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Organic Charge Transfer Salts; Absorption Spectra of Salts between the Pyrylium or Thiopyrylium Cation and the 1,1,3,3-Tetracyanopropenide or Tricyanomethanide Anion

Hiroshi Yasuba, Tatsuro Imai, Kenichi Okamoto,
Shigekazu Kusabayashi and Hiroshi Mikawa

Department of Chemical Technology, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka

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New organic charge transfer salts composed of an organic cation (pyrylium or thiopyrylium) and an organic anion (1,1,3,3-tetracyanopropenide or tricyanomethanide) were prepared. The absorption spectra were studied both in solution and in a solid. These salts have the charge transfer band in the visible region as a result of the electronic transition from the anion to the cation. The charge transfer bands of these salts in solution are sensitive to the nature of the solvent. The charge transfer band is observed in solvents with a low polarity; this band shifts toward a shorter wavelength in solvents with a high polarity. The increase in the polarity of the solvent causes a decrease in the apparent molar extinction coefficient. The charge transfer band in the solid shifts toward a shorter wavelength compared with that in the solution. In a single crystal, the polarized absorption spectrum shows a remarkable dichroism.

The absorption spectra of heteroaromatic onium iodide salts[1] have been studied in solution, and their features have been understood in terms of the interionic charge transfer. For example, with *N*-alkylpyridinium iodides two new absorption bands were observed in addition to the bands of the component ions in non-polar solvents[2]; the new absorption bands were attributed to the charge transfer from the anion to the cation. The charge

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[1] S. F. Mason, *J. Chem. Soc.*, **1960**, 2437; E. M. Kosower and P. E. Klinedinst, Jr., *J. Amer. Chem. Soc.*, **78**, 3493 (1956); G. Briegleb, W. Jung und W. Herre, *Z. Phys. Chem.* (Frankfurt), **38**, 253 (1963); A. T. Balaban, M. Mocanu and Z. Simon, *Tetrahedron*, **20**, 119 (1964).

[2] E. M. Kosower, J. A. Skorcz, W. M. Schwarz and J. W. Pattor, *J. Amer. Chem. Soc.*, **82**, 2188 (1960).

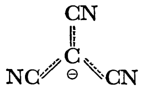
transfer band was sensitive to the nature of the solvent and shifted toward a shorter wavelength with an increase in the polarity of the solvent.[3]

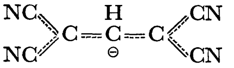
However, only a few brief studies have been reported concerning the absorption spectra of the organic charge transfer salts between the organic cation and the organic anion.[4] We have, therefore, attempted to make a systematic study of the organic charge transfer salts, and have reported the interionic organic charge transfer band and the crystal structure of the salt between 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide anion and quinolinium cation in previous papers.[5] From our consideration of the crystal structure and the optical studies in this salt, we confirmed that the charge transfer band was due to the electronic transition from the anion to the cation.

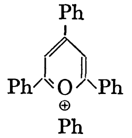
The present paper will deal with the charge transfer bands of the salts between the cyanocarbon-acid anion and the pyrylium or thiopyrylium cation.

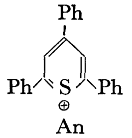
Experimental

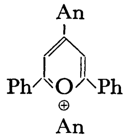
Materials. Tricyanomethanide (TCM) and 1,1,3,3-tetracyanopropenide (TCP) anions were used as the anions, while 2,4,6-triphenylpyrylium (TPP), 2,4,6-triphenylthiopyrylium (TPT), 4-anisyl-2,6-diphenylpyrylium (ADPP) and 4-anisyl-2,6-diphenylthiopyrylium (ADPT) cations were used as the cations.

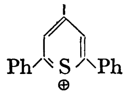

tricyanomethanide anion (TCM)

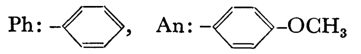

1,1,3,3-tetracyanopropenide anion (TCP)


2,4,6-triphenylpyrylium cation (TPP)


2,4,6-triphenylthiopyrylium cation (TPT)


4-anisyl-2,6-diphenylpyrylium cation (ADPP)


4-anisyl-2,6-diphenylthiopyrylium cation (ADPT)



Sodium-TCP (Na-TCP). Pyridinium-TCP (Py-TCP) was prepared by the method described in a previous paper.[6] Na-TCP was obtained from Py-TCP by the use of a cation-exchang resin, Amberlite CG 120 T-1.

