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On the Nature of the 5,10-Dimethyl-5,10-dihydrophenazine–Tetracyanoquinodimethane

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Synopsis. The 5,10-dimethyl-5,10-dihydrophenazine-tetracyanoquinodimethane appears to be largely ionic at room temperature. The results of various physical measurements of this compound can be explained without the reversible nonionic-to-ionic transition proposed by Soos *et al.*

The 1:1 compound between 5,10-dimethyl-5,10-dihydrophenazine (DMPH) and tetracyanoquinodimethane (TCNQ) has been prepared by Melby by the treatment of $DMPH^+I^-$ in hot absolute ethanol with a boiling solution of Li^+TCNQ^- dissolved in the same solvent.[1] He has suggested that the solid compound is represented as a pi-complex rather than as an ion-radical salt. The structure and the packing arrangement of this compound have been studied by Goldberg and Shmueli.[2] The structure consists of stacks in which the DMPH and TCNQ molecules alternate along the c axis. On the basis of the intrastack contacts and the molecular geometry of TCNQ, these authors have postulated the presence of rather strong charge transfer interactions.

Recently, Soos *et al.* have reported measurements of the ESR spectrum.[3] At room temperature, DMPH–TCNQ powder exhibits a very weak ESR signal at $g=2.0026$. An additional exchange-narrowed signal at $g=2.0035$ appears on heating. The intensity of the latter increases rapidly with a rise in the temperature. They have considered the compound to be largely neutral and diamagnetic at 300 K and to undergo an unusual reversible transition to a paramagnetic state at 390 K. The same group has reported an increase in the activation energy for semiconduction around 360 K.[4] Earlier, one of the present authors isolated two differently-colored forms of 7-methylbenzo[*a*]phenazinium–TCNQ.[5] The violet form is largely ionic, while the green form is not. Although the transformation of the green form to the violet one was observed in the presence of a solvent, the crystals were found to be stable once they were isolated. As it seemed unlikely to us that the nonionic-to-ionic transition proposed by Soos *et al.* occurs without hysteresis, a further study of this compound was undertaken.

5,10-Dimethyl-5,10-dihydrophenazine was prepared by means of the method described by Gilman and Dietrich[6] and was subsequently purified by sublimation in a vacuum. By the treatment of the phenazine with one equivalent of TCNQ separately dissolved in hot acetonitrile, dark violet DMPH–TCNQ crystals were precipitated. Found: C, 75.54; H, 4.37; N, 20.07%. Calcd for $C_{14}H_{14}N_2$–$C_{12}H_4N_4$: C, 75.28; H, 4.38; N, 20.28%.

The temperature dependence of the ESR signals examined at the X band exactly reproduced the observation described by Soos *et al.* Furthermore, three pairs of resonance lines characteristic of triplet-spin excitons could be recorded with the polycrystalline sample. The zero-field splitting parameters, $|D/g\beta|$ and $|E/g\beta|$, are 149 and 21 G ($1\ \mathrm{G}=10^{-4}\mathrm{T}$) at 327 K. As the temperature is increased, the lines are broadened and the splittings become less, the values at 380 K being 135 and 18 G. Our observation reasonably agrees with the results reported by Nöthe *et al.*, namely, 144 and 20 G at 339 K[4]. The room temperature resistivity of polycrystalline compactions measured by a four-probe method is in accord with the value of 6×10^6 ohm cm reported by Melby. The activation energy for semiconduction is 0.51 eV below 350 K and 0.65 eV in the higher-temperature region. The former value is in good agreement with the value of 0.50 eV obtained by two-probe single crystal measurements.[4] Consequently, we suppose that our DMPH–TCNQ sample is identical with that prepared by Soos *et al.*

The vibrational spectrum of TCNQ is known to be considerably modified by the addition of an extra electron;[7] therefore, it is not difficult to distinguish between the nonionic and ionic complexes by examining the spectrum. In Fig. 1, the spectrum of DMPH–TCNQ is compared with those of TCNQ and K^+-$TCNQ^-$, all examined as Nujol mineral oil mulls at room temperature. As the bands appearing at 1580, 1520, 1320, 1167, 844, and 710 cm^{-1} approximately constitute the pattern of the $TCNQ^-$ ion, the compound appears to be largely ionic under the conditions ex-

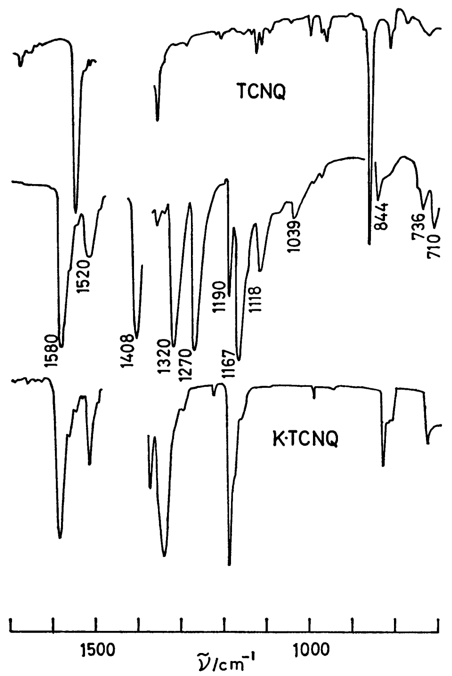

Fig. 1. Vibrational spectrum of the 5,10-dimethyl-5,10-dihydrophenazine–tetracyanoquinodimethane compared with those of TCNQ and K^+TCNQ^-.

amined. The measurements were performed at several temperatures up to 410 K; however, no change could be observed except for slight shifts to the lower-energy side.

