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Charge-Transfer and Proton-Transfer in the Formation of Molecular Complexes. I. The Complex Isomerization of Some Anilinium Picrates by Melting

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o-Chloroaniline, *m*-nitroaniline, 3-nitro-4-methylaniline, and *N*,*N*-dimethylamino-*p*-benzaldehyde form true phenolates with picric acid. However, their electronic and vibrational spectra were found to be drastically modified by melting. The appearance of a new electronic absorption located near the place where the corresponding *s*-trinitrobenzene complex exhibits the charge-transfer band is noted above the melting point. At the same time, the vibrational bands due to the anilinium ion observed at room temperature are replaced by those due to the aniline. On the basis of these observations, it was concluded that complex isomerization from a true phenolate to a charge-transfer complex takes place by melting in these cases. On the other hand, the spectra of *N*,*N*-diethylanilinium and *m*-chloroanilinium picrates were shown to remain the same below and above the melting points.

Many years ago, Pfeiffer suggested that the interaction between the two components in a molecular complex could be considered as an interaction between particular force fields to be assigned to some regions of the molecules.[1] If each of the component molecules had more than one type of force field, isomeric molecular complexes could be obtained, depending upon which pair of force fields predominated in the interaction. For example, when an aromatic amine is combined with a polynitrophenol, one type of force field produces an acid-base interaction, and the other, an electron donor-acceptor interaction. The former interaction leads to the formation of true phenolate by proton-transfer, and the latter, to a true molecular compound by charge-transfer (CT). The papers in the present series will deal with the phenomena characteristic of the molecular complexes composed of such bifunctional component molecules.

Hertel has assumed that the progressive weakening

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[1] P. Pfeiffer, "Organische Molekülverbindungen," 2 Aufl., Verlag von F. Enke, Stuttgart (1927), 341—346.

of the acid-base interaction and strengthening of the donor-acceptor interaction should produce molecular complexes which range in type from true phenolates at one end of the series to true molecular compounds at the other.[2] One may expect the presence of intermediate situations where the same components form either phenolates or CT complexes, depending upon ambient conditions. In fact, several combinations of the components giving such polymorphs were discovered by Hertel. This phenomenon was named "complex isomerism" by this author. The polymorphs differ distinctly from each other in their colors, melting points, molar volumes, phase diagrams, and X-ray diffraction patterns.[2-5] For example, the combination of 1-bromo-2-naphthylamine and picric acid gives a yellow-colored salt at room temperature. The color turns violet-red at 114°C, and then the complex melts at 178°C. The latter temperature is not far from the melting point of the corresponding brilliant red *s*-trinitrobenzene (TNB) complex, 195°C. Further evidence for the change in the type of interaction accompanying the transition has been provided by spectroscopic studies of the polymorphic phases of the two picrates carried out by Briegleb and Delle.[6,7] The infrared spectra of 1-bromo-2-naphthylamine- and 1,6-dibromo-2-naphthylamine-picric acid at room temperature have been shown to have the pattern assigned to NH_3^+ vibrations. When the complexes are heated to 140°C, which is well above the transition points, the intensities of this pattern are markedly diminished and the bands due to the NH_2 group are newly observed. The deep coloration at high temperatures has been attributed to the appearance of CT absorptions. The crystal and molecular structures of the red-colored form of the 1-bromo-2-naphthylamine complex are known.[8]

In principle, the melt of an anilinium picrate is an equilibrium mixture of not only the cation, the anion, and the ion-pair, but also the CT complex and the component molecules. When the equilibrium is favorable to the CT complex and its components, a marked deepening of the color may be observed at the melting point, as if the transition point were elevated to this temperature. A close examination of twenty-four anilinium picrates has revealed that a new phenomenon, complex isomerization by melting, can be observed if the amines are appropriately chosen.

Experimental

Materials. The picric acid and all the aromatic amines used in this work were commercially obtained. The sodium picrate mono hydrate was prepared by the neutralization of the acid with sodium carbonate. The amine hydrochlorides were made by means of a reaction between hydrochloric acid and the amines. They were washed with a small amount of water and then with ether. The anilinium picrates were precipitated by mixing the component compounds separately dissolved in benzene.

Measurements. To measure the reflectance spectra of molten samples, we employed the device proposed by J. Aihara of our laboratory.[9] A powdered sample sandwiched between two quartz plates was mounted on powdered sodium chloride embedded in a brass block. The reflectance given by this arrangement was recorded on a Beckman DK 2A spectroreflectometer. The temperature at the boundary between the quartz plate and the sodium chloride, which is somewhat higher than that of the sample, was regulated as has been described earlier.[10] The measurements are rather qualitative because of the change in the sample thickness and also because of the shift of the baseline caused by heating.

