Charge-transfer and Proton-transfer in the Formation of Molecular Complexes. IV.[1] Picric Acid Complexes with Benzidine and Its Derivatives

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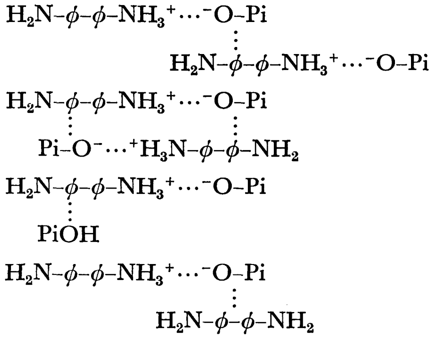
The preparation of picric acid complexes with benzidine, *o*-tolidine, 3,3′-dichloro-*o*-tolidine, 3,3′-dibromo-*o*-tolidine, *o*-dianisidine, and *N,N,N′,N′*-tetramethylbenzidine was attempted in the following three solvents: benzene, chloroform, and ethanol. From benzene and chloroform, 3,3′-dibromo-*o*-tolidine forms a 1: 1 complex of the charge-transfer type, but the other five diamines give yellow salts formed by means of proton-transfer. Some complexes prepared in ethanol are of an unfamiliar nature. The spectroscopic examination of the 1: 1 complexes with *o*-tolidine, *o*-dianisidine, and tetramethylbenzidine revealed that a half of the diamine molecule acts as a proton-acceptor, while the other half has a charge-transfer interaction with the picrate ion. The simultaneous operation of charge-transfer and proton-transfer interactions was also demonstrated in the black-colored complex with benzidine of a 2: 1 composition.

Our earlier study of the vibrational and electronic spectra of the orange-colored α-naphthylamine-picric acid (2: 1) complex revealed that a proton is transferred from picric acid to α-naphthylamine, and that the interaction between the picrate ion and the second α-naphthylamine molecule is capable of producing a charge-transfer absorption band.[2] For brevity, such a complex may be denoted as a complex of the CPT type because of the simultaneous operation of charge-transfer (CT) and proton-transfer (PT) interactions between the component molecules.

When an aromatic diamine such as benzidine is combined with picric acid in a mole ratio of 1: 1, one may imagine the classification of the resulting complexes into the following three types. If the pK_a value of the diamine is low, a complex of the CT type may be formed.[1,3] On the other hand, the PT interaction may take place when the pK_a value of the diamine is high. In addition, a third possibility may be conceived on the basis of the observation of the above-mentioned naphthylamine complex; that is, a half of the diamine molecule acts as a proton-acceptor, while the other half has a CT interaction with the picrate ion. In this way, the complex of a 1: 1 composition can be of the CPT type (Case 1 of CPT complexes). Of course, the hydroxy group of the acid must be in the proximity of the amino group acting as a proton-acceptor to make the PT interaction feasible, and the molecular stacking must allow the picrate ion to superpose upon the unprotonated half of the adjacent diamine molecule. Two ways of stacking, (a) and (b), may be produced by the orientation of this diamine molecule.

In the *s*-trinitrobenzene (TNB) complexes of *N,N,N′,N′*-tetramethylbenzidine and *o*-dianisidine, the mole ratio of the diamine to TNB has been known to be 1: 2.[4,5] Because of the structural similarity between TNB and picric acid, the picric acid complexes of a 1: 2 composition and of the CT type may exist. It is also highly likely that the diamine molecule accepts two protons. In a situation intermediate between these two, a complex of the CPT type may be obtained; that is, one of the two picric acid molecules may be a proton-donor, and the other, an electron-acceptor (Case 2 of CPT complexes). As has been found with the 2,4-dinitrophenol and picric acid complexes of aromatic monoamines,[1,6] a delicate balance between the pK_a value of picric acid and those of the diamine may be the major factor governing the formation of such a complex.

