Ultraviolet and Visible Absorption Spectra of the Solid States of Aromatic Amine Complexes with Iodine*

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It is well known that, from the interaction with an iodine molecule, a molecule of an amine forms a charge transfer complex which possesses optical absorption bands in addition to those observed for either component alone. Although many papers have been published on amine-iodine complexes in solution,[1-5] there have been few works on the electronic spectra of amine-iodine complexes in the solid state.

Blomgren and Kommandeur[6] reported that aromatic hydrocarbons become positive ions in aromatic hydrocarbon - antimony pentachloride complexes. If an aromatic amine - iodine complex is a strong charge transfer complex, its ground state is a dative state ($D^+ \cdot A^-$). It has been observed by numerous investigators that the spectrum of the aniline ions is very similar to that of benzene. Recently, Gallagher[7] has shown that the spectra of three mono-protonated isomeric phenylenediamine ions resemble that of aniline, and that the spectra of their divalent ions are similar to that of benzene. Their contention is that the addition of a proton to the lone electron pair on the nitrogen atom quenches the original effect of the amino groups upon the absorption spectrum. As an n-electron of nitrogen atom goes into the $\sigma_u(5P_z)$ antibonding molecular orbit of iodine, it is interesting to see how the electronic state in the aromatic amine changes. We have measured the ultraviolet and visible absorption spectra of the iodine complexes of five aromatic amines: aniline (ANI), *p*-phenylenediamine (*p*-PDA), 1, 5-naphthylenediamine (NDA), benzidine (BEN), *o*-tolidine (TOL) and *p*, *p'*-diaminodiphenylmethane (APM). The spectra of the solid states were measured by means of the KBr disk method.

Experimental

Materials.—The ANI-iodine complex does not precipitate from a non-polar solvent, so this complex was obtained by mixing ANI and iodine at a iodine/ANI mole ratio of 0.50 and 1.00. When the two components are blended, the temperature of the mixture was raised because of the heat of the complex formation. As the mixture is cooled, it becomes a solid which is apparently crystalline. These specimens were used as ANI-iodine complex systems. APM-iodine systems were also prepared in a similar way, and their iodine contents were varied from 0.75 to 1.50.[8]

The preparations of *p*-PDA, NDA, BEN and TOL complexes have been described in previous papers.[8,9]

The Ultraviolet and Visible Spectra in the Solid State.—The ultraviolet and visible spectra of these solid complexes were measured by means of the KBr disk method or with a squashed powder between quartz plates in the 222—2000 mμ wavelength region. The spectra were measured by using a Shimadzu SV50A recording spectrophotometer.

Results and Discussion

A. The Ultraviolet Spectra of ANI Complexes and Other Similar Compounds. — The ultraviolet spectra of ANI hydrochloride and ANI-iodine systems are shown in Fig. 1. The spectrum of the ANI-iodine complex has an extra maximum at 370 mμ which can not be found in the absorption spectra of either component alone. It seems that this extra band is a charge transfer band. It has been reported that the absorption spectrum of a mixture of ANI and iodine in a chloroform solution has a characteristic charge transfer band at 349 mμ.[5] It seems reasonable to presume that the 349 mμ band in solution is shifted to 370 mμ in a solid.

By putting the observed energy of the charge transfer transition of the ANI-iodine complex, hc/λ_{CT} (λ_{CT}=374 mμ), into the following equation,[10] the ionization potential, I_D, of ANI is estimated to be 7.9 eV.:

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1) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954).
2) H. Yada, J. Tanaka and S. Nagakura, This Bulletin, **33**, 1660 (1960).
3) H. Tsubomura, *J. Am. Chem. Soc.*, **82**, 40 (1960).
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5) A. K. Chandra and D. C. Mukherjee, *Trans. Faraday Soc.*, **60**, 62 (1964).
6) G. E. Blomgren and J. Kommandeur, *J. Chem. Phys.*, **35**, 1636 (1962).
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9) S. Nishizaki and H. Kusakawa, ibid., **36**, 1681 (1963).
10) G. Briegleb and J. Czekalla, *Angew. Chem.*, **72**, 401 (1960).

