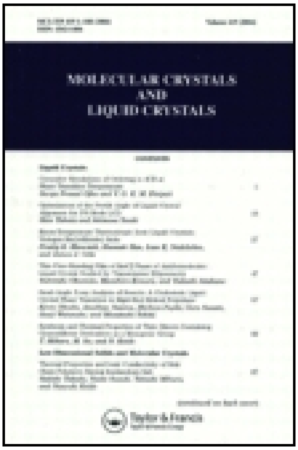

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Effect of Hydrogen Bonding in 2:3 TCNQ Compounds

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EFFECT OF HYDROGEN BONDING IN 2:3 TCNQ COMPOUNDS

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Abstract The Raman, IR, UV and VIS spectra of Quinuclidinium$_2$ TCNQ$_3$ (QND$_2$TCNQ$_3$) and triethylendiammonium$_2$ TCNQ$_3$ (TEDA$_2$TCNQ$_3$) are reported and compared to those of other known 2:3 compounds. In QND$_2$TCNQ$_3$ and Cs$_2$TCNQ$_3$ we have identified the presence of TCNQ$^-$ and TCNQ^0 species from their different Raman resonance behavior. In TEDA$_2$TCNQ$_3$, only one species, TCNQ$^{-2/3}$ is shown to be present. This difference in the electronic structure of the TCNQ chain in these salts will be correlated with the crystal structure, the conductivity and the electronic absorption. In particular, the hydrogen bond distribution in TEDA$_2$TCNQ$_3$ is shown to be quite different from that of other known compounds.

INTRODUCTION

The tertiary amines Quinuclidine (QND) and Triethylenediamine (TEDA) form 2:3 complexes with Tetracyano-quinodimethane (TCNQ). These cations form hydrogen bonds to the TCNQ ions or to themselves, thus permitting us to evaluate the relative importance of pinning of the electrons in the TCNQ conduction chains by the interactions with cations. Spectroscopic data should be useful to estimate the formal charge, and the interaction of the electron with phonons in these complexes.

In the present work, we report the Raman, IR, UV and VIS spectra of QND$_2$TCNQ$_3$,TEDA$_2$TCNQ$_3$ and compare these to an other known 2:3 compound, Cs_2TCNQ_3. A relative comparison of these spectroscopic results will help relate the various degrees of charge transfer in these semiconductors, i.e., localization of electrons on individual TNCQ molecules.

RESULTS AND DISCUSSION

The electronic absorption spectra of QND_2TCNQ_3 and $TEDA_2TCNQ_3$ are similar to other 2:3 salts. The two large bands at 15.8 and 28 x 10^3 cm^{-1} are assigned to the local excitations of TCNQ. In QND_2TCNQ_3 the band at 11.5 x 10^3 cm^{-1} and the shoulder around 7 x 10^3 cm^{-1} correspond to the charge transfer (C.T.) excitations. The crystal structure of QND_2TCNQ_3 has chains of isolated dimers of $(TCNQ_2)^{-2}$ (Fig. 1) with one C≡N hydrogen bonded to the Quiniclidinium cation. Between the dimer chains we find chains of neutral $TCNQ^{\circ}$. This structure favors stronger localization of electron on two $TCNQ^-$ molecules and a negligible interaction between the neutral and negative $TCNQ^-$. The weakness of the C.T. band around 7 x 10^3 cm^{-1} agrees with this inference.

The spectrum of $TEDA_2TCNQ_3$ has a small band around 4 x 10^3 cm^{-1} and a shoulder around 11 x 10^3 cm^{-1}. These are assigned to the C.T band. The energy of the lowest C.T band is obviously smaller than in other 2:3 salts, which implies that the electron configuration in this salt differs from those of Cs_2TCNQ_3 or Mor_2TCNQ_3. It is interesting that the whole feature of this spectrum resembles that of the spectra of $TEA.TCNQ_2$. $TEDA_2TCNQ_3$ forms chains of trimers separated by 3.45 Å whereas the TCNQ distances in dimer are 3.2 Å (Fig. 2). Of note, the charge distribution seems uniform (2/3e⁻ for TCNQ) and there is no hydrogen bonding to TCNQ chains because of the propensity of TEDA's to form hydrogen bond to themselves. The influence of the cation on the TCNQ chain is therefore negligible, which explains why this compound is the best conductor of the series (Table 1).

The infrared spectra of QND_2TCNQ_3 and $TEDA_2TCNQ_3$ were taken in nujol and in KBr to make sure there is no reaction between the sample with KBr dispersing material. Assignments of the vibrational bands of $TCNQ^-$ and $TCNQ^\circ$ are based on the recent report of Futamata et al [1]. The IR spectrum of QND_2TCNQ_3 was almost the same as that of Cs_2TCNQ_3. Three large bands observed at 1579, 1178 and 722 cm^{-1} are assigned to the A_g modes allowed by e.v coupling [1] as there is no infrared active TCNQ vibration in this frequency region. In the C=C vibration region, a small band at 1538 cm^{-1} is nearly identical to the 1543 cm^{-1} vibration of $TCNQ^\circ$, the corresponding $TCNQ^-$ band appears at 1502 cm^{-1}. Two sharp bands at 830 and 841 cm^{-1} correspond to the b_{1u} out of plane modes of $TCNQ^-$ and $TCNQ^\circ$ respectively. These results confirm the presence of neutral and negatively charge of TCNQ inferred in the X ray work [2]. The IR spectrum of $TEDA_2TCNQ_3$ showed broader A_g bands at 2166, 1567, 1343, 1756, 704 cm^{-1} in agreement with the more extensive electron delocalization determined from X ray result [3]. Furthermore, the IR dips occur near the frequency of charged species Raman 1410 (1416 cm^{-1}). We thus infer that the linear e.v coupling is not suitable in this case, and that correction such as quadratic interactions are necessary [3].