By analogy to the α-naphthylamine-picric acid (2: 1) complex, the diamine complexes of a 2: 1 composition can also be expected to be of the CPT type (Case 3 of CPT complexes). The three cases imagined above for the picric acid (PiOH) complexes of the CPT type may be schematically shown as follows:



Case 1 (a) $\mathrm{H_2N\text{-}\phi\text{-}\phi\text{-}NH_3^+\cdots{}^-O\text{-}Pi}$ $\vdots$ $\mathrm{H_2N\text{-}\phi\text{-}\phi\text{-}NH_3^+\cdots{}^-O\text{-}Pi}$

(b) $\mathrm{H_2N\text{-}\phi\text{-}\phi\text{-}NH_3^+\cdots{}^-O\text{-}Pi}$ $\vdots$ $\vdots$ $\mathrm{Pi\text{-}O^-\cdots{}^+H_3N\text{-}\phi\text{-}\phi\text{-}NH_2}$

Case 2 $\mathrm{H_2N\text{-}\phi\text{-}\phi\text{-}NH_3^+\cdots{}^-O\text{-}Pi}$ $\vdots$ PiOH

Case 3 $\mathrm{H_2N\text{-}\phi\text{-}\phi\text{-}NH_3^+\cdots{}^-O\text{-}Pi}$ $\vdots$ $\mathrm{H_2N\text{-}\phi\text{-}\phi\text{-}NH_2}$

This theorizing has led us to look into the picric acid complexes of benzidine and its five derivatives. As will be described below, the complexes belonging to most of the cases mentioned above, including Cases 1 and 3, were found by these combinations.

Experimental

Materials. The sources and handling of benzidine, *o*-tolidine, 3,3′-dichloro-*o*-tolidine, 3,3′-dibromo-*o*-tolidine, and *N,N,N′,N′*-tetramethylbenzidine have been described in a

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[1] Part III: N. Inoue and Y. Matsunaga, This Bulletin, **45**, 3478 (1972).

[2] Y. Matsunaga and G. Saito, *ibid.*, **45**, 963 (1972).

[3] E. Hertel, *Ann.*, **451**, 179 (1926).

[4] J. J. Sudborough, *J. Chem. Soc.*, **109**, 1339 (1916).

[5] T. Amano, H. Kuroda, and H. Akamatu, This Bulletin, **42**, 671 (1969).

[6] G. Saito and Y. Matsunaga, *ibid.*, **44**, 3328 (1971).

previous paper of ours.[7] In addition to this series, *o*-dianisidine obtained commercially was used in this work. The complexes were prepared in the following three solvents of different polarities: benzene, chloroform, and ethanol. Generally, the complexes were precipitated by mixing equimolar amounts of the component compounds separately dissolved in a hot solvent. However, preparation with an excess of either the diamine or picric acid was also attempted when ethanol was used as the solvent.

Measurements. The vibrational spectra of the solid complexes in the region from 2000 to 4000 cm^{-1} were determined as hexachloro-1,3-butadiene mulls with a JASCO IR–G infrared spectrophotometer, and the electronic spectra in the visible region, with a Beckman DK-2A spectroreflectometer. The procedure in the latter measurements was similar to that described in a previous paper.[8] All the complexes with one exception decompose rather gradually. Therefore, the temperatures recorded as the decomposition points are only approximate.

Results and Discussion

The characteristics of the picric acid complexes obtained in this work are displayed in Table 1. Only the following pK_a values are available in the literature: 4.95 and 3.85 for the first and second pK_a values of benzidine, and 4.5 and 3.3 for those of *o*-tolidine.[9] Therefore, the diamines in this table are arranged in the order in which the pK_a values of the related aniline derivatives decrease.

TABLE 1. COMPOSITION, COLOR, AND MELTING POINT OF THE PICRIC ACID COMPLEXES WITH BENZIDINE AND ITS DERIVATIVES

Diamine	Solvent		
	Benzene	Chloroform	Ethanol
N,N,N',N'-Tetramethylbenzidine	2:3 Bright yellow 196°(decomp)	2:5 Yellow 199°(decomp)	2:5 Yellow 195°(decomp) 1:2 Greenish yellow 199°(decomp) 1:1 Tan 198°(decomp)
Benzidine	1:2 Yellow 230°(decomp)	1:2 Yellow 215°(decomp.)	1:2 Dull yellow 225°(decomp) 2:1 Black or brown 124°
o-Dianisidine	1:2 Yellow 230°(decomp)	2:3 Dark yellow 216°(decomp)	1:1 Orange 220°(decomp)
o-Tolidine	2:3 Yellow 215°(decomp)	2:3 Yellow 223°(decomp)	1:1 Brick red 190°(decomp)
3,3'-Dichloro-*o*-tolidine	1:1 Yellow 194°(decomp)	1:1 Yellow 195°(decomp)	1:1 Yellow 195°(decomp)
3,3'-Dibromo-*o*-tolidine	1:1 Jet black 190°(decomp)	1:1 Jet black 190°(decomp)	—[a]

a) Only the cation-radical salt could be isolated.

