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SPECTROSCOPIC AND ELECTRICAL INVESTIGATIONS OF MeDABCO/TCNQ/$_2$ SALT

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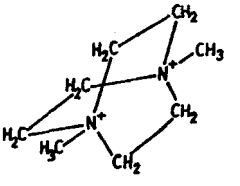
ABSTRACT. Spectral studies of MeDABCO/TCNQ/$_2$ salt were performed in the IR and visible regions respectively on KBr compactions at 85K-293K and in acetonitrile solutions. Electric conductivity was measured vs. temperature for polycrystalline MeDABCO/TCNQ/$_2$, permitting the calculation of the activation energy. Measurements of the thermoelectric force yielded the Seebeck coefficient.

The physical properties of tetracyano-p-quinodimethane/TCNQ/ with various electron donors, in particular with approximately planar molecules, have been studied and described in detail.[1,2] However, it was of interest to study the influence of the spatial structure of the donor on the type of ordering and physical properties of the salt.

Our present work bears on TCNQ with 1,4-diazobicyclo [2.2.2.]octane, methylated on both nitrogens,



to be referred to as MeDABCO/TCNQ/$_2$.

The choice of donor was mainly determined by its spatial structure. The "cage-like" structure of the donor makes the formation of parallel and separated donor chains difficult. The DABCO molecules, owing to the presence of two centers of basicity, easily forms complexes with charge transfer. In some cases the transfer can be complete, as for example in the complex of DABCO with TCNE.[3]

MeDABCO/TCNQ/$_2$ salt was obtained by a method similar to that described by Melby et al.[4,5] After threefold recrystallization from acetonitrile, the complex was obtained in the shape of dark blue crystals about 1 mm in size.

Spectral investigations in the visible regions, performed for solutions in acetonitrile, proved that no electroneutral $TCNQ^o$ molecules occur in MeDABCO/TCNQ/$_2$ salt. This conclusion was drawn from measurements of the optical densities of absorption bands performed at the wavelengths 400 nm and 842 nm.[6] The density ratio amounted to 0.79.

IR absorption spectra of MeDABCO/TCNQ/$_2$ salt taken in powder samples with KBr diverged strongly from the sum of the donor and acceptor spectra (Fig. 1). In the spectrum of MeDABCO/TCNQ/$_2$ salt, nine absorption bands predominate lying at 2970 cm^{-1}, 2182 cm^{-1} (triplet), 1580 cm^{-1}, 1340 cm^{-1} (doublet), 1182 cm^{-1}, 825 cm^{-1}, 723 cm^{-1}, 483 cm^{-1} and 332 cm^{-1}. The bands are very intense (except the one at 2910 cm^{-1}) and have no counterparts either in the spectrum of the donor or in that of the acceptor. We attribute the bands, on the theory of Rice,[7] to coupling between conductivity electrons of molecular orbitals and completely symmetric IR-inactive vibrations of TCNQ.

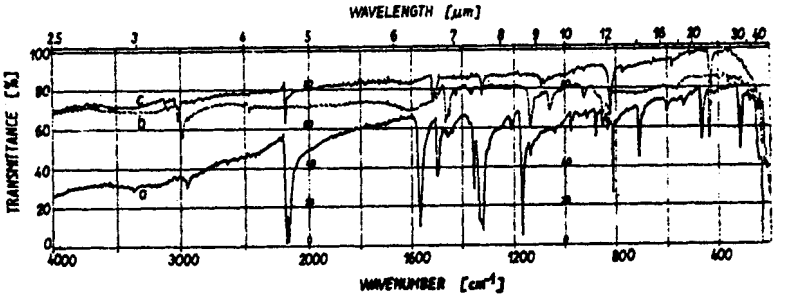


FIGURE 1. IR absorption spectrum of MeDABCO/TCNQ/$_2$ (a) and spectra of DABCO $2CH_3J$ (b) and TCNQ (c) of suitable concentrations.

Temperature-dependent studies of MeDABCO/TCNQ/$_2$ in IR failed to reveal anomalies. At liquid nitrogen temperature, the integral intensities of the bands increase by 10 to 100% compared to those measured at room temperature. Bands due to electron-phenon coupling behave similarly to the others.

The electrical measurements of MeDABCO/TCNQ/$_2$ were performed on cylindrical samples, compressed under about 7000 atm from finely ground salts. The compactions were placed in an appropriate cell and degased at 330 K for 16 hours in vacuum. The conductivities of the samples were determined using two-electrode technique, already described,[8] for temperatures ranging from 285 to 390K.

Fig. 2 shows the temperature-dependence of d.c. conductivity of MeDABCO/TCNQ/$_2$ for two different samples.

The experimental conductivity data can be expressed by the simple exponential temperature-dependence:

$$\sigma(T) = \sigma_o \exp(-E_a/kT).$$

By the least squares method, we obtained:

$$E_a = 0.44\,[eV] \quad \text{and} \quad \sigma_{25} = 3.08 \times 10^{-5}\,[\Omega^{-1}cm^{-1}].$$

The Seebeck coefficient, determined from thermoelectric measurements, was positive at room temperature (about 30 mV/deg).

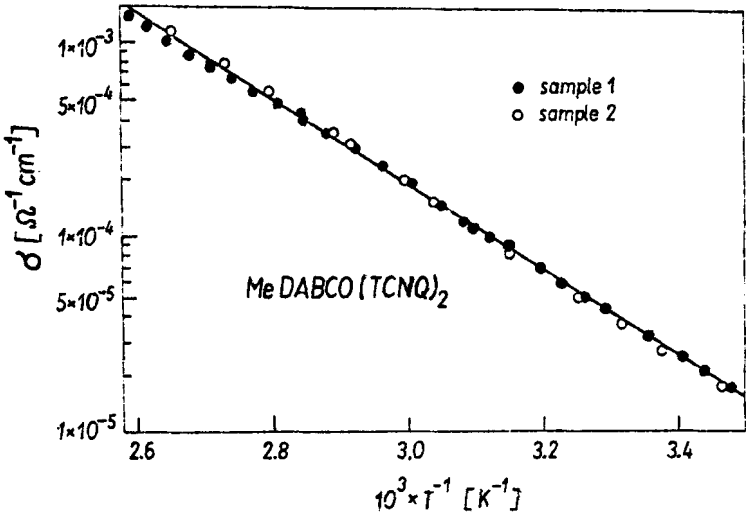


FIGURE 2. D.C. conductivity versus reciprocal temperature for two different samples of MeDABCO/ $TCNQ/_2$.

With regard to the criterion of J.J. André et al.,[1] the magnitudes of conductivity and thermal activation energy point to a low conducting linear system of our complex salts.

Our work hitherto performed in evidence that the

spatial structure of the donor affects spectral properties of the donor affects spectral properties of the complex essentially and has marked influence on the electric conductivity and its dependence on temperature.

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