The vibrational spectra of the powdered or molten sample sandwiched between two rock salt plates were examined in the region from 2000 to 4000 cm^{-1} using a Jasco IR-G infrared spectrophotometer equipped with a heating attachment. The temperature near the sample holder was monitored by means of a copper-constantan thermocouple and was kept constant using a Chino temperature-indicating controller, type E 500.

Results and Discussion

A preliminary survey was made by the visual examination of the color change at the melting point. *o*-Bromoanilinium and *o*-iodoanilinium picrates have been known to exhibit complex isomerism; therefore, the anilines having basicities close to or less than those of these two seemed to be the most hopeful component compounds. They are *o*-chloroaniline, *m*-nitroaniline, 3-nitro-4-methylaniline, *N,N*-dimethylamino-*p*-benzaldehyde, and *m*-chloroaniline (see Fig. 11). As expected, all these anilines except the last one were found to form picrates which show a marked color change upon melting. None of the other anilines gave picrates with such behavior.

The o-*Chloroaniline Complex* (*Figs. 1 and 2*). The complex precipitated from a red-colored benzene solution is a pale yellow powder which melts at 138—139°C (134°C by Hertel[2]). The color turns light red upon melting and then returns to yellow upon solidification. As is shown in Fig. 1, the reflectance spectrum at room temperature has a strong absorption below 450 mμ. Upon heating, a red-shift of this band is noted, as is indicated by curve b. Upon melting, a broad band covering the range from 450 to 600 mμ appears. Following the procedure employed by Briegleb and Delle,[7] the CT absorption of an imaginary complex formed between *o*-chloroaniline and picric acid was assumed to be approximated by that of the TNB complex, because the acceptor-strength of picric acid is comparable with that of TNB. The solid TNB complex is red and gives the spectrum shown by curve d. The close similarity

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[2] E. Hertel, *Ann.*, **451**, 179 (1926).
[3] E. Hertel and J. van Cleef, *Ber.*, **61**, 1545 (1928).
[4] E. Hertel and K. Schneider, *Z. Phys. Chem. B*, **13**, 387 (1931).
[5] E. Hertel and H. Frank, *ibid.*, **27**, 460 (1934).
[6] G. Briegleb and H. Delle, *Z. Elektrochem.*, **64**, 347 (1960).
[7] G. Briegleb and H. Delle, *Z. Phys. Chem. Neue Folge*, **24**, 359 (1960).
[8] E. Carstensen-Oeser, S. Göttlicher, and G. Habermehl, *Chem. Ber.*, **101**, 1648 (1968).
[9] J. Aihara, A. Sasaki, and Y. Matsunaga, This Bulletin, **43**, 3323 (1970).
[10] C. Dehari, Y. Matsunaga, and K. Tani, *ibid.*, **43**, 3404 (1970).

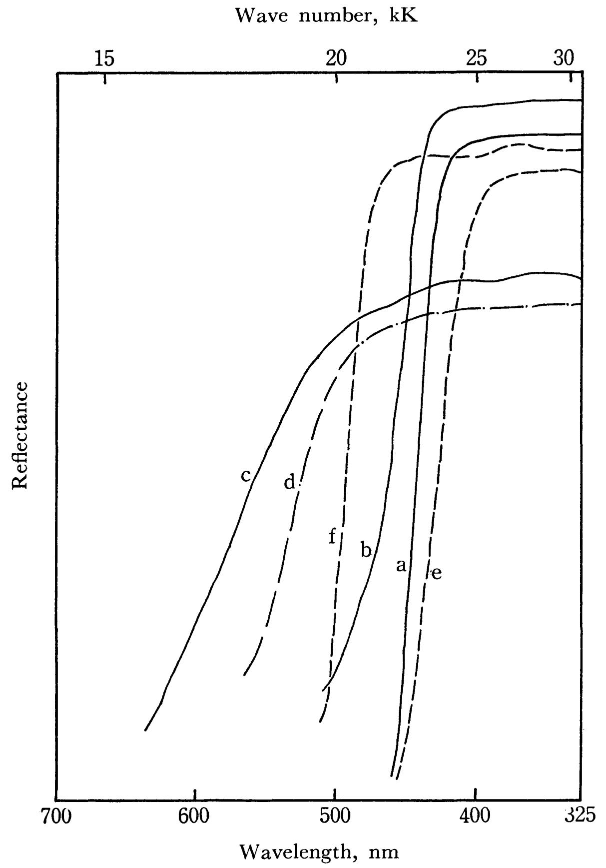

Fig. 1. Reflectance spectra, a) the *o*-chloroaniline-picric acid at room temperature, b) the same a little below the melting point, c) the same in the molten state, d) the TNB complex at room temperature, e) picric acid, and f) sodium picrate.

between curves c and d clearly indicates that the broad band appearing upon the melting of the complex arises from the CT interaction.

