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Charge-transfer and Proton-transfer in the Formation of Molecular Complexes. VI.[1] 3,3′,5,5′-Tetranitrobiphenyl-4,4′-diol Complexes with Aromatic Amines

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The 3,3′,5,5′-tetranitrobiphenyl-4,4′-diol complexes with twenty-eight aromatic monoamines were prepared and characterized on the basis of their compositions and vibrational and electronic spectra. Many amines were found to form yellow-colored complexes with a 1 : 1 composition and orange- or red-colored complexes with a mole ratio of 2 : 1 or higher. The former complexes appeared to be salts formed by means of the proton-transfer from the diol to the amine molecule, while the latter appeared to be complexes of a new type where charge-transfer and proton-transfer interactions simultaneously operate. The deep coloration of the latter complexes was interpreted in terms of a charge-transfer interaction between the anion derived from the diol and the second monoamine molecule. Furthermore, the complexes with ten aromatic diamines were examined. The 1 : 1 *o*-dianisidine complex was of particular interest in that it is either of the charge-transfer type or of the proton-transfer type, depending upon the preparative conditions.

Recently, we showed that, as is established on the basis of the vibrational and electronic spectra, the orange-colored α-naphthylamine-picric acid (2 : 1) complex previously prepared by Kofler consists of the picrate ion, the protonated amine, and the α-naphthylamine molecule.[2,3] The deep coloration of this complex was attributed to the charge-transfer interaction between the picrate ion and the naphthylamine molecule. For brevity, such a complex will be denoted as

1) Part V: Y. Matsunaga, This Bulletin, **46**, 998 (1973).

2) A. Kofler, *Z. Elektrochem.*, **50**, 200 (1944).

3) Y. Matsunaga and G. Saito, This Bulletin, **45**, 963 (1972).

a complex of the CPT type because of the simultaneous operation of charge-transfer (CT) and proton-transfer (PT) interactions between the component molecules.

With the hope of extending the scope of complexes of the CPT type, we then examined the picric acid complexes with benzidine and its five derivatives.[4] We suggested three possible cases of complexes of the CPT type in these combinations and found examples for two of them. In the 1 : 1 complexes with *o*-tolidine, *o*-dianisidine, and *N,N,N',N'*-tetramethylbenzidine, a part of the diamine molecule was found to act as a proton-acceptor, while the other part acted as an electron donor. This case may be schematically shown as follows:

$$\begin{array}{l} H_2N\text{-}\phi\text{-}\phi\text{-}NH_3^+ \cdots\cdots {}^-O\text{-}Pi \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \vdots \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad H_2N\text{-}\phi\text{-}\phi\text{-}NH_3^+ \end{array} \quad \text{(I)}.$$

Secondly, the black-colored complex with benzidine of a 2 : 1 composition was also found to be of the CPT type. The mode of interaction in this case may be analogous to that in the above-mentioned naphthylamine complex and may be shown by:

$$\begin{array}{l} H_2N\text{-}\phi\text{-}\phi\text{-}NH_3^+ \cdots\cdots {}^-O\text{-}Pi \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \vdots \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad H_2N\text{-}\phi\text{-}\phi\text{-}NH_2 \end{array} \quad \text{(II)}.$$

The last case is expected to be found among complexes of a 1 : 2 composition, where one of the picric acids is a proton donor and where the other is an electron acceptor. The constitution may be described by the following formula:

$$\begin{array}{l} H_2N\text{-}\phi\text{-}\phi\text{-}NH_3^+ \cdots\cdots {}^-O\text{-}Pi \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \vdots \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad PiOH \end{array} \quad \text{(III)}.$$

Unfortunately, no example of the complex represented by this formula could be found among the picric acid complexes. As has been demonstrated with the picric acid and 2,4-dinitrophenol complexes with aromatic monoamines,[5,6] a delicate balance between the pK_a value of picric acid and the first and second pK_a values of the diamine must be achieved to produce such a complex.