Potassium-TCM (K-TCM). This compound was prepared according to Trofimenko's method[7] and was purified by the column chromatography using active carbon as the adsorbent and methanol as the developing solvent.

TPP-perchlorate (TPP-ClO_4), TPT-ClO_4, ADPP-ClO_4 and ADPT-ClO_4. These compounds were prepared according to Ulrich's method.[8]

The following organic charge transfer salts were prepared and used for measurement.

TPP-TCM. This salt was prepared by a double decomposition reaction between TPP-ClO_4 and K-TCM in methanol and was purified by recrystallization from methanol - water (4 : 1) or methanol. Mp 197—199°C. Found: C, 81.05; H, 4.01; N, 10.40%. Calcd for $C_{27}H_{17}N_3O$: C, 81.20; H, 4.26; N, 10.53%.

The other salts were prepared by a similar method.

TPT-TCP. Mp 203—204°C, Found: C, 80.28; H, 3.34; N, 12.56%. Calcd for $C_{30}H_{18}N_4O$: C, 80.00; H, 4.00; N, 12.44%.

TPT-TCM. Mp 156.5—158°C, Found: C, 78.22; H, 3.90; N, 9.77%. Calcd for $C_{27}H_{17}N_3S$: C, 78.07; H, 4.10; N, 10.12%.

TPT-TCP. Mp 142—143°C, Found: C, 77.23; H, 3.40; N, 11.94%. Calcd for $C_{30}H_{18}N_4S$: C, 77.26; H, 3.86; N, 12.02%.

ADPP-TCM. Mp 201—202.5°C. Found: C, 78.39; H, 4.48; N, 9.64%. Calcd for $C_{28}H_{19}N_3O_2$: C, 78.32; H, 4.43; N, 9.78%.

ADPP-TCP. Mp 243—245°C. Found: C, 77.38; H, 4.10; N, 11.67%. Calcd for $C_{31}H_{20}N_4O_2$: C, 77.50; H, 4.18; N, 11.68%.

ADPT-TCM. Mp 65—67°C. Found: C, 72.82; H, 4.56; N, 9.26; S, 6.94%. Calcd for $C_{28}H_{19}N_3OS$: C, 75.51; H, 4.27; N, 9.45; S, 7.19%.

ADPT-TCP. Mp 175—177°C. Found: C, 75.24; H, 3.95; N, 11.36%. Calcd for $C_{31}H_{20}N_4OS$: C, 74.99; H, 4.03; N, 11.29%.

All the solvents used were purified according to the usual method of purification.[9]

Measurements. The absorption spectrum of the solution and the diffuse reflectance spectrum of the solid were measured with a Hitachi spectrophotometer, EPS 3. The diffuse reflectance spectrum was measured using potassium bromide powder as a standard; it was then plotted using the Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where R is the reflectance. The spectrum

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[3] E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3255 (1958).

[4] E. L. Goff and R. B. LaCount, *ibid.*, **85**, 1354 (1963).

[5] S. Sakanoue, T. Tamamura, S. Kusabayashi, H. Mikawa, N. Kasai, M. Kakudo and H. Kuroda, This Bulletin, **42**, 2407 (1969); S. Sakanoue, N. Yasuoka, N. Kasai, M. Kakudo, S. Kusabayashi and H. Mikawa, *ibid.*, **42**, 2408 (1969).

[6] A. Taniguchi, K. Suzuki and H. Mikawa, *ibid.*, **39**, 1605 (1966).

[7] S. Trofimenko, E. L. Little and H. F. Mower, *J. Org. Chem.*, **27**, 433 (1962).

[8] R. Winzinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 5 (1956); *ibid.*, **39**, 207 (1956).

[9] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston (1957); J. A. Riddick and E. E. Troops, Jr., "Technique of Organic Chemistry," Vol. 7, Organic Solvents, Interscience Publishers, Inc., New York, (1955).

in the single crystal was measured with a Shimadzu multipurpose spectrophotometer, MPS-50, with the use of a microspectrophotometer attachment.