In the case of the *N*,*N*-dimethylaniline-TNB complex reported earlier, it was found that the spectrum in the molten state is different from the solid-state spectrum, but much like the one in the dissolved state.[9] Consequently, we attempted to compare the high-temperature spectrum, curve c in Fig. 1, with the spectrum of the corresponding TNB complex in a chloroform solution. Unfortunately, the CT absorption of the *o*-chloroaniline-TNB complex in chloroform was not observable. Nevertheless, the location of its maximum may be estimated by the following method. In our previous work, the energy of the CT absorption maximum of a TNB complex was shown to be larger by 6 kK than that of the corresponding *p*-chloranil complex.[11] Since the CT band of the *o*-chloroaniline-*p*-chloranil complex in a chloroform solution is found at 19.1 kK, the required value may be about 25 kK. This value seems to be a little too high to be compared with curves c and d. Thus, the present results are not in accordance with the observations for the dimethylaniline-TNB complex.

Since *o*-chloroaniline is a weak electron donor and picric acid is a weak acceptor, the resulting CT complex may be expected to be non-ionic. Therefore, the vibrational bands due to the NH_3^+ group must be replaced by those due to the NH_2 group of the amine by melting if complex isomerization occurs. This change will drastically modify the spectrum in the region from 2000 to 4000 cm^{-1}. In Fig. 2, the vibrational spectra of the *o*-chloroaniline complex at room temperature and above the melting point are compared with those of the free amine, its hydrochloride, the free acid, and its sodium salt. All the bands but the one at 3150 cm^{-1} in the complex at room temperature are well approximated by a summation of the bands in the anilinium hydrochloride and those in the sodium picrate. The strong bands appearing near 3600 cm^{-1} in the sodium picrate are not observed in the *o*-chloroaniline complex. They may be assigned to the hydrated water.[12] It is easy to see that the broad bands located at 2040, 2550, and 2820 cm^{-1} in the complex at room temperature constitute the pattern characteristic of the anilinium ion. Although there is no band in the hydrochloride corresponding to the one at 3150 cm^{-1}, Mariella *et al.* have reported that the band appearing in the range from 3150 to 3310 cm^{-1} is characteristic

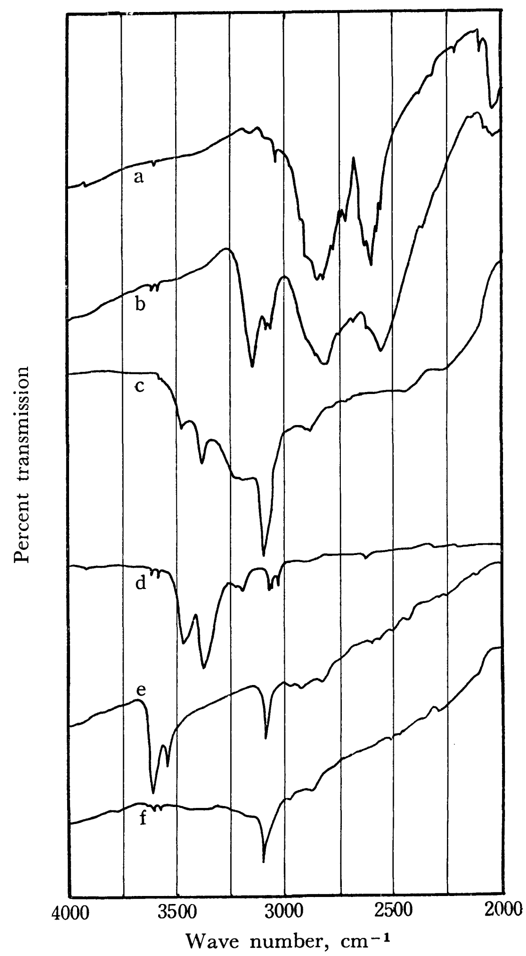

Fig. 2. Vibrational spectra, a) *o*-chloroaniline hydrochloride, b) the *o*-chloroaniline-picric acid at room temperature, c) the same above the melting point, d) *o*-chloroaniline, e) sodium picrate, and f) picric acid.

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11) Y. Matsunaga and G. Saito, *ibid.*, **44**, 958 (1971).

12) K. J. Pederson, *J. Amer. Chem. Soc.*, **56**, 2615 (1934).

of the picrates of primary amines. This band has been assigned to a NH_3^+ stretching frequency.[13] The bands in the room-temperature spectrum are not visible in the molten state. The rather weak bands now observable at 3215, 3380, and 3475 cm^{-1} can be ascribed to the amine, and the strong one at 3095 cm^{-1}, to the acid. The weakness of the former bands relative to the latter may be attributed, at least in part, to the vaporization of the amine during the heating. When the anilinium picrate dissociates into its neutral component molecules, the change in the vibrational spectrum may be expected to be the same as that observed. However, the presence of a strong CT band in the melt excludes such an explanation.