One may start a search for complexes of the CPT type by a visual examination. If the color is deeper than yellow, which arises from an absorption band due to the picrate ion, the presence of a CT interaction in some form is likely. As has been previously reported by us, the dissociation of picric acid does not much affect its electron affinity, which is close to that of TNB.[2,10] Consequently, the location of the CT absorption band in Case 3 of CPT complexes is expected to be not far from that of the corresponding TNB complex. On the other hand, a complex belonging to Case 1 or 2 cannot be so deep as the TNB complex because one of the two amino groups, which make the molecule a good electron-donor, is protonated.

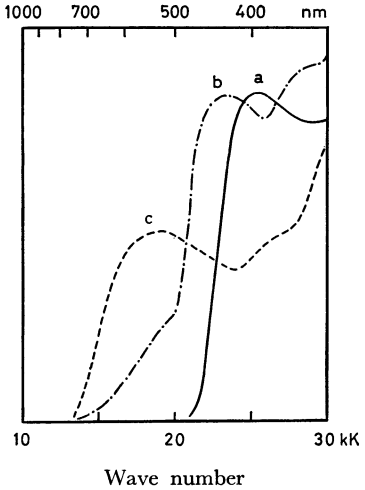

Fig. 1. Diffuse reflection spectra of a) the benzidine-picric acid (1:2) complex from benzene, b) the 2:1 complex from ethanol, and c) the corresponding TNB complex.

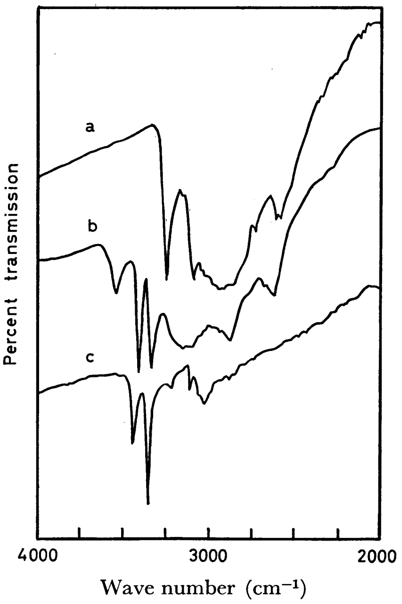

Fig. 2. Vibrational spectra of a) the benzidine-picric acid (1:2) complex from benzene, b) the 2:1 complex from ethanol, and c) the corresponding TNB complex.

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[7] Y. Matsunaga and G. Saito, This Bulletin, **44**, 958 (1971).

[8] K. Abe, Y. Matsunaga, and G. Saito, *ibid.*, **41**, 2852 (1968).

[9] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London (1965), p. 120.

[10] G. Saito and Y. Matsunaga, This Bulletin, **45**, 2214 (1972).

The Benzidine Complexes (Figs. 1 and 2). A yellow-colored powder precipitates from all the three solvents when the component compounds are mixed in equimolar proportions. The mole ratio of the diamine to the acid was found to be 1: 2. Found: C, 45.15; H, 2.93% (from benzene); C, 45.32; H, 2.96% (from chloroform); and C, 44.87; H, 3.03% (from ethanol). Calcd for $C_{12}H_{12}N_2 \cdot 2C_6H_3N_3O_7$: C, 44.86; H, 2.80%. Their electronic spectra are all the same. The absorption maximum located at about 25 kK can be assigned to the picrate ion (see Curve a in Fig. 1). Moreover, the vibrational spectra of all the three show the pattern characteristic of the picrates of primary amines, namely, broad bands in the region from 2500 to 3000 cm^{-1} and at about 3250 cm^{-1}.[11] This yellow-colored complex is undoubtedly a salt formed by the transfer of protons from two picric acid molecules to a diamine molecule.