Many aromatic monoamines are available and can cover a wider range of pK_a values than can benzidine and its derivatives; therefore, the chance of finding complexes of the CPT type represented by:

$$\begin{array}{l} HO\text{-}\phi\text{-}\phi\text{-}O^- \cdots\cdots H_3N^+\text{-}Ar \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \vdots \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad H_2N\text{-}Ar \end{array} \quad \text{(IV)}$$

may be much better than that of finding complexes represented by (III). 3,3',5,5'-Tetranitrobiphenyl-4,4'-diol, hereafter abbreviated as TNBP, seemed to be the best choice for this purpose. The pK_a value in methanol has been determined by Hart and Detroit to be 4.90±0.06.[7] As Schwarzenbach and Rudin have shown that the pK_a values of *o*- and *p*-nitrophenols measured in 49% ethanol, are smaller by as much as 2 than those measured in 95% ethanol,[8] we may predict that TNBP is a weaker acid than picric acid (pK_a= 0.42 in water), but is a stronger acid than 2,6-dinitrophenol (pK_a=3.71 in water).[9,10] As for the electron-acceptor strength, TNBP is as strong as picric acid and *s*-trinitrobenzene, as will be described in the following section.

Experimental

Materials. The TNBP was prepared, starting from benzidine, by the procedure of Kunze[11] or that of Borsche and Scholten.[12] Recrystallization from glacial acetic acid gave fine, yellow-colored needles. In the former procedure, biphenyl-4,4'-diol was isolated as an intermediate by the method given by Hirsch.[13] The complexes were precipitated by mixing various amounts of the component compounds separately dissolved in hot benzene. Their compositions were determined by elementary analysis.

Measurements. The vibrational spectra of the solid samples were recorded as hexachloro-1,3-butadiene mulls on a JASCO IR-G infrared spectrophotometer, and the electronic spectra, on a Beckman DK-2A spectroreflectometer.

Results and Discussion

Electron-acceptor Strength of TNBP. In order to estimate the electron-acceptor strength of TNBP, the energies of the CT absorption maxima in the TNBP complexes with a series of electron donors were compared with those in the corresponding complexes of picric acid, *s*-trinitrobenzene, and *p*-chloranil. The absorptions were mostly measured in solids, but some were also measured in chloroform. The values obtained are listed in Table 1. Here, the electron donors are arranged in terms of the energy of the CT absorption maximum observed with the *p*-chloranil complex in chloroform. The energy values in the complexes of three nitro compounds with a given electron donor are close to each other; therefore, the electron-acceptor strength of TNBP appears to be comparable with those of picric acid and *s*-trinitrobenzene. The plot of the energies of the CT absorption maxima in the complexes of TNBP (Y) against those in the corresponding *p*-chloranil complexes (X) is covered by this equation:

$$Y = X + (4.1 \pm 1.0) \quad (1)$$

The solid TNBP complexes with pyrene, anthracene, perylene, phenothiazine, and benzo[*c*]- and dibenzo[*c,h*]-phenothiazines were found by elementary analysis to be of a 1 : 1 composition. The compositions of the amine complexes in Table 1 will be discussed in the following sections.

Spectra of TNBP and Its Salts. The diffuse reflectance spectrum of TNBP shows an absorption maxi-

4) G. Saito and Y. Matsunaga, This Bulletin., **46**, 714 (1973).
5) G. Saito and Y. Matsunaga, *ibid.*, **44**, 3328 (1971).
6) N. Inoue and Y. Matsunaga, *ibid.*, **45**, 3478 (1972).
7) H. Hart and W. J. Detroit, *J. Amer. Chem. Soc.*, **74**, 5214 (1952).
8) G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, **22**, 360 (1939).
9) H. v. Halban and M. Seiler, *ibid.*, **21**, 385 (1938).
10) G. Kortüm and H. Wilski, *Z. Phys. Chem. N. F.*, **2**, 256 (1954).
11) E. Kunze, *Ber.*, **21**, 3331 (1888).
12) W. Borsche and B. G. B. Scholten, *ibid.*, **50**, 608 (1917).
13) R. Hirsch, *ibid.*, **22**, 335 (1889).

Table 1. Energies of CT absorption maxima in the complexes of TNBP, picric acid, *s*-trinitrobenzene, and *p*-chloranil (in kK).
The values in parentheses are those in the solid complexes.