Results and Discussion

The Electronic Absorption Spectra in Solution. The absorption spectrum of TPP-TCP in chloroform has four absorption bands (λ_{max}: 281, 351, 416, and 570 mμ), Na-TCP has one absorption band (λ_{max}: 345 mμ), and TPP-ClO$_4$ has three absorption bands (λ_{max}: 281, 372, and 414 mμ). The absorption band of Na-TCP is due to the TCP anion, and the absorption bands of TPP-ClO$_4$ are due to the TPP cation. Three absorption bands (λ_{max}: 281, 351, and 416 mμ) of TPP-TCP can be explained in terms of the superposition of the absorption bands of the parent cation and anion. The other absorption band (λ_{max}: 570 mμ) is characteristic of the TPP-TCP salt, because neither the parent cation nor the parent anion have any absorption in this region, as is shown in Fig. 1.

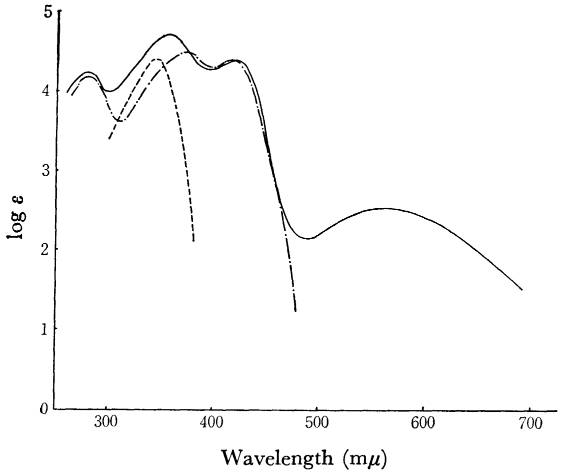

Fig. 1. Absorption spectra of TPP-TCP in chloroform and its component ions.
—— TPP-TCP in CHCl$_3$, — — — TPP-ClO$_4$ in CHCl$_3$ ------ Na-TCP in CH$_3$OH

Table 1. Absorption maxima of charge transfer band in chloroform and in solid state

Salts	λ_{max} in CHCl$_3$ (mμ)	λ_{max} in solid (mμ)
TPP-TCM	538	530
TPP-TCP	570	565
TPT-TCM	566	520 (S)
TPT-TCP	595	540
ADPP-TCM	530 (S)	520 (S)
ADPP-TCP	540 (S)	530 (S)
ADPT-TCM	540 (S)	520 (S)
ADPT-TCP	570 (S)	560 (S)

(S): shoulder

This fact suggests that the new band is an interionic charge transfer band. A new band of this type is also found in the absorption spectra of the other salts. The wavelengths of these new absorption bands are listed in Table 1.

The energies of the new bands in the TCM salts of TPP, TPT, ADPP, and ADPT are 2.30, 2.19, 2.34, and 2.30 eV respectively, while those in the TCP salts of TPP, TPT, ADPP, and ADPT are 2.18, 2.08, 2.30, and 2.18 eV respectively. These two series of energies have a linear relationship, as is shown in Fig. 2. Such a linear relationship has also been observed for usual donor-acceptor complexes between neutral molecules; it has been taken to be evidence of the absorption bands being charge transfer bands.[10] This consideration is thought to be applicable to the present organic salts, also.

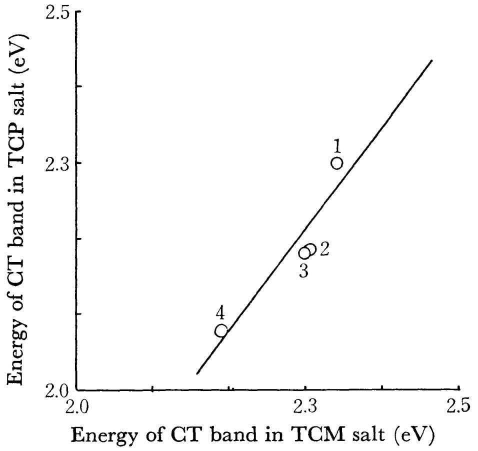

Fig. 2. Energies of charge transfer bands in salts of TCP with the cations: (1) ADPP, (2) ADPT, (3) TPP, (4) TPT, against the energies of the charge transfer bands in the salts of these cations with TCM.
1. ADDP, 2. ADDP, 3. TPP, 4. TPT

The new band is sensitive to the polarity of the solvent. The increase in the polarity of the solvent causes the absorption maximum to shift toward a shorter wavelength and the apparent molar extinction coefficient (ε_{app}) to decrease.