It must be noted that the melting point of the *o*-chloroanilinium picrate is essentially the same as that of the corresponding TNB complex—134°C *vs.* the 134.5°C reported by Hertel.[2] Such a coincidence is rather unusual because most anilinium picrates have been known to melt at temperatures higher by 30—70°C than the TNB complexes. Considering the possibility that the picrate isomerizes into the CT complex a little below the melting point, we examined this anilinium picrate by means of a differential scanning calorimeter. At the melting point, two overlapping endothermic peaks were recorded on the thermogram.

The m-*Nitroaniline Complex (Figs. 3 and 4).* A red benzene solution is obtained when the yellow component compounds are dissolved together. The complex crystallizes as yellow needles with a melting point of 149–150°C. With this complex, a reversible color change from yellow to red is observed. The reflectance spectrum at room temperature, curve a in Fig. 3, shows that this is an anilinium picrate formed by proton-transfer from the acid to the amine. Upon melting, a broad, strong band with its maximum around 500 mμ or 20 kK appears. As *m*-nitroaniline is rather strongly colored, the spectrum of its melt is presented by curve c for the sake of comparison. The newly-appeared band cannot be attributed to either the amine or the acid. The solid TNB complex gives the spectrum shown by curve d. When curves b and d are compared, it seems to be acceptable that the broad band appearing in the molten complex is a CT absorption. The energy of the CT band in the TNB complex in a chloroform solution is estimated to be 22.7 kK. The band observed with the melt is apparently shifted to the long-wavelength side. The above-mentioned estimation was made on the basis of the energy of the CT band in the *m*-nitroaniline-tetracyanoethylene (TCNE) complex, 14.2 kK, and the average difference in the energy of the CT absorption between TNB complexes and TCNE complexes, 8.5 kK.[11]

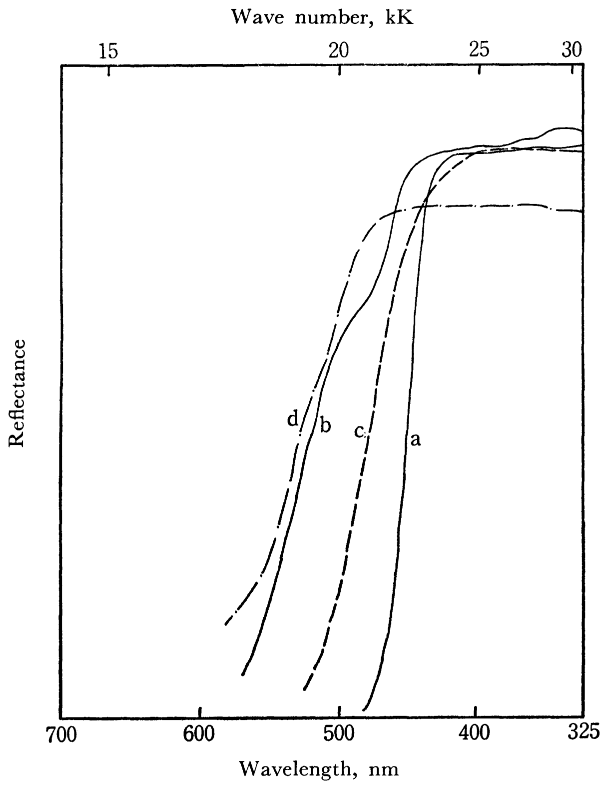

Fig. 3. Reflectance spectra, a) the *m*-nitroaniline-picric acid at room temperature, b) the same above the melting point, c) *m*-nitroaniline in the molten state, and d) the solid TNB complex.

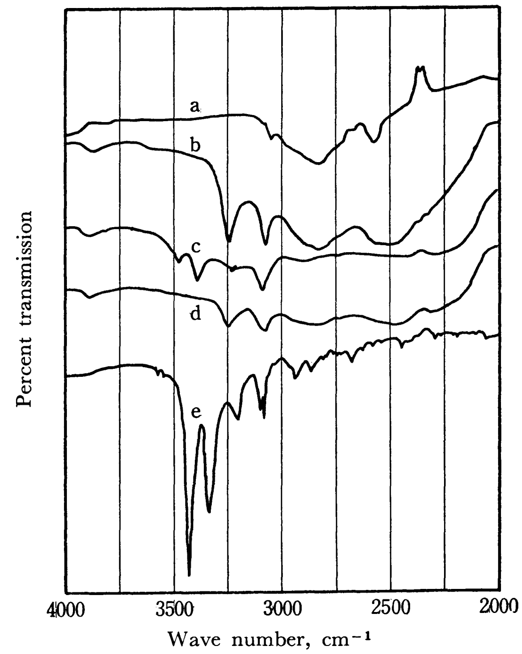

Fig. 4. Vibrational spectra, a) *m*-nitroaniline hydrochloride, b) the *m*-nitroaniline-picric acid at room temperature, c) the same above the melting point, d) the same after solidification, and e) *m*-nitroaniline.