Donor	TNBP	Picric acid	*s*-Trinitrobenzene	*p*-Chloranil
Hexamethylbenzene	23.1		25.3[a]	19.3
4,4′-Dimethoxybiphenyl	21.1			17.7
Pyrene	(20—21)		22.2 (22.5)[b]	16.2
N,*N*-Dimethylamino-*p*-benzaldehyde	(20—21)	*	(23.0)	16.0
Anthracene	(20)	(20)	(21.8)[b]	15.6
Diphenylamine	(19—20)		21.7[c]	15.3
3,3′-Dichloro-*o*-tolidine	(18.4)	*	21.3 (19.5)	14.3
3,3′-Dibromo-*o*-tolidine	(20.6)	(18.0)	20.4 (18.2)	14.1
Phenyl-α-naphthylamine	(18.8)	21.0	21.0	14.1
o-Dianisidine	(16.5)	*	(17.3)	13.4
Perylene	(18)	(18)	(20.4)[b]	13.2
Phenothiazine	(17.3)	(17.1)	19.1 (16.7)	12.3
Benzo[*c*]-phenothiazine	16.0 (16.6)	18.2 (14.7)	17.9 (15.7)	12.3
Dibenzo[*c*,*h*]phenothiazine	14.0 (15.4)	17.3 (14.1)	17.4 (18.2)	10.8

* Only the complexes of the PT type are available.
a) Taken from Ref. 14 (The solvent is carbon tetrachloride).
b) Taken from Ref. 15.
c) Taken from Ref. 16.

mum at 26.3 kK. In chloroform, the maximum is shifted to 27.6 kK. This value is a little lower than that of 28.2 kK observed in methanol by Hart and Detroit.[7] These authors located the absorption maximum of the monovalent anion at 22.4 kK when examining the spectral change upon the addition of sodium methoxide. The disodium salt was isolated as a bright red powder. The absorption maximum is located at 21.6 kK in the solid salt and at 22.0 kK when dissolved in acetone. In the vibrational spectra of the solid TNBP and the disodium salt, a band at about 3100 cm^{-1} assignable to the CH stretching is the only sharp one observed in the region from 2000 to 4000 cm^{-1}.

The Monoamine Complexes. The solid complexes were isolated; the twenty-eight aromatic monoamines are arranged in the order of decreasing pK_a value in Table 2.[17] An interesting result of the present study is the observation that the nine primary amines out of sixteen with pK_a values higher than 2.71 form yellow complexes of a 1 : 1 composition and also orange or red complexes of a 2 : 1 composition. Regardless of the composition, all of them show a vibrational pattern characteristic of phenolates of primary amines.

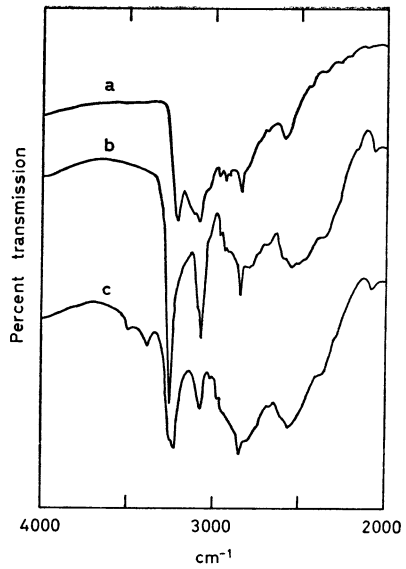

Fig. 1. Vibrational spectra; (a) *p*-anisidine-picric acid, (b) *p*-anisidine-TNBP (1:1), (c) *p*-anisidine-TNBP (2:1).

In other words, the spectra in the region from 2000 to 4000 cm^{-1} more or less resemble those of the corresponding picric acid complexes, which are known to be of the PT type. For example, the vibrational spectra of the 1 : 1 *p*-anisidine complex is compared with that of the picric acid complex in Fig. 1. Moreover, the similarity between the spectrum of the 1 : 1 complex and that of the 2 : 1 complex must be noted. Thus,

14) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955).
15) M. S. J. Dewar and A. R. Lepley, *J. Amer. Chem. Soc.*, **83**, 4560 (1962).
16) A. Bier, *Rec. Trav. Chim.*, **75**, 866 (1956).
17) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London (1965), pp. 58—91.