When an excess of the diamine was employed in ethanol, the 2: 1 complex was obtained as black needles or occasionally as a brown powder. Found: C, 61.70; H, 5.27%. Calcd for $2C_{12}H_{12}N_2 \cdot C_6H_3N_3O_7$: C, 60.30; H, 4.52%. As is shown in Fig. 1, this complex possesses an additional electronic absorption located below 20 kK. The comparison of this spectrum with that of the corresponding TNB complex clearly indicates that the diamine as a whole acts as an electron-donor. In this complex, the band to be assigned to the picrate ion appears at 23.5 kK. Such a location is not unusual, as we have seen in the cases of the α-naphthylamine- and pyridine-picric acid complexes.[2] The vibrational spectrum exhibits both the bands ascribed to the picrate of primary amine in the region from 2500 to 3250 cm^{-1} and those ascribed to the NH_2 group in the region from 3250 to 3500 cm^{-1}. The latter are well approximated by those in the spectrum of the TNB complex (see Curve c in Fig. 2). However, the assignment of the band appearing around 3500 cm^{-1} could not be settled. A sharp band at 3250 cm^{-1} observed in the 1: 2 complex is not seen in the 2: 1 complex. It may be added that a similar observation has been made in the α-naphthylamine-picric acid complexes.[2] These pieces of spectroscopic evidence lead to the conclusion that this 2: 1 complex is of the CPT type. Moreover, the intensity of the absorption band appearing below 20 kK is consistent with our earlier observation that the weakness of the CT absorption is characteristic of the complexes with picrates.[2,10] The same 2: 1 complex was isolated as black-colored plates when prepared in an aqueous solution containing a small amount of pyridine. Found: C, 60.87; H, 5.04%. It must be pointed out that the 2: 1 complex melts at a temperature about 110°C lower than the 1: 2 complex, reflecting the difference in the nature of intermolecular forces. The formation of the 1: 1 and 1: 2 complexes has been described by Rascanu.[12] Unfortunately, we could not obtain the former one, the melting point of which was reported to be 200—205°C.

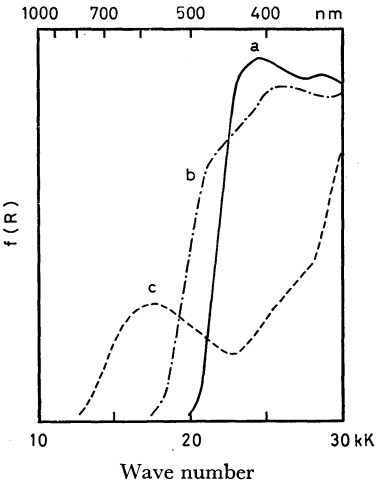

Fig. 3. Diffuse reflection spectra of a) the *o*-tolidine-picric acid (2: 3) complex from benzene, b) the 1: 1 complex from ethanol, and c) the corresponding TNB complex.

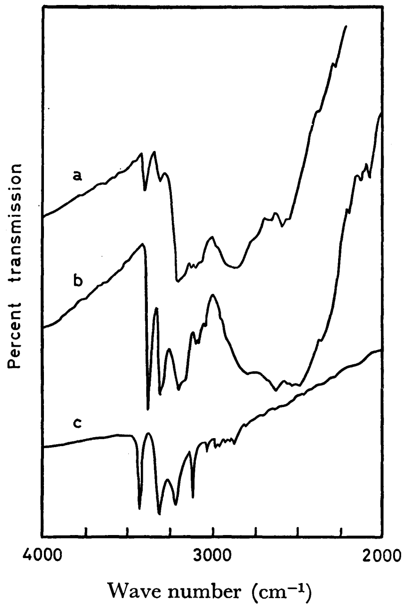

Fig. 4. Vibrational spectra of a) the *o*-tolidine-picric acid (2: 3) complex from benzene, b) the 1: 1 complex from ethanol, and c) the corresponding TNB complex.