As a distinct difference in the electronic spectrum has been seen between the nonionic and ionic forms of 7-methylbenzo[*a*]phenazinium–TCNQ, some changes may be expected in the specrtum of DMPH–TCNQ if the proposed transition takes place upon an increase in the temperature. The spectrum recorded as Nujol mineral oil mulls at room temperature shows absorption maxima at 6.8×10^3, about 16×10^3, and 27.5×10^3 cm^{-1}, with a shoulder around 23×10^3 cm^{-1}. These spectral features could be reproduced by diffuse-reflectance measurements of a sample diluted with sodium chloride. The maxima are located at 6.8×10^3, 17.2×10^3, and 27.5×10^3 cm^{-1}, with a shoulder around 24×10^{-3} cm^{-1}. By means of the latter technique, we examined the spectrum at several temperatures up to 473 K; nonetheless, no change could be detected in the spectral pattern.

The Seebeck coefficient, as measured with a polycrystalline compaction, is negative throughout the range from room temperature to 385 K, as is shown in Fig. 2. The open and shaded circles indicate points taken in the processes of increasing and decreasing the temperature respectively. A broad minimum of about -100 μV K^{-1} is located near 350 K. Such a change in the slope is commonly found when the contribution of impurities or imperfections cannot be ignored in the lower-temperature region.[8] If this interpretation is correct, the change in the activation energy of semiconduction may be attributed to the extrinsic conduction dominant below 350 K rather than to the nonionic-to-ionic transition around that temperature.

Differential scanning calorimetric measurements carried out up to 420 K showed that no enthalpy change takes place, at least not in a relatively narrow temperature range. Moreover, the X-ray diffraction pattern of the polycrystalline sample recorded at about 390 K was found to be the same as that recorded at room temperature.

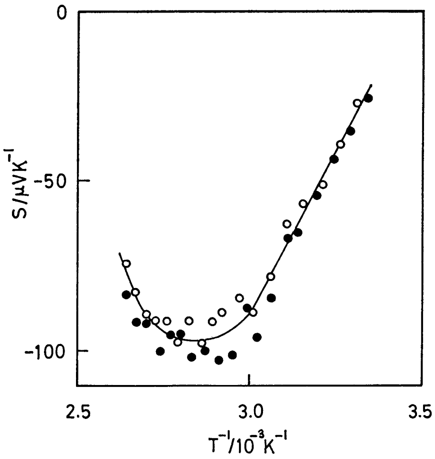

Fig. 2. Seebeck coefficient of the 5,10-dimethyl-5,10-dihydrophenazine–tetracyanoquinodimethane.

The newly obtained results lead to the conclusions that, basically, the DMPH–TCNQ is ionic at room temperature and that the nonionic-to-ionic transition does not occur in this solid complex. The former conclusion seems, though, to be inconsistent with the number of electrons per TCNQ molecule (0.30) estimated by Flandrois and Chasseau based on the bond lengths in the TCNQ molecule determined by Goldberg and Shmueli.[9] The ground state of the DMPH–TCNQ is supposed to be singlet because of an antiferromagnetic exchange interaction, as has been found for a number of ionic charge-transfer complexes. A change in the weak ESR signals appearing near $g=2.00$ with the temperature is not unknown for such complexes. Faucher and Robert have examined the ESR spectrum of powder and single crystals of the *p*-phenylenediamine–*p*-chloranil and have found two magnetic species in it.[10] One of them has an isotropic *g*-factor of 2.0035, and its intensity varies following the classic Curie law. The other species exhibits temperature-dependent *g*-factor splittings, and the spin density shows an exponential dependence with an activation energy of 0.22 eV. Because of this complication, the powder spectrum is markedly dependent on the temperature.

The observations described above were supplemented with some measurements of a related compound; that is, the 5,10-diethyl-5,10-dihydrophenazine–TCNQ is largely ionic, judging from the vibrational spectrum. Triplet-spin excitons can also be found in this compound. The zero-field splitting parameters are 147 and 19 G at 310 K and 141 and 18 G at 380 K. In this case, too, a weak signal in the $g=2.00$ region at room temperature is reversibly replaced by a rapidly growing signal with a little larger *g*-value when the temperature is increased. The zero-field splitting parameters obtained here compare well with those observed for the ionic form of 7-methylbenzo[*a*]-phenazinium–TCNQ and also with those reported for a number of simple TCNQ salts.

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