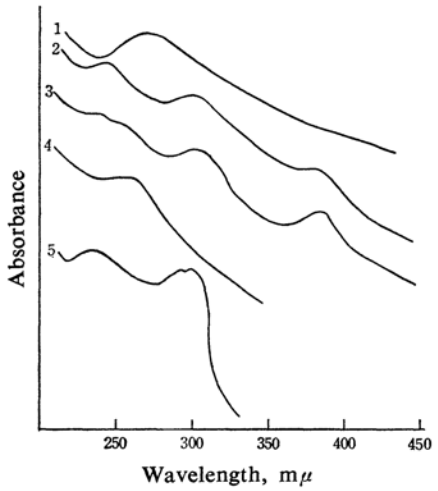

Fig. 1. Ultraviolet spectra of ANI complexes, other similar compounds and iodine in KBr disk.
1 Iodine 2 ANI-I_2 (1 : 0.50)
3 ANI-I_2 (1 : 100) 4 $C_6H_5NH_3^+Cl^-$
5 ANI (liquid membrane between quartz plates)

$$hc/\lambda_{CT}=I_D-C_1+C_2/(I_D-C_1) \qquad (1)$$

This value is in agreement with the findings of Briegleb and Czekalla,[11] but slightly larger than that of Watanabe's[12] determination with photoionization. In Eq. 1, C_1 and C_2 are constants; they are 5.20 and 1.5 eV. respectively for iodine complexes.

The 1 : 1 ANI-iodine complex possesses another new absorption band at 255 mμ, which coincides with the position of an absorption band of ANI hydrochloride. Considering this, in the 1 : 1 ANI-iodine complex one part of ANI must be in an electronic state, like the anilinium ion. The following equilibrium may represent standing in a solid state as well as in solution:

$$C_6H_5NH_2\cdot I_2 \rightleftarrows C_6H_5NH_2^+\cdot I_2^- \qquad (2)$$

The lone electron pair of the nitrogen atom is localized on the iodine molecule, and the n-π resonance within the ANI molecule disappears; therefore, it is reasonable to presume that one part of ANI in the iodine complex shows an absorption spectrum like that of benzene.

B. The Ultraviolet and Visible Spectra of Aromatic Diamine - Iodine Complexes. — The ultraviolet spectra of amine crystals and the spectra of iodine complexes are shown in Fig. 2 and Fig. 3 respectively. The wavelength of the spectral maxima of aromatic diamine complexes with iodine in the solid state and other

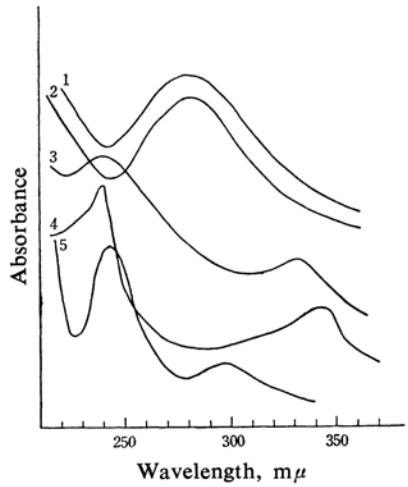

Fig. 2. Ultraviolet spectra of aromatic diamines in KBr disk.
1 BEN, 2 TOL, 3 *p*-PDA, 4 NDA, 5 APM

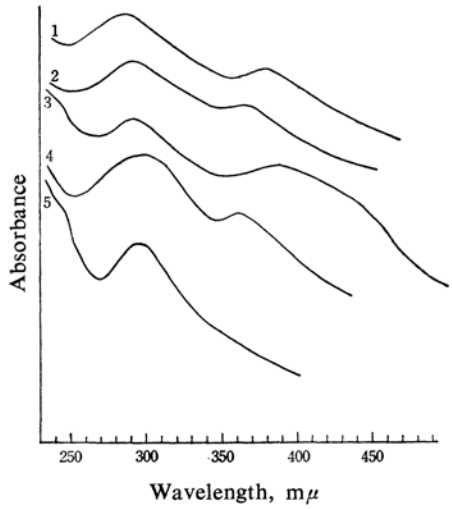

Fig. 3. Ultraviolet spectra of iodine complexes.
1 BEN, 2 TOL, 3 NDA, 4 *p*-PDA, 5 APM

similar compounds are summarized in Tables I to V.

It can be seen from these tables that, in the absorption spectrum of the 0.1 N hydrochloric acid solution, each aromatic diamine, including *p*-PDA,[7] has an absorption band which coincides with that of the aromatic hydrocarbon corresponding to its aromatic skeleton. Judging from those facts, it can be deduced that the spectrum of each mono-protonated diamine is similar to that of the mono-amino substituted derivative of the aromatic hydrocarbons.

