Solid Molecular Complexes of Phenothiazine & N-Methylphenothiazine with 7,7,8,8-Tetracyanoquinodimethane

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Phenothiazine and N-methylphenothiazine interact with tetracyanoquinodimethane to form solid 1:1 molecular complexes. The optical absorption spectra and the electrical properties show that these complexes are not ionic salts, but neutral molecular complexes. N-Methylphenothiazine is a poorer electron donor as compared to phenothiazine.

Several workers have reported the formation of charge-transfer complexes between some electron acceptors and phenothiazine (PTZ) or its derivatives[1-5]. Phenothiazine (PTZ) and its derivatives are of considerable interest in view of their physiological activities. These activities depend on the geometrical and conformational properties of the compounds[6]. The comparatively low ionization potential of PTZ and the high electron affinity of 7,7,8,8-tetracyanoquinodimethane (TCNQ) are expected to make their charge-transfer complex strong. Some of the complexes reported are so strong that they are ionic in the ground state[5,7]. Recent single crystal studies have shown that PTZ, which is bent along the $N-S$ axis, becomes planar in PTZ-TCNQ complex[8-10]. As PTZ cation is known to be planar, the PTZ-TCNQ complex is expected to be ionic[11]. However, in the case of PTZ-TCNQ complex, the planarity of PTZ is claimed to be due to hydrogen bonding[12]. So it was thought interesting to find out whether the PTZ-TCNQ complex is neutral or ionic and whether there is any hydrogen bonding between N $-$H of PTZ and N of TCNQ. It was also of interest to find whether N-methylphenothiazine (MePTZ) forms a stronger complex as reported by Matsunaga[3] or it is a weaker electron donor as claimed by Bloor *et al*[2].

Materials and Methods

Phenothiazine, which is commercially available, was purified by crystallization using ethanol, followed by sublimation *in vacuo* (m.p. 181°C). Methylphenothiazine was synthesised from PTZ, following the procedure of Bernthsen[13] (m.p. 100°). TCNQ was sublimed *in vacuo* before using.

Minute crystals of PTZ-TCNQ and MePTZ-TCNQ complexes were obtained on cooling hot CH_2Cl_2 and CH_3CN solutions containing the appropriate amounts of the donor and acceptor. The composition of each molecular complex was found to be 1:1 on the basis of elemental analyses.

The absorption spectra of the samples in nujol were recorded using Hitachi EPS-24 and Beckman DU spectrophotometers. The polarized absorption spectra of minute single crystals were measured with a microspectrophotometer, the details of the apparatus and the procedure of measurements have been reported elsewhere[14]. The infrared spectra of the samples in nujol were recorded using Hitachi EPI-2 and Perkin-Elmer 621 IR spectrophotometers.

The electrical conductivities, σ, of the crystalline samples, which were packed in a cell and compressed under a pressure of 116 kg/cm^2 were measured by the DC method. The temperature of the specimen was controlled with an electric furnace placed around the cell.

Results and Discussion

Electronic spectra—The electronic spectra of PTZ-TCNQ and MePTZ-TCNQ show two main bands at 8.2, 18.5 kK and 8.7, 20 kK respectively. These bands can be assigned as the first and second charge-transfer bands as neither of the reactants has any absorption in these regions. We could not detect any band around 14.7 kK, which indicates that there is no TCNQ$^-$ species in the complexes[7,15]. This shows that the complex is essentially of non-bonding type in the ground state.

There is a red shift in the first charge-transfer (C.T.) band in going from solution to the solid state. The shifts are 0.17 and 0.23 eV for PTZ-TCNQ and MePTZ-TCNQ respectively. These results compare well with those for the neutral TNB-aromatic hydrocarbon complexes, where the charge-transfer excitation energy in solid state is lowered by

~ 0.17 eV[16]. The red shift in the band position may be due to crystal packing and it has been explained by Gott and Maish[17] in terms of change in refractive indices. In weaker complexes, the effect of pressure is expected to be more than that in the stronger complexes and this is indeed observed in the case of MePTZ-TCNQ complex.

Polarized absorption spectra: (*a*) *PTZ-TCNQ complex*—The crystal structure of the complex has been reported by Kobayashi[8,12]. It is monoclinic with $a = 7.04$ Å, $b = 25.38$ Å, $c = 10.51$ Å and $\beta = 92.1°$. The space group is $C2/C$; $Z = 2$.

We observed the long axis (*b*) and short axis (*a*) polarized spectra from the direction normal to the developed plane. There are two absorption bands in the visible and near IR regions. The absorption maximum of first CT band could not be detected due to the limitations of our experimental set up. The first CT band (obtained from mull spectra) at 8.2 kK is exclusively polarized along the long axis. In the first CT band, the transition moment is parallel to the direction of alternate stacks of donor and acceptor molecules (PTZ and TCNQ are stacked alternately in infinite columns along the *a* axis[12]).

The second absorption band appears at ~ 18.5 kK. This band is stronger in the short axis of the crystal. The second CT band may be associated with the interaction of donor molecule with the second nearest acceptor molecule (as the second ionization potential of the donor is quite high[6]), and hence it has low intensity. There is an absorption maximum in the long axis direction also; so it appears that it may not be a pure CT band, but CT band mixed with local excitation of the components.