The solid complex exhibits a vibrational spectrum containing two broad bands, located at 2500 and 2850 cm^{-1}, which are characteristic of the anilinium ion (see Fig. 4). The relatively sharp bands appearing at 3388 and 3475 cm^{-1} upon melting correspond well to those in the spectrum of the free amine. The band at 3247 cm^{-1} has no corresponding band in the spectrum of the hydrochloride; however, it is in the range reported by Mariella *et al.* for the picrates of primary amines. The spectrum recorded after

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

solidification is included in Fig. 4 to show how reversible the change is. The hypothesis that this anilinium picrate transforms essentially into a CT complex at the melting point is firmly supported by these pieces of spectroscopic evidence. Finally, we may add that the present complex melts at a temperature about 50°C higher than the TNB complex, which has been reported to melt at 98°C by Sudborough and Beard.[14]

The 3-Nitro-4-methylaniline Complex (Figs. 5 and 6). When the red-colored amine is combined with yellow-colored picric acid, the complex is obtained in the form of yellow needles. The color turns red reversibly upon melting at 156–157°C. The reflectance spectrum was measured a little below and above the melting point. As is shown by curve c in Fig. 5, the molten amine absorbs strongly in the region from 350 to 500 mμ. Therefore, the absorption band characteristic of the complex in the molten state is observed as a shoulder around 525 mμ or 19 kK. This value should be compared with that of 21.1 kK estimated for the energy of the CT absorption of the complex in a chloroform solution. In the room-temperature spectrum of the TNB complex, the CT absorption covers the range from 530 to 600 mμ. The intensity of this band is markedly diminished by melting, as is indicated by curve e. This change is possibly to be attributed to the partial dissociation of the molecular complex in the molten state. The resultant spectrum bears a resemblance to curve b.

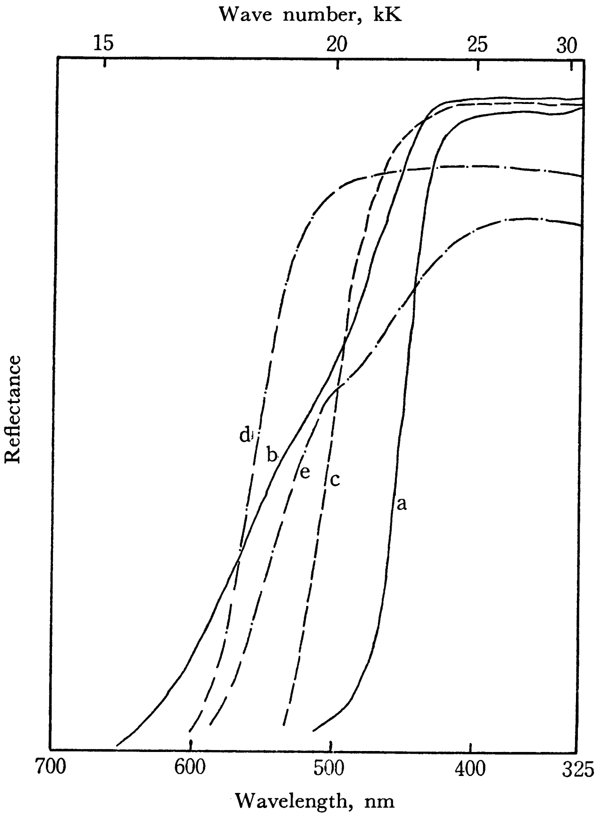

Fig. 5. Reflectance spectra, a) the 3-nitro-4-methylaniline-picric acid a little below the melting point, b) the same above the melting point, c) the amine in the molten state, d) the solid TNB complex, and e) the molten TNB complex.

Fig. 6. Vibrational spectra, a) 3-nitro-4-methylaniline hydrochloride, b) the solid 3-nitro-4-methylaniline-picric acid, c) the same in the molten state, and d) the amine.

The vibrational spectrum of the complex is drastically modified by the change in the state, as is shown in Fig. 6. Below the melting point, the two broad bands at 2570 and 2850 cm^{-1} attributable to the anilinium ion dominate. When melted, they are replaced by those at 3390 and 3478 cm^{-1} attributable to the amine. Thus, the spectroscopic observations indicate that the acid-base interaction predominates in the solid complex, and the electron donor-acceptor interaction, in the molten complex. The band near 3100 cm^{-1} remains through the phase change and is to be assigned to picric acid or picrate anion. The absorption characteristic of the picrates of primary amines is observed at 3210 cm^{-1}. The melting point of the TNB complex is found to be 82°C.