Table 2. TNBP complexes with aromatic monoamines

Amine	pK_a	Color	Mole ratio	Elementary analysis			
				Found		Calcd	
				C%	H%	C%	H%
N,*N*-Diethyl-*m*-toluidine	7.12	Red	2 : 1	57.74	5.55	58.96	5.78
		Red	3 : 1	63.55	6.76	63.16	6.67
N,*N*-Diethylaniline	6.61	Orange	1 : 1	51.14	3.92	51.26	4.08
		Dark orange	5 : 3	56.04	5.04	56.00	5.05
N,*N*-Dimethyl-*o*-toluidine	6.11	Orange	1 : 1	50.22	3.76	50.30	3.79
p-Anisidine	5.34	Yellow	1 : 1	46.39	3.05	46.63	3.07
		Yellow	2 : 3	44.76	2.83	44.64	2.68
		Brown	2 : 1	50.95	3.99	50.98	3.92
N,*N*-Dimethyl-*m*-toluidine	5.34	Orange	1 : 1	50.34	3.92	50.30	3.79
		Dark orange	5 : 2	59.08	5.35	58.85	5.47
p-Phenetidine	5.20	Bright yellow	1 : 1	47.33	3.44	47.71	3.38
		Russet	2 : 1	52.60	4.36	52.50	4.38
N,*N*-Dimethylaniline	5.15	Bright russet	1 : 1	49.56	3.54	49.28	3.49
p-Toluidine	5.09	Bright yellow	1 : 1	48.31	3.14	48.20	3.17
		Dark russet	2 : 1	53.97	4.30	53.79	4.14
2,4-Dimethylaniline	4.90	Bright yellow	1 : 1	48.16	3.15	48.20	3.17
		Brown	2 : 1	53.60	4.16	53.79	4.14
N-Methylaniline	4.85	Bright yellow	1 : 2	44.38	2.42	44.34	2.50
m-Toluidine	4.68	Bright yellow	1 : 1	48.16	3.15	48.20	3.17
		Dark russet	2 : 1	53.60	4.16	53.79	4.14
Aniline	4.59	Bright yellow	1 : 1	46.15	2.76	47.06	2.83
		Dark russet	2 : 1	52.24	3.62	52.17	3.62
o-Anisidine	4.52	Yellow	1 : 1	46.81	3.19	46.63	3.07
		Reddish orange	5 : 2	52.64	4.21	52.56	4.23
		Red	5 : 1	57.24	5.16	57.49	5.20
o-Phenetidine	4.43	Yellow	3 : 2	49.92	3.72	50.31	3.94
		Yellowish orange	2 : 1	52.41	4.35	52.50	4.38
o-Toluidine	4.39	Bright yellow	1 : 1	48.33	3.35	48.20	3.17
		Orange red	2 : 1	53.71	4.18	53.79	4.14
m-Anisidine	4.20	Yellow	1 : 1	46.62	3.09	46.63	3.07
		Brownish yellow	2 : 1	51.27	4.05	50.98	3.92
β-Naphthylamine	4.16	Light orange	1 : 1	51.82	2.97	51.87	2.95
p-Chloroaniline	3.99	Bright yellow	1 : 1	44.07 (Cl 7.06	2.50	43.77 7.19)	2.43
		Orange	5 : 1	50.20	3.79	50.22	3.59
α-Naphthylamine	3.92	Orange	2 : 1	57.72	3.67	58.90	3.68
m-Chloroaniline	3.33	Yellow	1 : 1	(Cl 7.15		7.19)	
		Orange	2 : 1	46.19	2.92	46.38	2.90
3-Nitro-4-methylaniline	2.96	Bright yellow	1 : 1	44.34	2.79	43.68	2.68
o-Chloroaniline	2.71	Orange	2 : 1	46.38	2.91	46.38	2.90
o-Iodoaniline	2.60	Red	1 : 1	36.96	2.15	36.92	2.05
o-Bromoaniline	2.55	Dull yellow	4 : 1	41.08 (Br 30.58	2.88	40.99 30.36)	2.85
m-Nitroaniline	2.46	Yellow	3 : 2	43.82	2.63	43.98	2.62
		Orange	2 : 1	45.03	2.80	44.86	2.80
N,*N*-Dimethylamino-*p*-benzaldehyde	1.62	Red	1 : 1	49.19	3.29	48.93	3.30
Diphenylamine	0.79	Black	1 : 1	53.85	3.30	53.83	3.18
Phenyl-*α*-naphthylamine	?	Jet black	1 : 2	50.71	2.81	50.47	2.63