Figure 3 shows the plot of the λ_{max} energies of the new bands of TPT-TCP in various solvents *versus* the *Z*-value,[3] the empirical parameter of the solvent polarity. The linear relationship shows that the absorption maximum shifts to a shorter wavelength with an increase in the solvent polarity. The other salts give similar results. The solvent shift of the absorption bands in these salts can be explained by Kosower's theory presented in his

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[10] R. Foster, *Tetrahedron,* **10**, 96 (1960); K. Abe, Y. Matsunaga and G. Saito, This Bulletin, **41**, 2852 (1968).

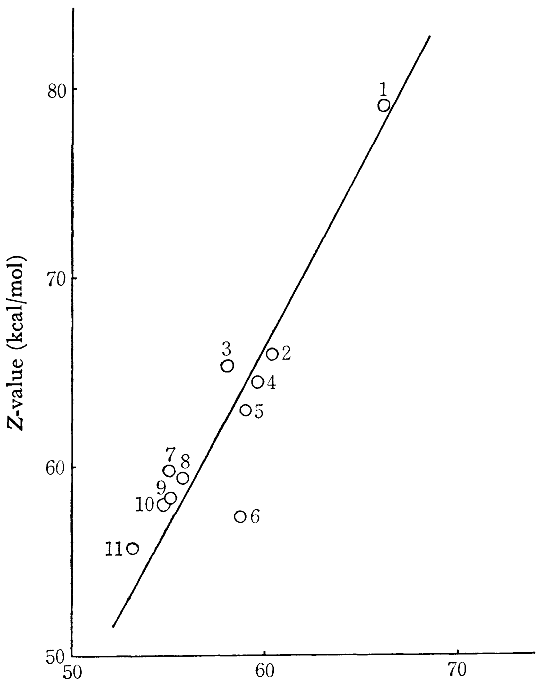

Fig. 3. Energies of the charge transfer bands of TPT-TCP against the Z-value for the solvents used.

(1) Acetic acid, (2) Methyl acetate, (3) Anisole, (4) Dichloromethane, (5) Chloroform, (6) Ethyl acetate, (7) Bromobenzene, (8) Chlorobenzene, (9) Dioxane, (10) Toluene, (11) Benzene.

consideration of the solvent effect of the absorption spectrum of organic iodides.[3] That is, the solvent shift of the absorption maximum depends on the stabilization in the ground state and the destabilization in the excited state. From the above results, it can be concluded again that the new bands of these salts are due to the electronic charge transfer from the anion to the cation. The slope in Fig. 3 is associated with the solvent sensitivity of the charge transfer band. If the slope is steep, the solvent sensitivity is low. In these salts, the slope of this straight line is 1.5—2.0. In tropylium iodide[11] and *N*-methylacridinium iodide,[12] the slope of this line is unity. It has been reported that the solvent sensitivity depends on the size of the anion and the delocalization of its charge, the increase in size and the increase in the delocalization of its charge causing the decrease in the solvent sensitivity.[12] In the present case, the size and the delocalization of the charge in TCM or TCP anion are larger than those of the iodide anion. It can, therefore, reasonably be understood that the solvent sensitivity for TCM or TCP is inferior to that of iodides. In ADPP and ADPT systems the new band was observed as a shoulder. It was, therefore, not possible in these salts to investigate the solvent effect in detail.

As these charge transfer bands are due to the interaction between the anion and the cation, both ions must be in the ion-pair form in order to exhibit charge transfer interactions. The salts are in the following equilibrium in solution:

$$\mathrm{AD} \rightleftarrows \mathrm{D}^- + \mathrm{A}^+$$

where DA is an organic charge transfer salt in an ion-pair form and where D^- and A^+ are the component ions. In polar solvents the dissociation of the ion-pair proceeds and the concentration of the ion-pair from decreases, thus decreasing the apparent molar extinction coefficient ($\varepsilon_{\mathrm{app}}$). At a certain concentration the $\varepsilon_{\mathrm{app}}$ values were measured in several different solvents. As is shown in Fig. 4, the $\varepsilon_{\mathrm{app}}$ values decrease with the increase in the dielectric constant of the solvent. The dissociation constants of these salts were calculated as follows from the concentration dependence of the charge transfer bands by a method similar to that used for *N*-dodecylpyridinium iodide.[13] Provided that the absorbance of the solution at the charge transfer