The o-*Tolidine Complexes (Figs. 3 and 4).* The complexes precipitated from benzene and chloroform are in the form of a yellow powder and have a mole ratio of 2: 3, whereas the brick red-colored powder precipitated from ethanol is of a 1: 1 composition. Found: C, 50.39; H, 3.78% (from benzene); C, 50.29; H, 4.10% (from chloroform), and C, 54.59; H, 4.48% (from ethanol). Calcd for $2C_{14}H_{16}N_2 \cdot 3C_6H_3N_3O_7$ and for $C_{14}H_{16}N_2 \cdot C_6H_3N_3O_7$: C, 49.68; H, 3.69% and C, 54.42; H, 4.31% respectively. As the spectra of the 2: 3 complexes are identical, only that of the sample made in benzene is presented in Fig. 3. The bands above 23 kK are common to both 2: 3 and 1: 1 complexes and can be ascribed to the picrate ion. An extra absorption band at about 21 kK apparently accounts for the deep coloration of the 1: 1 complex. A comparison with the spectrum of the corresponding TNB complex shown by Curve c indicates that the

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11) R. P. Mariella, M. J. Gruber, and J. W. Elder, *J. Org. Chem.*, **26**, 3217 (1961).

12) R. Rascanu, *Ann. Sci. Univ. Jassy.*, **26**, 3 (1940), through *Chem. Abstr.*, **34**, 4385 (1940).

electron-donor is not a neutral *o*-tolidine molecule. If the electron-donor strength of the monoprotonated *o*-tolidine cation is essentially determined by that of the unprotonated half, the CT absorption is expected to appear near that of the *o*-toluidine-TNB complex, 23.1 kK. The close similarity of the locations strongly suggests that this 1: 1 complex belongs to Case 1 of CPT complexes. This speculation is supported by the vibrational spectral analysis. Both the 2: 3 and 1: 1 complexes show patterns characteristic of the picrates of primary amines and also the NH_2 group. The latter pattern consists of bands appearing at 3300 and 3390 cm^{-1}, as evidenced by the spectrum of the corresponding TNB complex (see Fig. 4). The intensity of this pattern in the 2: 3 complex is definitely weaker than that in the 1:1 complex; therefore, all the picric acid molecules in the former complex seem to participate in the PT interaction. Although the free amino group must be left in the 2: 3 complex, no CT absorption could be detected.

The melting point observed by us for the 1: 1 complex differs considerably from that reported by Rascanu, 110°C. Furthermore, we failed to obtain the 1: 2 complex described by her.[12]

*The 3,3'-Dichloro-*o*-tolidine Complexes.* All the yellow-colored complexes precipitated from the three solvents were found to be of a 1: 1 composition. Found: C, 47.31; H, 3.23% (from benzene); C, 46.67; H, 3.16% (from chloroform); and C, 47.16; H, 3.35% (from ethanol). Calcd for $C_{14}H_{14}N_2Cl_2 \cdot C_6H_3N_3O_7$: C, 47.06; H, 3.33%. Contrary to the case of the *o*-tolidine-picric acid (1: 1) complex, no band to be assigned to the CT absorption could be detected. As would be expected from the color and the composition, the coexistence of the NH_3^+ and NH_2 groups is demonstrated by the vibrational spectrum.

By the prolonged heating of an ethanolic solution of the complex on a water-bath, a green powder of a 1: 1 composition deposited. On the basis of the spectral behavior, we suppose that the product is a picrate of the 3,3'-dichloro-*o*-tolidine cation-radical.

*The 3,3'-Dibromo-*o*-tolidine Complexes (Fig. 5).* Jet black-colored needles were crystallized from benzene and chloroform. Their compositions appear to be 1:1. Found: C, 40.29; H, 2.90% (from benzene); C, 39.98; H, 2.92% (from chloroform). Calcd for $C_{14}H_{14}N_2Br_2 \cdot C_6H_3N_3O_7$: C, 40.08; H, 2.84%. Not only the electronic spectrum, but also the vibrational spectrum, strikingly resemble those of the TNB complex (see Fig. 5 for the reflection spectra). Thus, the complex is certainly of the CT type. In accordance with this conclusion, dibromo-*o*-tolidine is supposedly the poorest proton-acceptor among the diamines studied here.