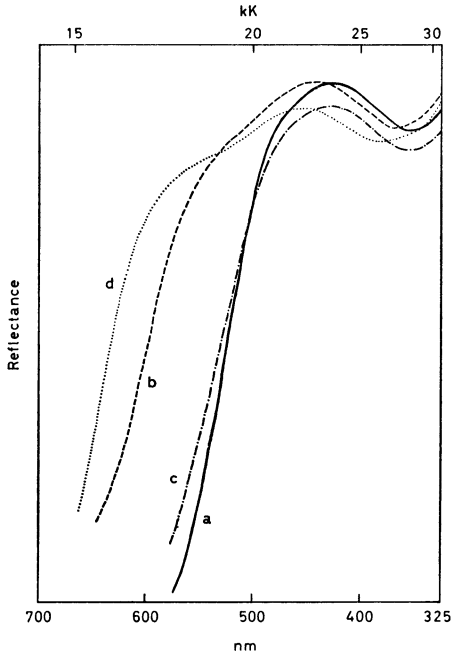

Fig. 2. Reflectance spectra; (a) *p*-anisidine-TNBP (1:1), (b) *p*-anisidine-TNBP (2:1), (c) aniline-TNBP (1:1), (d) aniline-TNBP (2:1).

the presence of PT from TNBP to the amine molecule in both the 1 : 1 and 2 : 1 complexes seems to be certain. In addition, the presence of two weak bands at 3380 and 3480 cm^{-1} in the spectrum of the 2 : 1 complex clearly indicates that the second amine is not protonated.

In general, the 1 : 1 complex exhibits a broad absorption band with a maximum at about 23.1—24.6 kK, which may be attributed to the TNBP monovalent anion. On the other hand, an additional absorption appears in most of the 2 : 1 complexes as a shoulder located on the lower-energy side of the main band. Obviously the deep coloration of the 2 : 1 complex is due to the appearance of this low-energy band. Fig. 2 presents the reflectance spectra of the 1 : 1 and 2 : 1 *p*-anisidine complexes. The absorption maximum appearing at 23.5 kK (425 nm) in the 1 : 1 complex is shifted a little towards the lower-energy side by combination with the second amine molecule. Furthermore, a new absorption can be seen in the region from 500 to 650 nm. The shoulder is located around 19 kK (525 nm). By analogy with the case of picric acid,[3,18] we may assume that the electron-acceptor strength of TNBP is not much affected by the dissociation. The location of the above-mentioned shoulder is fairly close to the energy value given by Eq. (1) with $X=16.2$. This result is strikingly different from the observation made for complexes represented by (I) and also from what would be expected for the complexes represented by (III). We established in a previous paper that the electron-donor strength of the monoprotonated diamine cation is essentially determined by that of the unprotonated half. The present result leads to the conclusion that the 2 : 1 *p*-anisidine complex is of the CPT type represented by Formula (IV). Although the vibrational bands to be assigned to the neutral amines are hardly detectable in the other eight 2 : 1 complexes, the fact that these amines are weaker bases than *p*-anisidine leaves little doubt as to the absence of PT in the second amine molecules. These complexes are probably of the same nature, judging from the deep coloration or the appearance of a new absorption on the lower-energy side of the main band; see the other example presented in Fig. 2. The deeply colored 2 : 1 complexes of *o*-phenetidine, *o*-chloroaniline, and α-naphthylamine with the characteristic vibrational pattern of phenolates of primary amines may also be of the same CPT type. On the other hand, the 2 : 3 complex of *p*-anisidine and the 3 : 2 complex of *o*-phenetidine are both yellow. Their vibrational spectra indicate the presence of PT. No additional electronic absorption band to be assigned to the CT interaction can be detected in them.

Upon heating, the 2 : 1 complex easily loses one molecule of the amine. However, further heating results in decomposition. These processes can be well demonstrated by the vibrational spectra. For example, the spectrum of the 2 : 1 *p*-toluidine complex turns into that of the 1 : 1 complex when it is heated to about 160 °C. This change is accompanied, of course, by the loss of the low-energy absorption band characteristic of the 2 : 1 compoex. After heating to 220 °C, the vibrational pattern differs substantially from that of TNBP. Thus, the amine participating in the CT interaction with the TNBP anion is much more easily removable than the one acting as a proton acceptor.

