Electronic Spectra of Organic Charge Transfer Salts of 2-Dicyanomethylene-1,1,3,3-tetracyanopropane

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In some compounds charge transfer bands between organic cation and organic anion have been observed in the electronic spectrum.[1] However, there has been no explanation of these charge transfer bands on the basis of the crystal structure.

The absorption spectra of quinolinium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide (Q_2DMTP) in various solvents are shown in Fig. 1. In chloroform-ethanol solution, two new shoulder bands appeared near 380 and 410 mμ in addition to the absorption of the component ions. The apparent extinction coefficient of these shoulder bands decreased with the increase of the polarity of the solvents. In the same solvent the apparent extinction coefficient of the absorption in 410 mμ increased with the increase of the concentration, while that of the absorption in 380 mμ decreased. This may be explained from the equilibrium between the dissociated ions and the ion-pairs, Q_2DMTP and/or QDMTP$^-$, and the new absorption bands due to the ion-pairs.

To elucidate the origin of the new absorption band, the polarized absorption spectrum of a single crystal was measured by means of a microspectrophotometer. The crystal of this salt is orthorhombic with the unit cell dimensions, $a=13.18$, $b=15.40$, $c=11.56$ Å; $Z=4$, and the space group, *Pbcn*. In the crystal, one unit consists of the propeller-shaped DMTP anion sandwiched with two planar quinolinium cations on both sides, and the unit is stacked in finitely along the *a*-axis. The tilt angle of the plane of the cation to the *a*-axis is about 60°. In the solid absorption spectrum, a new band was also observed. The spectrum of *a*-polarization and that of *c*-polarization are shown in Fig. 2. It can be seen that the optical density is higher in the *a*-polarization spectrum than in the *c*-polarization spectrum. In connection with the crystal structure, this result proves that the new band in solid is a charge transfer band between ions within an ion-pair.

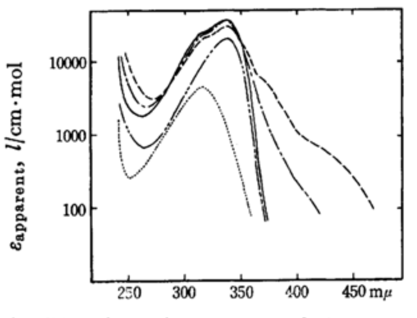

Fig. 1. The absorption spectra of Q_2DMTP in various solvents and its component ions (Q^+, DMTP^{2-}) in water.
…… Quinoline in HCl aqueous solution
—·— Na_2DMTP in H_2O
—— Q_2DMTP in H_2O 3.24×10^{-4} mol/l
— — Q_2DMTP in C_2H_5OH 3.16×10^{-4} mol/l
---- Q_2DMTP in $CHCl_3$-C_2H_5OH 5.00×10^{-4} mol/l

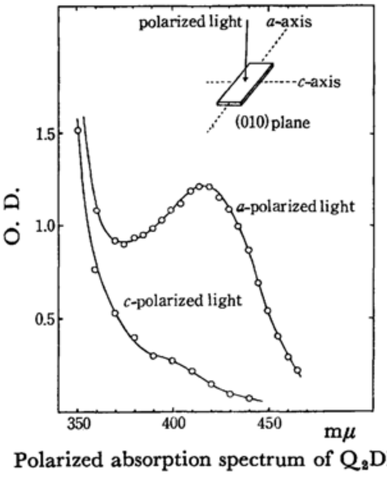

Fig. 2. Polarized absorption spectrum of Q_2DMTP.

Several other salts of DMTP were also prepared with *N*-heteroaromatic cations, such as pyridinium, quinolinium and *N*-methylacridinium. These salts showed characteristic colors, white, yellow and red, respectively. The wavelengths of the new absorption bands of these salts increased as the electron affinity of the *N*-heteroaromatic cations increased. Therefore the color of the salts may be also attributed to the electronic transition from the anion to the cation.

The results show that the new absorption band both in solid and in solution is a charge transfer band between ions within an ion-pair.

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[1] M. Feldman and S. Winstein, *Tetrahedron Letters*, **19**, 853 (1962); E. L. Goff and R. B. LaCount, *J. Am. Chem. Soc.*, **85**, 1354 (1963).