) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

(5) H. A. Benesi and J. H. Hildebrand, ibid., **71**, 2703 (1949); **72**, 2273 (1950).

(6) R. M. Keefer and L. J. Andrews, ibid., **74**, 458, 1891, 4500 (1952); **75**, 3561 (1953).

(7) C. Reid and R. S. Mulliken, ibid., **76**, 3869 (1954).

(8) R. M. Keefer and L. J, Andrews, ibid., **77**, 2164 (1955).

(9) N. Ogimachi, L. J. Andrews and R. M. Keefer, ibid., **77**, 4205 (1955).

(10) T. M. Cromwell, ibid., **72**, 3825 (1950).

(11) S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, ibid., **75**, 2900 (1953).

(12) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

carbon tetrachloride in the visible region is shown in Fig. 1, the concentration of the former being constant. It shows an apparent isosbestic point, which proves the formation of 1 : 1 complex. Regrettably enough, as benzylideneaniline absorbs light considerably in the region below 400 mμ, and the equilibrium constant of the complex at the room temperature is found to be very small, no charge-transfer band could be observed on account of experimental difficulty. But the shift of I_2 band is considerable, from which the equilibrium constant could be calculated.

The equilibrium constant can be calculated by means of the equation

$$d=C_1\varepsilon_c+(C_1\varepsilon_i-d)/C_2K$$

where d is the optical density of the mixture solution at the measured wavelength, C_1 and C_2 are the concentrations of iodine and benzylideneaniline, respectively, ε_i and ε_c are the molar extinction coefficients of iodine and complex, respectively, at the wavelength, and K is the equilibrium constant. This equation can easily be derived from the law of mass action of 1 : 1 complex, with the consideration that the concentration of benzylideneaniline is actually not altered, as it is so high compared with that of iodine, and that the observed optical density is the sum of those of iodine and a complex. As the absorption due to benzylideneaniline can not be ignored, measurements were carried out with the benzylideneaniline solutions as references.

The values of d are plotted against $(C_1\varepsilon_i-d)/C_2$ (Fig. 2). They fall on straight lines which are parallel to each other, of which the slope indicates $1/K$.

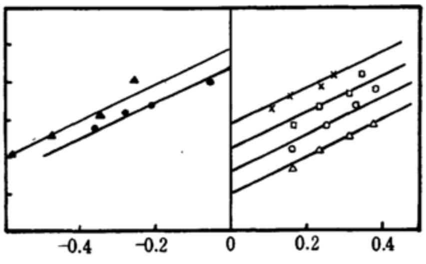


Fig. 2. Plots of d values against $(C_1\varepsilon_i-d)/C_2$.

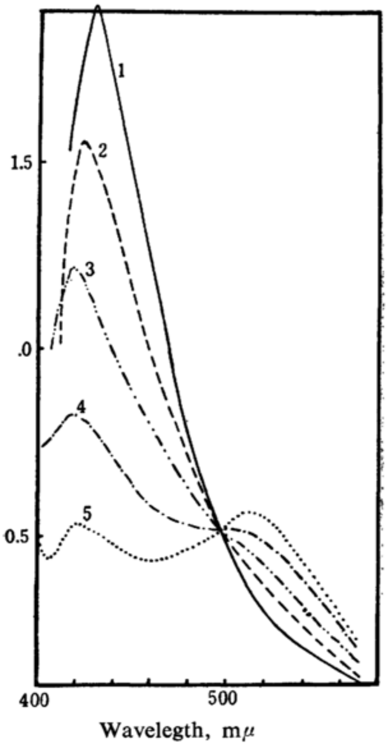


Fig. 4. Spectra of benzylidene-o-anisidine+I_2 in CCl_4; Base concentration: 1, —— 0.83; 2, ---- 0.42; 3, ·-·-·-0.21; 4, ·--·- 0.10; 5, ······ 0.05 mol./l. I_2 concentration 1.93×10^{-4} mol./l.

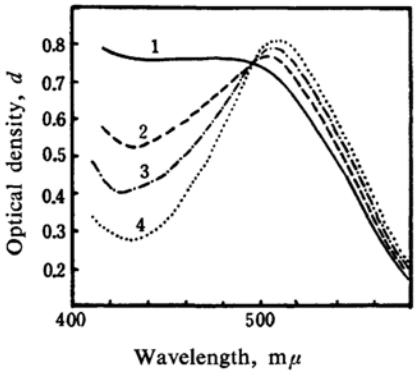


Fig. 3. Spectra of benzylidene-p-anisidine+I_2 in CCl_4; Base concentration: 1, —— 0.83; 2, ---- 0.42; 3, -·-· 0.21; 4, ······ 0.10 mol./l. I_2 concentration 2.68×10^{-4} mol./l.