In the iodine complexes of *p*-PDA and NDA, the positions of the absorption bands maxima change from 303 mμ to 285 mμ, and from 342 mμ to 296 mμ. From a comparison of these wave-

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12) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

TABLE I. ABSORPTION MAXIMA λ_{max} OF *p*-PDA, ITS COMPLEX AND OTHER COMPOUNDS (mμ)

p-PDA	ANI	*p*-PDA in 0.1 N HCl	C_6H_6**	Iodine complexes I_2/*p*-PDA (mole ratio)					
				0.45	0.67	0.82	1.03	1.36	1.62
243	231	255	255					(237)*	(234)
303	294			283	283	283	288	284	282
				350	354	350	348	350	350
								394	
				830	780	720	750	730	750

* Brackets represent shoulders.
** Quoted from "Organic Electronic Spectral Data," Vol. II, Ed. by H. E. Ungnade, Interscience Publishers Inc., New York (1960).

TABLE II. ABSORPTION MAXIMA λ_{max} OF NDA, ITS COMPLEX AND OTHER COMPOUNDS (mμ)

NDA	α-Naphthyl-amine	NDA in 0.1 N HCl	$C_{10}H_{10}$**	Iodine complexes I_2/NDA (mole ratio)			
				0.70	0.86	0.90	1.01
237	236	221	221				
342	303	268	265	300	296	294	292
		277	275				
		286	286				
				(370)	(370)	(370)	(370)
				700	700	700	700

TABLE III. ABSORPTION MAXIMA λ_{max} OF BEN, ITS COMPLEX AND OTHER COMPOUNDS (mμ)

BEN	*p*-Phenylaniline	BEN in 0.1 N HCl	$C_6H_5 \cdot C_6H_5$**	Iodine complexes I_2/BEN (mole ratio)			
				0.78	0.94	1.26	1.49
281	278	248	248	294	293	294	292
				390	380	379	375
				620	610	600	630
				1620	1650	1500	1500

TABLE IV. ABSORPTION MAXIMA λ_{max} OF TOL, ITS COMPLEX AND OTHER COMPOUNDS (mμ)

TOL	TOL in 0.1 N HCl	Iodine complexes I_2/TOL (mole ratio)			
		0.94	1.02	1.29	1.53
283	250	300	298	296	294
		368	366	358	366
		(470)	(470)	(470)	(470)
		640	640	640	640
		(900)	(900)	(900)	(900)
		1400	1400	1400	1400

TABLE V. ABSORPTION MAXIMA λ_{max} OF APM, ITS COMPLEX AND OTHER COMPOUNDS (mμ)

APM	$C_6H_5CH_2C_6H_5$**	APM in 0.1 N HCl	Iodine complexes I_2/APM (mole ratio)			
			0.75	1.00	1.25	1.50
246			(255)	(255)	(255)	(255)
299	254	254	299	299	301	301
	256					
	260	261				
	263	265				
	269	270				
			384	384	392	386
			(450)	(450)	(450)	(450)
			585	580	580	580

lengths, 285 mμ and 296 mμ, with those of the absorption bands of aniline and α-naphthylamine, it can be presumed that *p*-PDA and NDA become mono-positive ions in solid iodine complexes. The ground states of *p*-PDA-iodine and NDA-iodine complexes are dative states:

$$p\text{-PDA}^+ \cdot I_2^- \quad \text{and} \quad \text{NDA}^+ \cdot I_2^- \qquad (3)$$

In *p*-PDA-iodine and NDA-iodine complexes, an iodine molecule exists in the visinity of an amino group and localizes the lone electron pair of the nitrogen atom as in the ANI-iodine complex.

On the other hand, in the case of the BEN-iodine complex, a bathochromic shift is found. The maximum of the absorption band at 281 mμ shifts to 294 mμ. Of course, it does not correspond to that of *p*-phenylaniline[13] at 278 mμ. A similar phenomenon is found on the TOL-iodine complex, where the band maximum at 283 mμ shifts to 298 mμ. At the present time we can not explain why the bathochromic shift occurs in the case of a polyphenylene-diamine-iodine complex system.

When APM, a non-conjugated aromatic diamine, is used as the donor, there is no conspicuous change in the ultraviolet spectra of this complex system. The shoulder at 255 mμ probably arises from the reaction of the anilino group with iodine.

Excepting the APM-iodine system, the color of aromatic diamine complexes with iodine is blue at a low iodine content; it becomes black with an increase in the iodine content. As these specimens were dissolved in such polar solvents as alcohols or ketones, the color of the solution was green at first, but it changed brown with the lapse of time.