o-Anisidine was found to form complexes of 5 : 2 and 5 : 1 compositions in addition to that of a 1 : 1 composition. The coexistence of NH_2 and NH_3^+ groups is proved by their vibrational spectra (see Fig. 3). The intensities of the bands due to the NH_2 group are rather weak; therefore, we may explain the earlier observation that the corresponding bands are hardly observable in most of the 2 : 1 complexes of the CPT type. The shift of the strong absorption band at 23.8

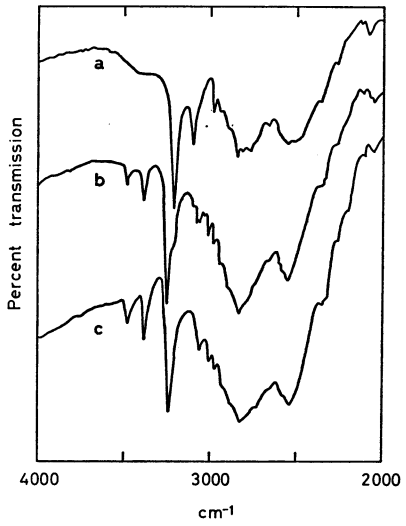

Fig. 3. Vibrational spectra of *o*-anisidine-TNBP; (a) the 1:1 complex, (b) the 5:2 complex, (c) the 5:1 complex.

18) G. Saito and Y. Matsunaga, This Bulletin, **45**, 2214 (1972).

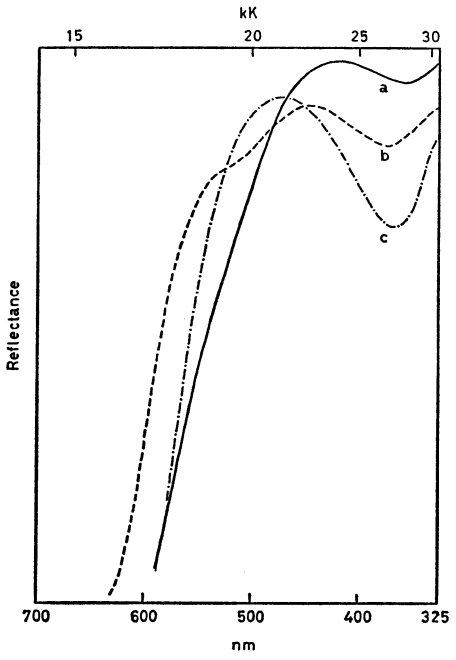

Fig. 4. Reflectance spectra; (a) *o*-anisidine-TNBP (1:1), (b) *o*-anisidine-TNBP (5:2), (c) *N,N*-diethyl-*m*-toluidine-TNBP (3:1).

kK in the 1 : 1 complex by about 1 kK towards the lower-energy side in the 5 : 2 complex and the appearance of a low-energy absorption in the latter complex may be seen in Fig. 4. In view of the magnitude of the pK_a value of the amine, and also the location of the band arising from the proton-donor component, TNBP may be supposed to be in the form of the monovalent anion; however, it is not clear how many anisidine molecules are involved in the CT interaction. The spectroscopic examination of the 5 : 1 *p*-chloroaniline complex showed that this complex can be classified into the same group as the above-mentioned *o*-anisidine complexes.

Of the amines with pK_a values below 2.60, some complexes are of the CT type and some are of the CPT type. No PT interaction was detected in the complexes of the following four bases: *o*-iodoaniline, *N,N*-dimethylamino-*p*-benzaldehyde, diphenylamine, and phenyl-α-naphthylamine. The pK_a value of the last mentioned is not known. As we may see in Table 2, naphthylamines are weaker bases than aniline; therefore, this amine is undoubtedly weaker than diphenylamine, and so the weakest among the amines employed. By contrast, the vibrational spectra of complexes of *o*-bromoaniline and *m*-nitroaniline, which have pK_a values slightly lower than that of *o*-iodoaniline, indicate the occurrence of PT in the complex formation. This irregularity reflects the fact that *o*-iodoaniline is the strongest electron donor among these three; $X=18.6$ for *o*-iodoaniline, compared with the values of 20.0 and 22.7 for *o*-bromoaniline and *m*-nitroaniline respectively. In accordance with the assumption made earlier, these observations suggest that the first pK_a value of TNBP in water is close to the pK_a values of these amines: 2.46—2.60. Although both diphenylamine and phenyl-α-naphthylamine have been known to form 1 : 2 complexes with *s*-trinitrobenzene,[19] the compositions of the TNBP complexes differ from each other, reflecting the size of the component molecules.