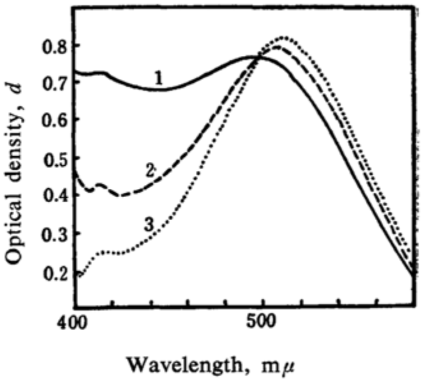
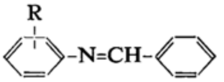


Fig. 5. Spectra of benzylidene-o-chloroaniline+I_2 in CCl_4; Base concentration: 1, —— 0.83; 2, ---- 0.42; 3, ······ 0.21 mol./l. I_2 concentration 2.68×10^{-4} mol./l.

The spectra of iodine complexes of benzylidene-*p*- and *o*-anisidine are shown in Figs. 3 and 4. There is a maximum near 420∼430 mμ for the latter, which is too intense to be a perturbed iodine transition, and probably it is the charge-transfer band. For the former compound, this band seems to appear at shorter wavelength. The spectra of the chlorine derivatives also show the same peculiarity for the ortho-compound (Fig. 5).

The appropriate values are listed in Table I.

TABLE I. EQUILIBRIUM CONSTANTS OF IODINE COMPLEXES OF BENZYLIDENEANILINES IN CCl_4 AT 11.0°C



R	*K*
H	2.0
o-OCH_3	10.6
p-OCH_3	9.2
o-Cl	2.4
m-Cl	2.0
p-Cl	2.7

The positions of I_2 absorption maxima could not strictly be defined, as, at the shorter wavelengths, the absorption due to the free base and presumably due to the charge-transfer band becomes large and the exact calculations are not feasible. But the color of the solutions is bright golden yellow and the calculation shows that their positions should not be above 460 mμ. As the shifts of I_2 band in aromatic hydrocarbons are usually not more than 10∼20 mμ, it can probably be safe to say that the iodine molecule attaches predominantly to the lone-pair orbital, which is to be more favored, if the steric requirement is fulfilled.

The influence of the methoxyl group in the aniline ring is remarkable. One explanation is that the iodine molecule attaches to the oxygen atom of the substituent, but this is not likely to be the case, because the increment of *K* is too large to be interpreted under this assumption. Moreover, it can not account for the larger values of *K* and longer wavelengths of the charge-transfer bands of ortho-derivatives.

If the proposed structure is assumed, it may be said that the methoxyl group will reduce the ionization potential of the lone-pair electron of the nitrogen atom and facilitate complex formation, and for *o*-methoxy-derivative, in addition to this, the two parallel and closely standing non-bonding orbitals with almost the same size will interact strongly with the iodine molecule and stabilize the complex. For the chlorine derivatives, the effects of the substituent would be small and the *K* values not much different from that of the unsubstituted molecule as expected, and for the *o*-chloro-compound, owing to the large size of chlorine atom, the steric hindrance will predominate over other factors affecting the equilibrium.

The equilibrium constant of benzylideneaniline is unexpectedly small and can be compared with those of the hydrocarbons. But for dimethylaniline, *K* is also small[13], and this is probably partly due to the increase of the ionization potential of the lone-pair electron caused by its migration into the benzene ring and partly due to the steric inhibition rather than to the complex formation with π-orbital as the donor, as other evidences tend to support the former model.

When the almost perpendicular structure is assumed, the hybridization of nitrogen-valence-orbitals will approach largely to the *sp*-type, then the non-bonding orbital will be almost of the *p*-type. Furthermore, as the interaction of the latter with the benzene ring is of the order of perturbation, it must retain largely its original *p* structure. This orbital is less concentrated along one direction than sp^2 orbital, and can not overlap well with I_2 orbital unless this comes nearer. This would cause the increase of steric hindrance and decrease the equilibrium constants.

Experimental

Preparations of benzylideneanilines were described in the previous paper. Iodine was sublimed two times from the G. R. grade commercial substance.

Absorption spectra were measured by a Cary self-recording spectro photometer model 14 M and a Hitachi EPU 2 type spectrophotometer using 1 cm. quartz cell. Measurements were made as soon as the solutions were prepared, so as to avoid the change due to the reaction. Reaction occurs in considerable extent when the mixture is left standing for a long time, but in the course of measurement no remarkable change was observed.

Summary

Absorption spectra of the mixtures of iodine with benzylideneanilines in various concentrations have been measured, and from the optical densities of the solutions the equilibrium constants have been calculated.

The equilibrium constants are unexpectedly small. But for methoxy-derivatives and especially for ortho-compound, the equilibrium constants are considerably large.

For *o*-methoxy- and *o*-chloro-derivatives, the charge-transfer bands appear at the longer wavelengths.

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[13] H. Tsubomura, Private communication to Professor S. Nagakura to whom the author is very much indebted for having been allowed to refer to it.

These experimental evidences are also adequately explained by the perpendicular structure of benzylideneaniline.

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