BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (10), 3071—3072 (1978)

Complex Isomerism in 7-Methylbenzo[*a*]phenazinium Tetracyano-*p*-quinodimethanide

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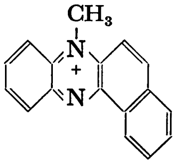
(Received May 1, 1978)

Synopsis. 7-Methylbenzo[*a*]phenazinium tetracyano-*p*-quinodimethanide is dark green when it is prepared in boiling ethanol and violet when it is prepared in acetonitrile. Examination of the electronic, vibrational, and ESR spectra revealed that the former form is essentially non-ionic, and the latter, ionic.

N-Methylphenazinium tetracyano-*p*-quinodimethanide, (NMP-TCNQ) is among the highest conducting TCNQ anion radical salts.[1] On the basis of the strong similarity of the electronic spectra of a wide variety of conducting TCNQ salts to each other and to $Cs_2(TCNQ)_3$ Torrance, Scott and Kaufman have suggested that NMP-TCNQ is not fully ionic.[2] The degree of ionicity has been estimated to be 0.94 by an NMR study and about 0.9 by measurements of the Seebeck coefficient.[3,4] These values are definitely larger than those reported for the well-known organic metal, TTF-TCNQ, 0.48—0.67.[5,6] Earlier, the present author demonstrated that the crystal charge-transfer complexes can be rather clearly classified into two groups, namely, non-ionic and ionic complexes.[7] NMP-TCNQ and TTF-TCNQ may be supposed to be in the region of non-ionic-to-ionic transitions of crystal charge-transfer complexes. Furthermore, it was shown that the probability of finding non-ionic complexes can be increased by choosing component molecules with larger differences in size and shape. Consequently, if the 7-methylbenzo[*a*]-phenazinium ion ($NMBP^+$) is employed in place of the NMP^+ ion, a smaller degree of ionicity in the resulting complex may be foreseen. The recent work by Soos *et al.* indicating that phenazine–TCNQ systems are close to the non-ionic-to-ionic separation[8] prompted the present author to study the above-mentioned combination.



Benzo[*a*]phenazine was prepared by means of a condensation reaction between 1,2-naphthoquinone and *o*-phenylenediamine dissolved in 50% acetic acid at 0 °C,[9] and was purified by sublimation in a vacuum. NMBP methyl sulfate was obtained by boiling a benzene solution of the base and excess dimethyl sulfate for several hours. By the treatment of the methyl sulfate in hot absolute alcohol with a boiling ethanolic solution of one equivalent of LiTCNQ, dark green NMBP-TCNQ crystals were precipitated. Found: C, 77.14; H, 3.71; N, 18.52%. Calcd for $C_{17}H_{13}N_2$–$C_{12}H_4N_4$: C, 77.49; H, 3.81; N, 18.70%. Metathesis in acetonitrile instead of ethanol gave dark violet crystals. Found: C, 77.44; H, 3.64; N, 18.69%. The former form could be transformed into the latter by recrystallization from acetonitrile.

The electronic spectra recorded as Nujol mineral oil mulls are shown in Fig. 1. The sharp peaks located at 10.6 and 12.2×10^3 cm^{-1} in the spectrum of the green form (Curve a) may be assigned to the monomeric $TCNQ^-$ anion radicals trapped in the crystals. Such peaks are not observed in the spectrum of the violet form. The shoulder appearing near 5×10^3 cm^{-1} suggests that the sample is contaminated with the green form. If this shoulder is ignored, the rest of the spectrum is that of a typical simple TCNQ salt, *e.g.*, pyridinium-TCNQ. Because of the close resemblance between this spectrum and that of the dimeric ion $(TCNQ)_2^{2-}$ in an aqueous solution,[10] the anion radicals in the violet form appear to be in predominantly pair-by-pair interaction. The two forms of NMBP-TCNQ exhibit spectra considerably different from each other. The lowest-energy absorption shown by the green form is at 6.0×10^3 cm^{-1}. Assuming that this absorption arises from the charge transfer from 7-methylbenzo[*a*]phenazin-7-yl radical to TCNQ molecule, the ionization potential of the former species may be estimated to be about 6.6 eV. This value is so low that the combination can form an ionic complex provided the molecules are closely packed in the crystal.