C. The Change Transfer Bands of Semiconductive Complexes and the Ionization Potentials of Aromatic Diamines.—The visible and near infrared absorption bands, which are assumed to be the charge transfer bands of aromatic diamine-iodine complexes, are shown in Fig. 4. In order to estimate the ionization potential of these aromatic diamines, the observed wavelength of the charge transfer band was placed into Eq. 1. However, it was not possible to calculate the ionization potential by this equation because the observed values of the energy of the charge transfer transition are so small that Eq. 1 does not give a real number. Therefore, instead of Eq. 1, the following equation are used[14] to estimate the ionization potential:

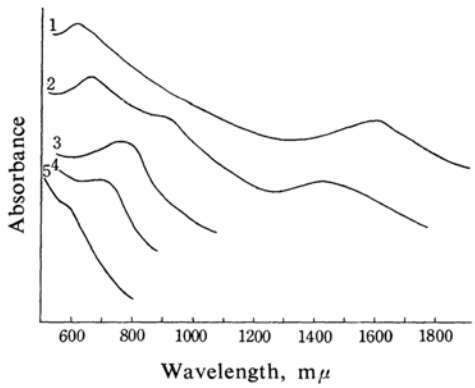

Fig. 4. The spectra of iodine complexes.
1 BEN, 2 TOL, 3 *p*-PDA, 4 NDA, 5 APM

TABLE VI. IONIZATION POTENTIAL ENERGIES ESTIMATED FROM EQS. 4 AND 5 OF AROMATIC AMINES (eV.)

Donor	From Eq. 4	From Eq. 5	Corresponding methyl substituted amine
ANI	7.9	7.9	7.2[6]
p-PDA	6.1	7.2	6.7[6]
NDA	6.1	7.2	—
BEN	5.1	6.8	6.7[7]
TOL	5.2	6.8	—
APM	6.5	7.4	7.1[6]

$$hc/\lambda_{CT} = 0.87 I_D - 3.6 \qquad (4)$$

The values obtained are shown in Table VI. In comparison with *N*, *N*, *N'*, *N'*-tetramethyl-*p*-phenylenediamine (TMPD) or *N*, *N*, *N'*, *N'*-tetramethyl-*p*, *p'*-diaminodiphenylmethane,[15] it seems that these values are underestimated. Similar results may be obtained from an emprical linear relation between the ionization potential I_D and the wave number of the charge transfer band, $\tilde{\nu}_{CT}$.[15] Such a relationship have been determined for the complexes of donors of a reliably know ionization potential (namely, 7.9 eV. for ANI[11] and 7.2 eV. for *p*-PDA[11]). This is:

$$I_D = 6.5 + 5.19 \times 10^{-4} \tilde{\nu}_{CT} \qquad (5)$$

for aromatic amine - iodine complexes in solid states. From measurements of the wave numbers of charge transfer bands of specimens, the ionization potential may be evaluated. The results are quoted in the second column of Table VI. However, Foster and Thomson reported that the *N*, *N*, *N'*, *N'*-tetramethylbenzidine is as strong as TMPD as an electron donor for chloranil.[16]

The results of this investigation imply that

13) E. Sawicki and F. E. Ray, *J. Org. Chem.*, **19**, 1903 (1954).
14) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).
15) R. Foster, *Nature*, **183**, 1253 (1959).
16) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 1059 (1963).

the charge transfer bands of aromatic diamine-iodine complexes, above all, of the polyphenylenediamine-iodine system, unusually appear in the very long wavelength region, and that the order of the energies of the charge transfer transition is in agreement with that of the electrical resistivities of these specimens.[8,9]

Summary

The ultraviolet and visible spectra of aromatic amine complexes with iodine in the crystalline state have been investigated by means of the KBr disk method or with a squashed powder between quartz plates.

Part of the aniline (ANI) ions in the ANI-iodine system become positive, and the maximum of the spectrum band appears at 255 mμ. *p*-Phenylenediamine (*p*-PDA) and 1,5-naphthylenediamine (NDA) complexes with iodine possess the band maxima at the same position as those of ANI and α-naphthylamine. The ground states of these complexes seem to be dative states.

In benzidine (BEN) and *o*-tolidine (TOL) from polyphenylenediamines, and iodine complex systems bathochromic shifts are observed.

By estimating the ionization potential I_D of these aromatic amines from the energies of the charge transfer transition, low values of I_D, except for ANI, are obtained.

The electrical resistivities of these specimens are in the order BEN$<$TOL$<$NDA$\approx$*p*-PDA, which is in agreement with that of the energies of the charge transfer transition.

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