(*b*) *MePTZ-TCNQ*—The crystal structure of this complex has been reported by Kohayashi[8,12]. It is monoclinic and its dimensions are: $a = 10.904$ Å, $b = 13.321$ Å, $c = 7.086$ Å, $\beta = 91.06$ and the space group is $C2/m$; $Z = 2$.

The variation of absorption with the direction of polarization of incident light throws light on the polarization axis. The crystal which we chose for the polarized absorption measurements had the *ac* developed plane. Out of the two CT bands, the one at 8.7 kK is polarized along the long axis *c*; the second CT band at ~ 20 kK (which is again a mixture of CT band and the local excitation of the components) is largely polarized along the small axis.

The dihedral angle along the N − S axis in MePTZ-TCNQ complex is $\sim 163°$ whereas for the pure MePTZ this is expected to be $\sim 151°$ (ref. 20). Using a microscope, we could see two types of crystals, namely, very thin crystals which are polarized along the *bc* plane, and thick flat crystals polarized along *ac* plane.

Infrared absorption spectra—Vibrational spectroscopy has principally been used to distinguish a neutral 'outer' complex from the radical ion pair formed by electron transfer. The spectrum of the complex is nearly the superimposition of the spectra of pure components. The $\nu C \equiv N$ mode is observed at 2220 cm^{-1} and it is not split. In the case of TCNQ anion radicals, the corresponding band appears at 2203 cm^{-1}, and it is broadened and split[19]. A band expected around 1540 cm^{-1} due to the superimposition of ring $\nu C = C$ mode and ethylene $\nu C = C$ mode of TCNQ appeared at 1538 cm^{-1} indicating the absence of radical salts. The band in the case of TCNQ$^-$, is split and the bands appear at 1507 and 1580 cm^{-1}. The splitting is considered to be due to the difference in bond lengths of the ring and ethylenic C = C bonds in TCNQ and its anion radical. Moreover, we could not detect any band around 1183 cm^{-1} which is observed in the case of TCNQ$^-$. So, from IR spectra, it is evident that both PTZ-TCNQ and MePTZ-TCNQ are not ionic salts in the ground state and they are neutral molecular complexes.

In PTZ, the $\nu N - H$ mode appears at 3380 cm^{-1} and after complexation it shifts to 3320 cm^{-1}. This shift is caused by the hydrogen bonding between N − H of PTZ and N of TCNQ. The average N − H...N distance is 3.285 Å (3.20-3.37 Å) and using the empirical relation proposed by Pimental[20] for N − H....N hydrogen bonded crystals, we have,

$$\Delta\nu = 1.05 \times 10^3 (3.38 - R)$$

The expected shift comes out to be 100 cm^{-1}. The present experimental value ($\Delta\nu = 60$ cm^{-1}) is of the same order as the expected shift clearly indicating the presence of hydrogen bonding between N − H of PTZ and N of TCNQ. However, its lower than expected value indicates that the hydrogen bonding between PTZ and TCNQ is not strong.

Electrical conductivity—The solid molecular complexes, PTZ-TCNQ and MePTZ-TCNQ, behave as semiconductors[21]. The energy gap, Eg, for the system is calculated using the equation,

$$\sigma = \sigma_0 C^{-Eg/2kT}$$

The results are summarized in Table 1.

It can be seen from the data in Table 1 that the conductivity of MePTZ-TCNQ is lower and Eg is higher than those of PTZ-TCNQ. It may be mentioned

Table 1—Electrical Conductivity Data of the Complexes

System	Conductivity σ (ohm^{-1}cm^{-1}) 25°C	Eg (eV)	$h\nu_{CT}$ (eV) (Solid)	$h\nu_{CT}$ (eV) (Solution)
PTZ-TCNQ	1.35×10^{-8}	1.35 ± 0.1	1.01 ± 0.01	1.18 ± 0.01
MePTZ-TCNQ	5.8×10^{-10}	1.65 ± 0.15	1.07 ± 0.01	1.30 ± 0.01

that the width of a forbidden band is expected to reflect the strength of the interactions amongst the molecular orbitals; this strength in turn depends on the shape and the extent of overlap of its donor orbitals with those of the acceptors. The relatively high resistivity and energy gap in MePTZ-TCNQ complex may be attributed to the poor overlapping of the component molecules (sterically unfavourable potential barrier) compared to those of PTZ and TCNQ. Uchida and Akamatu[22] have pointed out that strong charge-transfer complexes (i.e., those which have ionic ground state) have very low resistivities and the weaker interactions lead to room temperature resistivities which are very much higher but lower than those encountered in ordinary molecular crystals.

So the above results, namely the low electrical conductivity and high energy gap in MePTZ-TCNQ compared to those in PTZ-TCNQ corroborate the spectroscopic observations that MePTZ-TCNQ is weaker complex as compared with PTZ-TCNQ.

The complexes do not show any ESR signal at the room temperature which again indicates that the complexes are neutral. The preliminary experimental results of magnetic susceptibility measurements also show that the complexes are neutral.

The absence of any absorption bands due to TCNQ$^-$ in the electronic and IR regions, the low electrical conductivities, high energy gaps and the unsuccessful attempts to detect any magnetic properties indicate that PTZ-TCNQ and MePTZ-TCNQ complexes are neutral complexes in the ground state and MePTZ-TCNQ complex is weaker compared to PTZ-TCNQ.

Acknowledgement

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