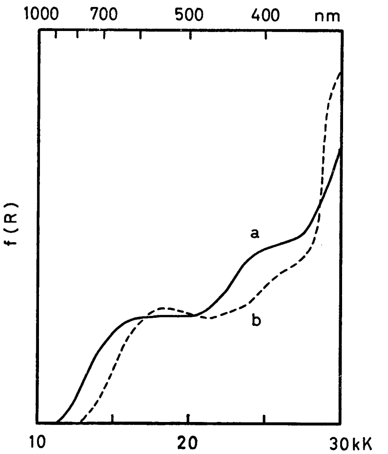

Fig. 5. Diffuse reflection spectra of a) the dibromo-*o*-tolidine-picric acid (1: 1) complex and b) the corresponding TNB complex.

Upon storage for months in air, the color turned green. A bright green product was directly obtained if the component compounds were mixed in ethanol. These two samples show spectra similar to each other. The behavior of this and the above-mentioned diamine cation-radical salt will be reported in detail later.

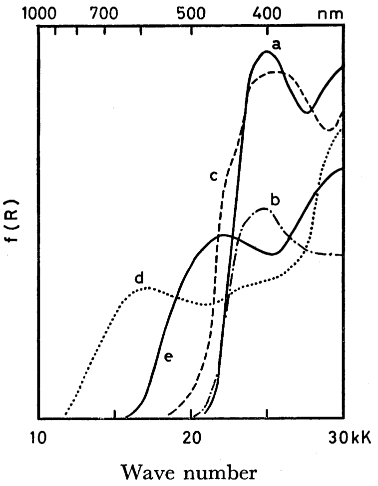

Fig. 6. Diffuse reflection spectra of the *o*-dianisidine-picric acid (1: 2) complex from benzene, b) the 2: 3 complex from chloroform, c) the 1: 1 complex from ethanol, d) the corresponding TNB (1: 2) complex, and e) the *o*-anisidine-TNB complex.

*The *o*-Dianisidine Complexes (Fig. 6).* The yellow-colored complex crystallized from a benzene solution has a 1: 2 composition. Found: C, 44.35; H, 3.27%. Calcd for $C_{14}H_{16}N_2O_2 \cdot 2C_6H_3N_3O_7$: C, 44.44; H, 3.13%. The vibrational spectrum is dominated by the pattern to be ascribed to the NH_3^+ group, indicating that the two amino groups in an *o*-dianisidine molecule are protonated. This complex is undoubtedly of the same nature as the benzidine-picric acid (1: 2) described above.

When chloroform is employed as the solvent, a yellow-colored powder was precipitated. The mole ratio is more complicated; namely, 2: 3. Found: C, 47.05; H, 3.46%. Calcd for $2C_{14}H_{16}N_2O_2 \cdot 3C_6H_3N_3O_7$: C, 46.97; H, 3.49%. The presence of the NH_2 group is indicated by the appearance of vibrational bands at 3300 and 3380 cm^{-1}. Nevertheless, the electronic spectrum is essentially the same as that of the 1: 2 complex. The possibility that this complex is a mixture of the 1: 2 and the 1: 1 complexes was ruled out by the X-ray diffraction measurements. Presumably this belongs to the same category as the *o*-tolidine complex of a 2: 3 composition.

The 1: 1 complex prepared in ethanol is orange-colored. Found: C, 50.69; H, 4.14%. Calcd for $C_{14}H_{16}N_2O_2 \cdot C_6H_3N_3O_7$: C, 50.74; H, 4.02%. The reflection spectrum shown in Fig. 6 has an absorption in addition to those of the above-mentioned 1: 2 and 2: 3 complexes. This new band is at a location higher than the CT absorption band in the corresponding TNB complex, 17.3 kK, while close to that in the *o*-anisidine-TNB complex, 22.2 kK. Further evidence that the electronic absorption arises from the CT interaction between the monoprotonated *o*-dianisidine cation and the picrate anion comes from the coexistence of the vibrational patterns due to the NH_2 and NH_3^+ groups. This is a second example of Case 1 of CPT complexes.