The N,N-*Dimethylamino*-p-*benzaldehyde Complex (Figs. 7 and 8).* When this white amine and picric acid are dissolved together in benzene, a dark red color develops. Bright yellow prisms crystallize from it. This complex melts at 98—99°C, and it turns red. Upon solidification, the complex turns yellow again. The reflectance spectrum recorded below the melting point, curve a in Fig. 7, is similar to that of sodium picrate; therefore, this complex is considered to be a true phenolate in the solid state. As is shown by curve b, a very pronounced absorption appears upon melting. The maximum seems to be shifted to the long-wavelength side compared with the estimated value for the CT band of the TNB complex in a chloroform solution, 22.0 kK. The spectrum of the reddish brown solid TNB complex is shown by curve c, and that of the melt, by curve d. The larger decrease in

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

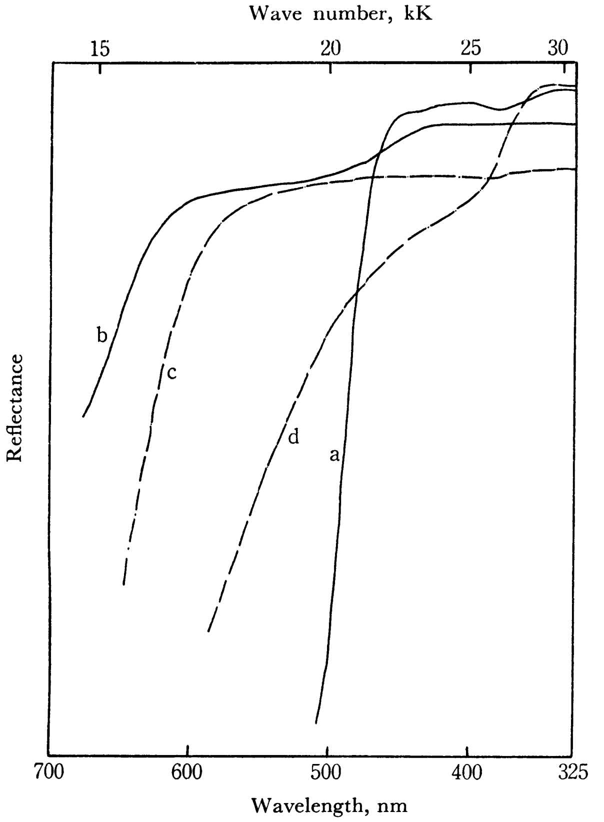

Fig. 7. Reflectance spectra, a) the dimethylamino-*p*-benzaldehyde-picric acid, b) the same in the molten state, c) the solid TNB complex, and d) the same in the molten state.

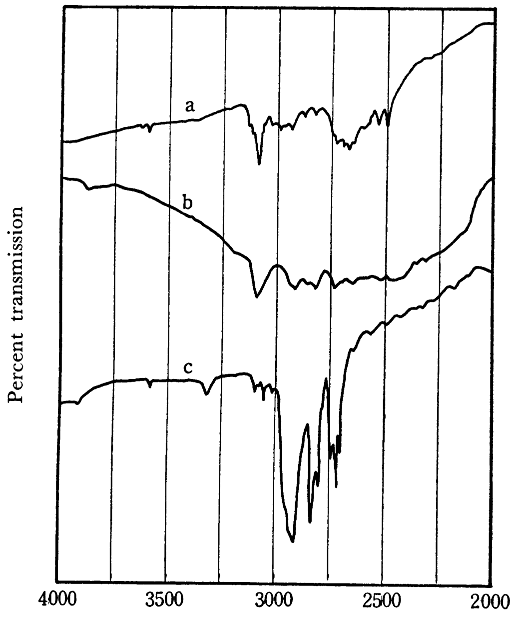

Fig. 8. Vibrational spectra, a) the dimethylamino-*p*-benzaldehyde-picric acid at room temperature, b) the same above the melting point, and c) the amine.

the intensity of the CT band of the TNB complex suggests that this complex dissociates appreciably into its components in the molten state. The similarity between curves b and c is considered to be evidence that the complex in the molten state is of the electron donor-acceptor type.

The vibrational spectra of the solid and molten complexes are presented in Fig. 8. As the amine hydrochloride is not available, the room-temperature spectrum has no reference. According to Mariella *et al.*, tertiary amine picrates have characteristic bands in the range from 2500 to 2670 cm^{-1}.[13] The spectroscopic feature observed at room temperature seems to be of the acid-base interaction. The bands at 2740, 2825, and 2920 cm^{-1} in the melt can be well compared with the strong bands observed in the free amine. Hence, an interaction of the electron donor-acceptor type apparently dominates in the molten complex. The TNB complex melts at 66°C. As is found in many other cases, the melting point of the picrate is definitely higher than this temperature.