Now let us turn our attention to the complexes of *N*-substituted anilines, which are the strongest proton acceptors among the amines examined. They form deeply colored 1 : 1 complexes with TNBP, despite the occurrence of PT, as is indicated by their vibrational spectra. For example, the russet 1 : 1 *N,N*-dimethylaniline complex exhibits the vibrational pattern characteristic of phenolates of tertiary amines, with bands located in the region from 2250 to 2750 cm^{-1}.[20] A strong absorption located at 22.0 kK is observed in the electronic spectrum. The deep coloration must be wholly attributed to the breadth of this band. Besides the 1 : 1 complex, these amines give 5 : 3, 5 : 2, 2 : 1, and/or 3 : 1 complexes. Their color is deeper than that of the 1 : 1 complexes. In the case of the complexes of *N,N*-diethyl-*m*-toluidine, the strongest proton acceptor studied here, red powders with 2 : 1 and 3 : 1 compositions were obtained. Their electronic spectra are similar to each other and show a strong absorption at 21.3 kK (see Fig. 4). If the complexes are of the CPT type, the CT band can be predicted to appear at about 17 kK, according to Eq. (1). Nonetheless, we cannot see any indication of the presence of such a band. As the location of a strong absorption band is a little lower than that in complexes of the CPT type, and as the amine has a high pK_a value, the TNBP in this complex may be in the form of a divalent anion. If so, the second pK_a value of TNBP must be as high as the range covered by these amines. Thus, the difference between the first and second pK_a of the biphenyldiol is appreciably larger than that found for benzidine. This may be the reason why we can easily find complexes of the CPT type represented by (IV), but not those of the type represented by (III). *N*-Methylaniline, the only *N*-monosubstituted aniline used in this work, gives samples containing more amine than 1 : 2. Such preparations easily lose the amine even at room temperature; therefore, we could isolate no other stoichiometric complex.

The Diamine Complexes. The complexes prepared are listed in Table 3. They may be classified into two groups, those of the PT type and those of the CT type. *o*-Dianisidine can form complexes of both the PT and CT types.

The 1 : 1 complexes with *o*-tolidine, *p*-phenylenediamine, 1,5-diaminonaphthalene, and 1,6-diaminopyrene clearly exhibit the vibrational bands characteristic of the NH_3^+ group, but not those characteristic of the NH_2 group. On the other hand, the appearance of the electronic absorption band in the range from 22.5 to 23.6 kK may be accounted for by proposing that the 1 : 1 complex is composed of the TNBP monovalent anion and the monoprotonated diamine cation. The reason why the vibrational bands due to NH_2 group are not detectable remains unknown; however, we have

19) J. J. Sudborough and S. H. Beard, *J. Chem. Soc.*, **97**, 773 (1910).

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

Table 3. TNBP complexes with aromatic diamines

Amine	Color	Mole ratio	Elementary analysis			
			Found		Calcd.	
			C%	H%	C%	H%
p-Phenylenediamine	Orange	1 : 1	45.39	2.92	45.57	2.95
Diaminodurene	Orange	3 : 2	52.23	4.40	52.92	4.91
1,5-Diaminonaphthalene	Orange	1 : 1	50.55	3.18	50.38	3.05
1,6-Diaminopyrene	Dark orange	1 : 1	55.57	3.11	56.19	3.01
Benzidine	Orange	3 : 2	55.05	3.56	56.07	3.74
N,N,N',N'-Tetramethylbenzidine	Light red	1 : 2	50.70	3.68	49.38	3.29
o-Tolidine	Light red	1 : 1	54.03	3.84	53.98	3.81
o-Dianisidine	Yellowish orange	1 : 1	50.95	3.60	51.15	3.61
	Black	1 : 1	51.34	3.67	51.15	3.61
3,3'-Dichloro-*o*-tolidine	Jet black	1 : 1	48.56	3.09	48.22	3.09
3,3'-Dibromo-*o*-tolidine	Brown	1 : 1	42.61	2.67	42.39	2.72

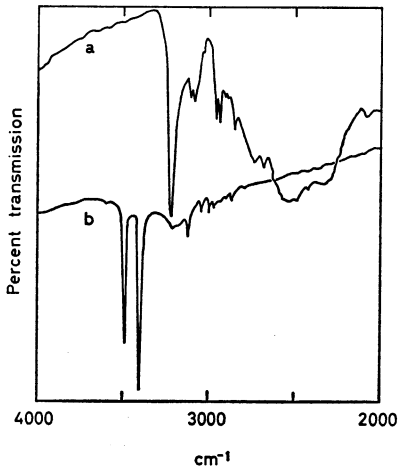

Fig. 5. Vibrational spectra of *o*-dianisidine-TNBP (1:1) complex; (a) the yellow form, (b) the black form.