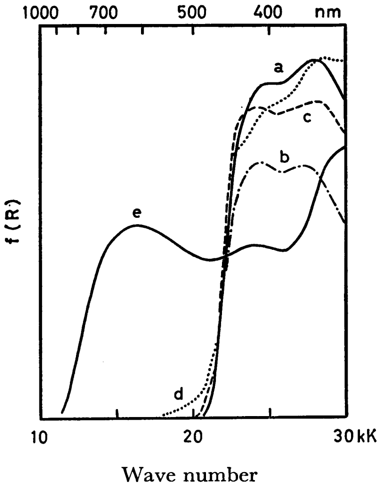

Fig. 7. Diffuse reflection spectra of a) the tetramethylbenzidine-picric acid (2: 3) complex from benzene, b) the 2: 5 complex from chloroform, c) the 1: 2 complex from ethanol, d) the 1: 1 complex from ethanol, and e) the corresponding TNB (1: 2) complex.

The Tetramethylbenzidine Complexes (Fig. 7). The bright yellow complex deposited from benzene is of a 2: 3 composition. Found: C, 51.21; H, 4.15%. Calcd for $2C_{16}H_{20}N_2 \cdot 3C_6H_3N_3O_7$: C, 51.41; H, 4.20%.

From chloroform a yellow-colored complex was precipitated. The mole ratio was found to be 2: 5. Found: C, 45.43; H, 3.61%. Calcd for $2C_{16}H_{20}N_2 \cdot 5C_6H_3N_3O_7$: C, 45.78; H, 3.38%.

When ethanol was employed, the following three complexes were isolated, depending upon the ratio of the component compounds mixed. One of them was the 2: 5 complex previously obtained from chloroform. Found: C, 45.93; H, 3.53%. The complex of a 1:2 composition is greenish yellow. Found: C, 47.39; H, 3.36%. Calcd for $C_{16}H_{20}N_2 \cdot 2C_6H_3N_3O_7$: C, 48.14; H, 3.72%. The last one has a 1: 1 composition and is tan-colored. Found: C, 56.69; H, 5.09%. Calcd for $C_{16}H_{20}N_2 \cdot C_6H_3N_3O_7$: C, 56.29; H, 4.90%. The intensity of the electronic absorption unique to this complex is weak. However, its location is very clearly observable by the original recording in reflectance and can be well compared with that of the CT absorption in the solid *N,N*-dimethylaniline-TNB complex, 19.3 kK. Consequently, this may be considered as the third complex belonging to Case 1 of CPT complexes. Broad bands characteristic of the picrates of the tertiary amines in the region from 2300 to 2750 cm^{-1} are dominant in the vibrational spectra of all the complexes. Of course, the higher the picric acid content, the more dominant these bands are.

The ionization potentials of the diamines estimated by the energies of the CT absorption bands developed by mixing with *p*-chloranil in chloroform increase in this order: tetramethylbenzidine$<$*o*-dianisidine$\sim$*o*-tolidine$<$dibromo-*o*-tolidine$\sim$dichloro-*o*-tolidine$<$benzidine. The location of benzidine is dependent on the particular electron-acceptor chosen and is somewhat ambiguous.[13] The electron-donor strength seems to have no direct correlation with whether or not a diamine forms a solid complex of the CPT type. This is not at all surprising, since the stabilization by the CT interaction is only a minor fraction of the total ground-state binding energy in the complexes where both the CT and PT interactions simultaneously operate. The two which do not form such complexes are 3,3′-dihalo-*o*-tolidines; therefore, the steric effect of the two substituents introduced *ortho* to an amino group may be considered as a primary factor.

It must be noted that all the complexes of the CPT type were prepared in ethanol, the most polar solvent among the three. Even though the association of electron-donor and acceptor is expected to be poor in this solvent, the dissociation of the ion-pair formed by means of the PT interaction may facilitate the CT interaction between the picrate anion and the diamine molecule or the monoprotonated diamine cation.

No example of Case 2 of CPT complexes could be found in the present work. If the difference between the first and second pK_a values is as small as those in benzidine and *o*-tolidine, it may not be easy to find such a complex.

Very recently, Thewalt and Bugg have reported the crystal and molecular structures of red-colored serotonin picrate monohydrate.[14] The protonated serotonin cation and the picrate anion are arranged in alternatingly stacked arrays to form continuous columns. The interaction between these two components has been concluded by them to be of the CT type. This salt may be considered another example of Case 1 of CPT complexes.

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13) G. Saito and Y. Matsunaga, This Bulletin, **44**, 1788 (1971).

14) U. Thewalt and C. E. Bugg, *Acta. Crystallogr.*, **B 28**, 82 (1972).