TABLE 1. Resistivities, activation energies of somes 2:3 compounds.

Compounds	Powder resistivity (Ωm)	Activation energies
QND_2TCNQ_3	10^4	0.29 ev
$TEDA_2TCNQ_3$	1.2	0.23
Cs_2TCNQ_3	10^3	0.32
Mor_2TCNQ_3	10^3	0.31

Raman spectroscopy is considered a good technique to estimate the degree of charge transfer owing to the linear dependency of TCNQ frequency on the formal charge [4,5]. In QND_2TCNQ_3 and Cs_2TCNQ_3, the Raman bands corresponding to ν_4 were observed at 1453, 1435, 1386 cm^{-1}. This shows clearly the presence of TCNQ neutral (1453 cm^{-1}) and $TCNQ^-$ (1386 cm^{-1}) (Fig. 3). Resonance effects indicate that the $TCNQ^-$ vibration at 1386 cm^{-1} is enhanced in intensity with yellow and red lines excitation, in contrast to $TCNQ^\circ$ neutral 1453 cm^{-1} vibration, which is resonant with the blue and violet lines. This observation shows the localized nature of these Raman bands, hence the localization of the conducting electron on TCNQ chains.

The Raman spectra of $TEDA_2TCNQ_3$ on the other hand does not exhibit this resonant effect (Fig. 4). Only one Raman band corresponding to ν_4 is observed at 1416 cm^{-1}, this band being shifted by about 38cm^{-1} as compared to $TCNQ^\circ$. The formal charge is therefore estimated to be 38/60 (.64e^-), which value agrees well with the X ray results. The presence of only one Raman band at the intermediate frequency 1416 cm^{-1} means that the fluctuation of charge in the trimer unit is very rapid in the case of $TEDA_2TCNQ_3$, in constrast to the slow fluctuation of charge in QND_2TCNQ_3 and Cs_2TCNQ_3. This is taken as evidence of more charge delocalization in $TEDA_2TCNQ_3$.

SUMMARY AND CONCLUSIONS

1. In the case of $TEDA_2TCNQ_3$, the single Raman frequency observed at 1416 cm^{-1} (characteristic of the C=C vibration) indicates the charge density to be uniform in this system. This uniformity in charge density may be induced by weak proton interaction in the cation chain which is commensurate

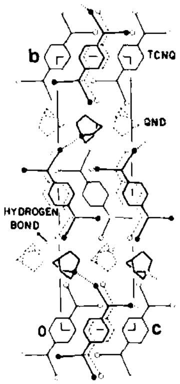

FIGURE 1 Projection of QND_2TCNQ_3 along a axis

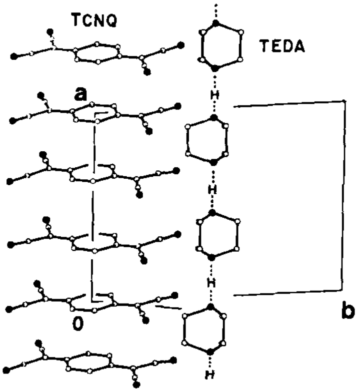

FIGURE 2 Projection of $TEDA_2TCNQ_3$ along c axis.

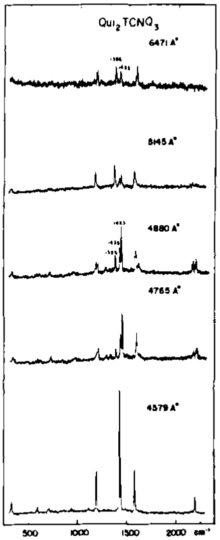

FIGURE 3 Raman spectra of QND_2TCNQ_3.

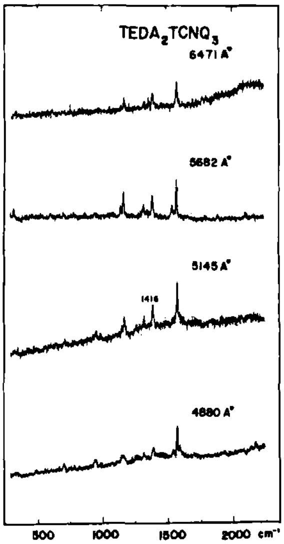

FIGURE 4 Raman spectra of $TEDA_2TCNQ_3$.

with the TCNQ chain. Thus this compound is free of any charge pinning by the cations.

2. $TEDA_2TCNQ_3$ is the best conductor in the series considered here owing to *least TCNQ cation interaction and also* minimum electron repulsion. This compound undergoes trimerization, i.e., one would expect a charge density wave ($\Delta\rho = \sin\left(\frac{2\pi x}{3a} - \frac{\pi}{6}\right)$) to occur.
3. Raman spectra of QND_2TCNQ_3, Cs_2TCNQ_3 *indicate unambiguosly* the presence of TCNQ° (1453 cm^-) and $TCNQ^-$ (1386 cm^{-1}), in agreement with the X ray; the charges are pinned on dimers by the cations or H-bonds, thus leaving a neutral TCNQ. This results in poor conduction.
4. $TCNQ^-$ vibration at 1386 cm^{-1} shows a resonant effect with yellow, red line excitations, in contrast to the TCNQ° vibration at 1453 cm^{-1} whose intensity is enhanced in the blue and violet region. This permits us to assign readily the $TCNQ^-$ vibrations.
5. The present Raman and IR spectra point out the need to introduce quadratic electron - vibration coupling in the theory of organic conductors.

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