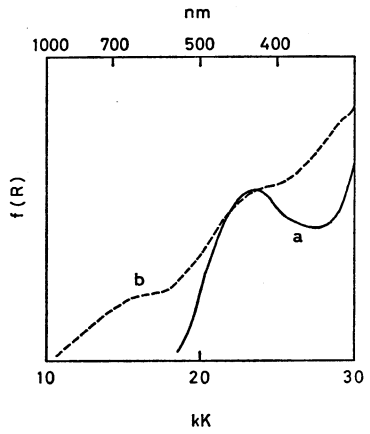

Fig. 6. Diffuse reflection spectra of *o*-dianisidine-TNBP (1:1) complex; (a) the yellow form, (b) the black form.

encountered the same problem in the 2 : 1 monoamine complexes. The yellowish-orange form of the *o*-dianisidine complex is another member of this group. As is shown in Fig. 5, the protonation of the diamine is firmly established by the broad vibrational bands appearing below 3000 cm^{-1}. The electronic absorption band arising from the proton-donor component is located at 23.5 kK; see Curve a, plotted using the Kubelka-Munk function, in Fig. 6. On the basis of a comparison between the pK_a values of benzidine, 4.95 and 3.85, and that of aniline, 4.59, the second pK_a value of *o*-dianisidine is expected to be below 4. Consequently, the possibility that two protons are transferred from the TNBP to the *o*-dianisidine molecule may be eliminated. If this complex is of the CPT type, the electronic spectrum may be similar to that of the 5 : 2 *o*-anisidine complex, shown in Fig. 4, as the electron-donor strength of the monoprotonated *o*-dianisidine may be anticipated to be close to that of *o*-anisidine. No absorption ascribable to the CT interaction between the TNBP monovalent anion and the monoprotonated diamine cation was observed in the *o*-dianisidine complex. This conclusion also applies to the 1 : 1 diamine complexes discussed above.

The coexistence of NH_2 and NH_3^+ groups in the 3 : 2 complexes with benzidine and diaminodurene is evidenced by the vibrational spectra, which are in accordance with a high ratio of the NH_2 group to NH_3^+ group. Nevertheless, no CT absorption band can be found in them. Tetramethylbenzidine combines with TNBP in a mole ratio of 1 : 2. As this diamine is a strong base, the constitution may be expressed by $[(CH_3)_2NH\text{-}\phi\text{-}\phi\text{-}NH(CH_3)_2]^{2+}(HO\text{-}\phi\text{-}\phi\text{-}O^-)_2$. The location of a strong electronic absorption at 22.8 kK seems not to be inconsistent with this expression.

A further result of importance in this study is that *o*-dianisidine can form not only a PT complex, but also a CT complex, with TNBP. On the mixing of benzene solutions containing equimolar amounts of the component compounds, a yellow complex was precipitated, while a small amount of fine, black needles appeared together with the yellow precipitate when the solutions were diluted and when a large excess of the diamine was employed. The black needles were separated from the mixture with tweezers. Surprisingly, the mole ratio of the diamine to TNBP was found to be identical in these two specimens. The black form exhibits vibrational bands assignable to the NH_2 group at 3395 and 3490 cm^{-1} and an electronic absorption assignable

to the CT interaction at 16.6 kK (see Figs. 5 and 6). The shoulder appearing at about 23 kK suggests that our black specimen is slightly contaminated with the yellow form. The band maximum located at 28.5 kK may be attributed to the TNBP molecule. The transitions from the black form to the yellow one, and *vice versa*, have so far not been observed. 3,3′-Dihalo-*o*-tolidines are the weakest bases among the diamines employed. The 1 : 1 complexes with TNBP are of the CT type. The energies of the CT absorption bands in these complexes are given in Table 1.