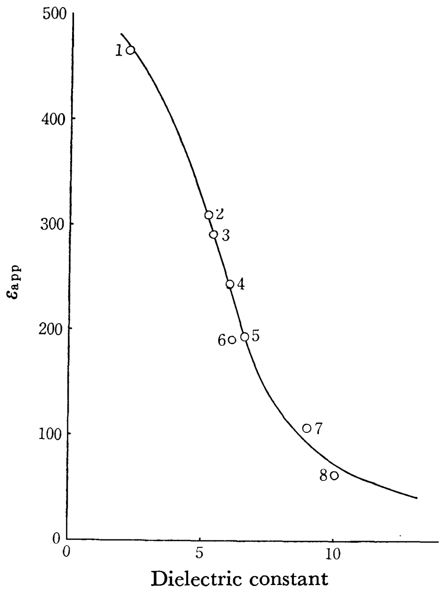

Fig. 4. Apparent molar extinction coefficient of TPT-TCP against the dielectric constants for the solvents used.

(1) Dioxane, (2) Chlorobenzene, (3) Bromobenzene, (4) Methyl acetate, (5) Ethyl acetate, (6) Acetic acid, (7) Dichloromethane, (8) 1,2-dichloroethane.

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[11] E. M. Kosower, *J. Org. Chem.*, **29**, 956 (1964).

[12] T. G. Beaumont and K. M. C. Davis, *J. Chem. Soc.*, *B*, **1968**, 1010.

[13] A. Ray and P. Mukerjee, *J. Phys. Chem.*, **70**, 2138 (1966).

band is due entirely to the charge transfer absorption of the ion-pair present, and provided that the absorption due to the component ions is negligible in this wavelength region, the following equation is obtained:

$$D/C_0 = \varepsilon - (K\cdot\varepsilon)^{1/2}\cdot D^{1/2}/C_0$$

where D is the optical density for an optical length of 1 cm; C_0, the total concentration of the salt; ε, the molar extinction coefficient of the ion-pair, and K, the dissociation constant of the salt. The values of K and ε were calculated from the slope and intersection of the plots of D/C_0 *vs.* $D^{1/2}/C_0$; they are shown in Table 2 for chloroform solution. The values of K in Table 2 clearly show that, in chloroform, the anion and the cation exist as an ion-pair form. These results are also supported by the measurement of the conductivity of the solution. In a polar solvent the equivalent conductivity is proportional to $C^{1/2}$, and in a non-polar solvent, to $1/C^{1/2}$, where C is the concentration of the salt. This conductivity behavior suggests that these salts dissociate highly in a polar solvent and do not dissociate so much in a non-polar solvent.

TABLE 2. DISSOCIATION CONSTANT AND MOLAR EXTINCTION COEFFICIENT IN CHLOROFORM

	K	ε
TPP-TCM	$\sim10^{-5}$ below	340
TPP-TCP	$\sim10^{-5}$	310
TPT-TCM	$\sim10^{-5}$ below	470
TPT-TCP	$\sim10^{-4}$	370

In conclusion, the solvent shift of the charge transfer band can be explained by the term of Z-values, and the dissociation of the salt is closely related to the dielectric constant of the solvent.

In the interionic charge transfer salts, the following equation is also applicable:

$$E_{ct} = I_p(\mathrm{D}^-) - E_a(\mathrm{A}^+) + E_{coul}$$

where E_{ct} is the energy of the charge transfer transition; $I_p(\mathrm{D}^-)$, the ionization potential of the donor anion; $E_a(\mathrm{A}^+)$, the electron affinity of the acceptor cation, and E_{coul}, the coulomb energy for the separation of ions. The term of the coulomb energy (E_{coul}) is probably nearly the same in different interionic charge transfer salts. For the salts having the same cation, the difference in E_{ct}, therefore, represents the difference in $I_p(\mathrm{D}^-)$, that is, the energy difference between the highest occupied molecular orbitals of the anions. The values of Table 1 suggested that the ionization potential of TCM is larger than that of TCP. The simple Hückel LCAO calculation also supports this suggestion. A similar treatment to the salts composed of the same anion suggested that the electron affinity of TPP is smaller than that of TPT. It has been suggested that the polarographic half-wave potential is correlated with the electron affinity and, hence, with the charge transfer energy.[14] The half-wave potentials of these cations, measured as usual against the saturated calomel electrode, gave the values of -0.24 V for TPP and