The N,N-*Diethylaniline and* m-*Chloroaniline Complexes (Figs. 9 and 10).* For comparison with the complexes mentioned above, we will describe here the spectral behavior of two complexes which do not isomerize at their melting points. *N,N*-Diethylaniline has been chosen as an example because it is one of the strongest bases and also one of the strongest electron donors among the derivatives of aniline. The other example, *m*-chloroaniline, is a base only a little bit stronger than *o*-chloroaniline. Moreover, the electron-donor strengths of these two position isomers are almost equal to each other. Both the diethylaniline and *m*-chloroaniline complexes are yellow in the solid and molten states. The reflectance spectrum of the former complex is shown in Fig. 9. Only a slight shift to the long-wavelength side is observed

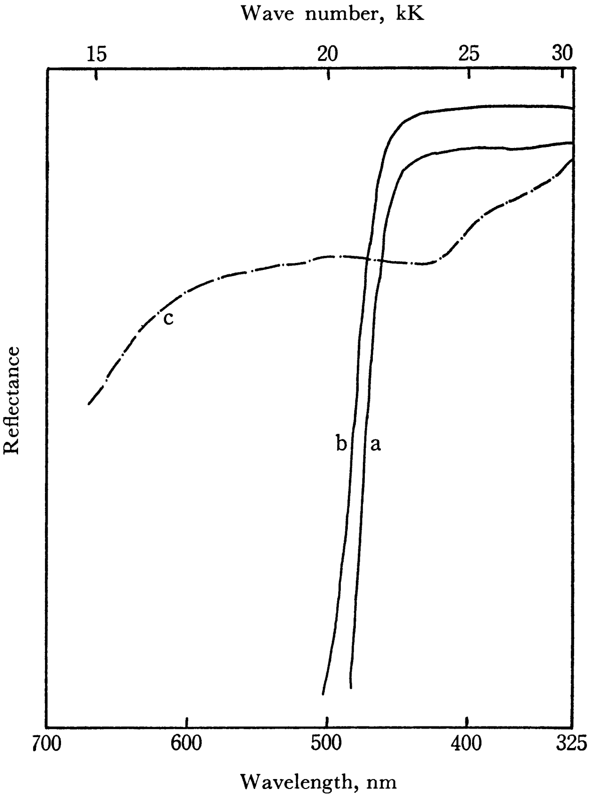

Fig. 9. Reflectance spectra, a) the *N,N*-diethylaniline-picric acid at room temperature, b) the same in the molten state, and c) the TNB complex at room temperature.

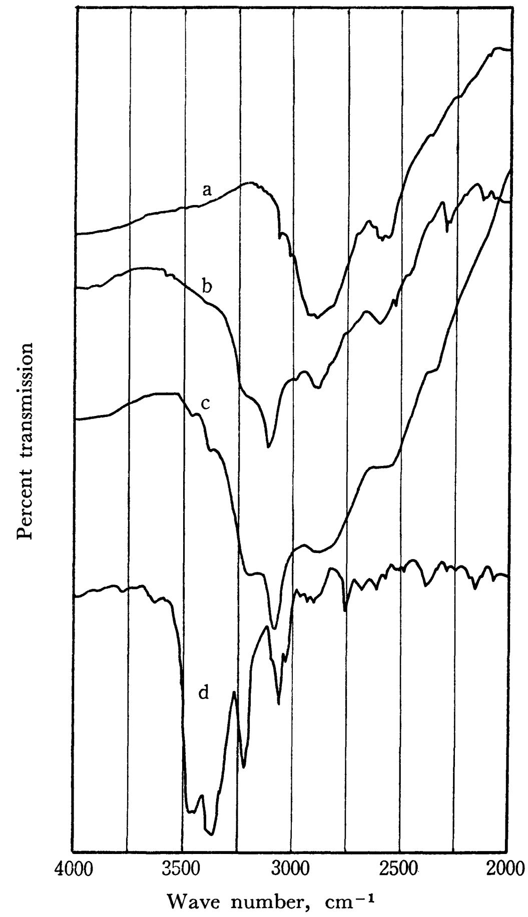

Fig. 10. Vibrational spectra, a) *m*-chloroaniline hydrochloride, b) the *m*-chloroaniline-picric acid at room temperature, c) the same in the molten state, and d) the amine.

when the complex is heated. The spectrum is quite different from that of the corresponding TNB complex. The latter shows a CT absorption covering nearly all the visible region (see curve c).

Figure 10 presents the vibrational spectra of the *m*-chloroaniline complex at room temperature and above the melting point. Both the spectra have two broad strong bands, located at 2575 and 2875 cm^{-1}, which can be compared with those in the amine hydrochloride. The band common to the picrates of primary amines appears at about 3160 cm^{-1}, and the one to be assigned to the picrate ion, at about 3100 cm^{-1}. However, two weak bands visible in the molten complex at 3360 and 3450 cm^{-1} suggest the presence of a small amount of the amine. Nevertheless, it is unquestionable that these complexes are largely of the acid-base type, even in the molten state. The diethylaniline and *m*-chloroaniline complexes melt at 133°C and 173°C (177°C was the value reported by Hertel[2]) respectively. The latter temperature is appreciably higher than the melting point of the corresponding TNB complex, 114.5°C, which is taken from the work by Sudborough and Beard.[14]