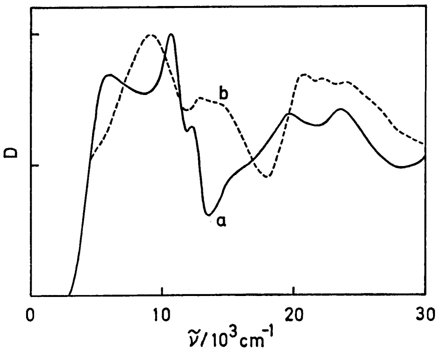


Fig. 1. Electronic spectra of 7-methylbenzo[*a*]phenazinium tetracyano-*p*-quinodimethanide, (a) the green form and (b) the violet form.

The vibrational spectra of the green and violet forms examined as Nujol mulls are compared in Fig. 2. No band assignable to an N–H stretching vibration could be detected in the region from 3000 to 3500 cm^{-1}. Therefore, the reduction of the diamagnetic $NMBP^+$ ion to the $HNMBP^+$ cation radical during the course of preparation may be excluded from possible causes of the dimorphism. Although the relative intensities of

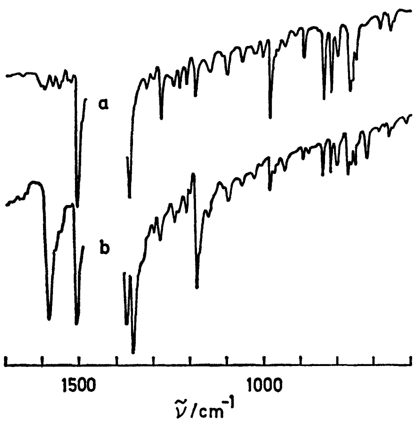


Fig. 2. Vibrational spectra of 7-methylbenzo[*a*]phenazinium tetracyano-*p*-quinodimethanide, (a) the green form and (b) the violet form.

bands are different, the locations in the region below 1300 cm^{-1} are rather similar to each other. In the spectrum of the violet form, strong bands appearing at about 1580, 1360, and 1180 cm^{-1} approximately constitute the pattern of the TCNQ$^-$ anion observed with the solid lithium salt. They are absent in the spectrum of the other form. However, no strong band is found in the latter spectrum near 1550 cm^{-1}, where solid TCNQ is known to give a relatively strong band.

The ESR spectra of the two forms were examined at the X-band. The green form gives a single resonance. The distance between the points of maximum slope is about 1.0 G. In addition to a strong narrow center line, three pairs of resonance lines characteristic of triplet-spin excitons were observed with the violet polycrystals. As the temperature is increased, the resonance lines broaden and the zero-field splitting parameters, $|D/g\beta|$ and $|E/g\beta|$, become smaller. The values obtained on the assumption that the isotropic g value is equal to the free electron value are 147 and 24 G at −30 °C and 140 and 20 G at 90 °C respectively. They are comparable to those reported for a number of the simple TCNQ salts, namely, 143—165 G for $|D/g\beta|$ and 17—25 G for $|E/g\beta|$.[11] The collapse of the three pairs into a single broad line was noted around 140 °C. The singlet-triplet separation was estimated to be 0.16 eV by relative-intensity measurements in the range from −30 to +10 °C.

The electrical resistivities measured with polycrystalline compactions were in the order of 10^5 ohm cm at room temperature for both the forms. The plots of the logarithm of the resistivity recorded between −125 and 110 °C against $1/T$ are not straight, indicating that the extrinsic conduction is dominant below room temperature. The activation energies for semiconduction were estimated to be about 0.3 eV for the high-temperature region. Thus, all the results presented above lead to the conclusion that the violet form of NMBP-TCNQ is essentially ionic, while the green form is not. The two forms may be called complex isomers, and this phenomenon, complex isomerism.

The author wishes to express his thanks to Mr. Nobuhiko Miyajima for the preparation of benzophenazine and to Mr. Shigeo Ikeura for the electrical resistivity measurements. The work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education (No. 234028).

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