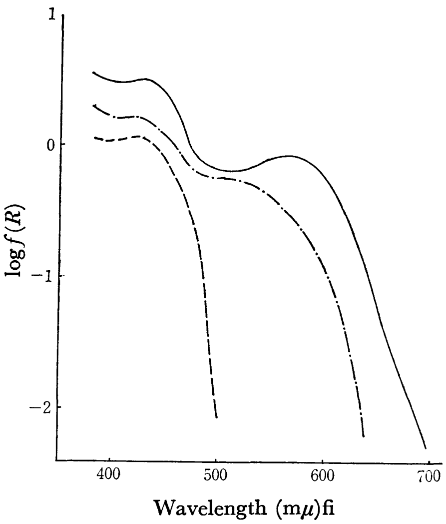

Fig. 5. Diffuse reflectance spectra of TPP-TCP (——), TPP-TCM (– – –) and TPP-ClO$_4$ (-----).

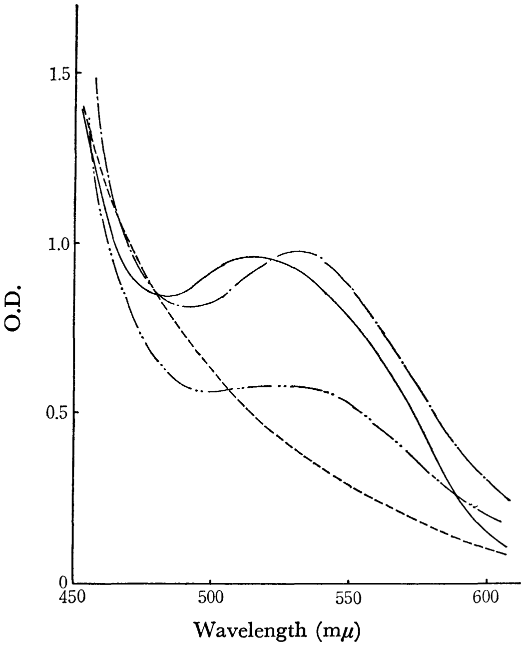

Fig. 6. Polarized absorption spectra of single crystals of TPP-TCP and TPP-TCM.
TPP-TCP: – – – 1//, –·–·– 1⊥
TPP-TCM: —— 1//, ----- 1⊥

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[14] M. Feldman and S. Winstein, *Tetrahedron Lett.*, **1962**, 853.

-0.17 V for TPT in absolute ethanol. The electron affinity of TPP is, therefore, smaller than that of TPT. From these results, it can reasonably be understood that the charge transfer bands of TPP-TCM and TPP-TCP are in a shorter wavelength region than those of TPT-TCM and TPT-TCP respectively.

The Electronic Absorption Spectrum in Solid. The absorption spectra in a solid were measured by diffuse reflectance spectroscopy. The spectra of TPP-TCM, TPP-TCP, and TPP-ClO_4 are shown in Fig. 5. The absorption band is at 530 mμ in TPP-TCM and at 565 mμ in TPP-TCP. These absorption bands in a solid are considered to correspond to the charge transfer bands in solution. The absorption peaks of other salts in the solid state are shown in Table 1.

The charge transfer band in the solid state lies in a somewhat shorter wavelength region than does the corresponding charge transfer band in the solution, as is shown in Table 1. This suggests that the stabilization by the neighboring ions in the solid state is larger than the stabilization by the neighboring solvent molecules in the solution. The data in Table 1 also suggest that the stabilization of the TPP system is smaller than that of the TPT system. This difference may be due to the differences in the crystal structure and the polarizability of the component ions.

The polarized absorption spectra of the single crystals of TPP salts show a remarkable dichroism in the charge transfer band, the optical density being large in the direction of the crystal growth (Fig. 6). Although the crystal sturcture has not yet been determined in this case, it seems certain that the cation and the anion are stacked in an alternating face-to-face arrangement in the growth direction, and that the charge transfer transition occurs from an anion to the nearest cation in this direction. A similar phenomenon has also been observed in quinolinium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide (Q_2DMTP). The crystal structure of Q_2DMTP is orthorhombic, and the cation and the anion are stacked alternately along the *a*-axis.$^{5)}$ The optical density is higher in the *a*-polarization spectrum than in the *c*-polarization spectrum.$^{5)}$

All the results show that the new absorption band, both in a solid and in solution, is a charge transfer band between the anion and the cation.