General Remarks. When a strong acid is combined with a strong base, the acid-base interaction is expected to predominate. The strength of the former component is expressed by the pK_a, and that of the latter, by the pK_b. As the acid is picric acid throughout the present work, only the pK_b of the amines will be taken into consideration here. On the other hand, the quantity to be considered in the electron donor-acceptor interaction is the ionization potential, I_P, of the amines. As proposed in our previous works,[11,15] the energy of the CT band in the complexes with a common acceptor observed in a chloroform solution will be taken as a measure of I_P. In this work, *p*-chloranil is selected for this purpose. This energy, hν_{CT}, is approximately given by the I_P-E_A-constant, where E_A is the electron affinity of *p*-chloranil. In Fig. 11, the amines are arranged, with $14-\mathrm{p}K_b=\log[\mathrm{R_1R_2R_3NH^+}]/[\mathrm{R_1R_2R_3N}][\mathrm{H^+}]$ placed on the ordinate, and hν_{CT} on the abscissa.[16] We see here that an amine with a high (14−pK_b) value, that is, a strong base, tends to have a low hν_{CT} value, that is, a strong electron donor. As a result, there seems to be a linear relationship between these two quantities, especially among the amines with (14−pK_b) values higher than 3. The only exception is *N,N*-dimethyl-*o*-toluidine, in which the conjugation between the dimethylamino group and

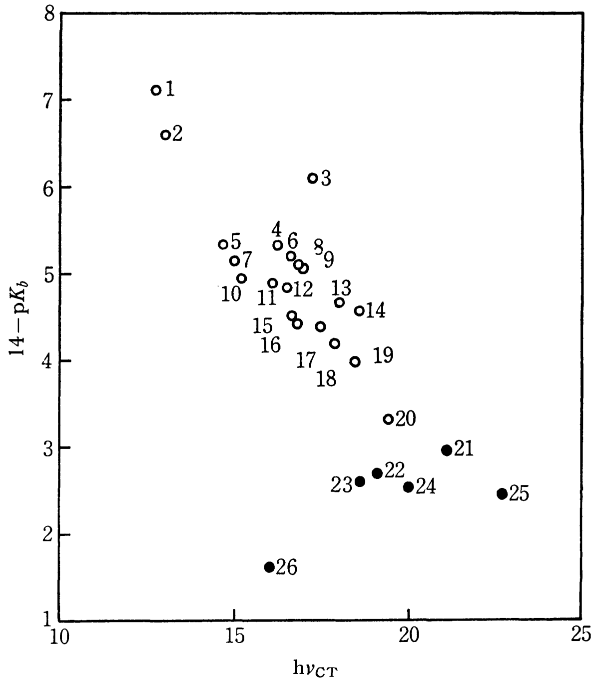

Fig. 11. Plot of (14−pK_b) of the amines against the energy of the CT band of the *p*-chloranil complexes of : 1, *N,N*-diethyl-*m*-toluidine; 2, *N,N*-diethylaniline; 3, *N,N*-dimethyl-*o*-toluidine; 4, *p*-anisidine; 5, *N,N*-dimethyl-*m*-toluidine; 6, *p*-phenetidine; 7, *N,N*-dimethylaniline; 8, *N*-ethylaniline; 9, *p*-toluidine; 10, *N*-ethyl-*o*-toluidine; 11, 2,4-dimethylaniline; 12, *N*-methylaniline; 13, *m*-toluidine; 14, aniline; 15, *o*-anisidine; 16, *o*-phenetidine; 17, *o*-toluidine; 18, *m*-anisidine; 19, *p*-chloroaniline; 20, *m*-chloroaniline; 21, 3-nitro-4-methylaniline; 22, *o*-chloroaniline; 23, *o*-iodoaniline; 24, *o*-bromoaniline; 25, *m*-nitroaniline; 26, *N,N*-dimethylamino-*p*-benzaldehyde. As to the meaning of open and shaded circles, see text.

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[15] Y. Matsunaga, This Bulletin, **42**, 2490(1969).

[16] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London (1965), pp. 58—91.

the benzene nucleus may be supposed to be sterically hindered. In their complexes with picric acid, the acid-base interaction is found to predominate in both the solid and molten states. The amines to form such complexes are indicated by open circles. On the other hand, the amines which were found to form CT complexes above the transition or melting points are those with $(14-\mathrm{p}K_b)$ values less than 3. In Fig. 11, they are indicated by shaded circles. Furthermore, it must be noted that many of these amines do not fit the relationship mentioned above and tend to be electron donors better than would be expected from the relationship. The results summarized in Fig. 11 reinforce Hertel's view.

In conclusion, it must be pointed out that the possibility of finding monotropic phases, where the four amines studied here and picric acid form CT complexes, still remains. When the red-colored melts are solidified, a part of the solid was often observed to be transitorily red-colored.