Evidence of Back Charge Transfer in DMBP-TCNQ$_3$

Geoffrey J. Ashwell, Graham H. Cross, and Ian M. Sandy
Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, England

Witold Waclawek* and Maria Zabkowska
Institute of Physics, Pedagogical University of Czestochowa, Al. Zawadzkiego 13/15,
42-200 Czestochowa, Poland

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The single crystal conductivity of (N,N′-dimethyl-4,4′-bipyridinium)$^{2+}$(7,7,8,8-tetracyano-p-quinodimethanide)$_3^{2-}$, DMBP-TCNQ$_3$, exhibits an anomaly at 170 K which may be attributed to a phase transition and, also, a change in activation energy at 135 K which may be attributed to the onset of extrinsic behaviour. Above 135 K the conductivity varies as $\sigma = \sigma_0 \exp(-E_a/kT)$ where $\sigma_{300\,K} = 1$ S cm^{-1} and $E_a = 0.18$ eV. In the high temperature region the thermoelectric e.m.f. saturates to a temperature independent value of $S = -20$ µV K^{-1} whereas for the related monoquaternised salt, [N-phenyl-4-(4′-pyridyl)-pyridinium]$^+$(TCNQ)$_2^-$, ØBP-TCNQ$_2$, $S = -55$ µVK^{-1}. The thermoelectric data may be interpreted in terms of the Chaikin and Beni model and the results indicate 92% charge transfer in DMBP-TCNQ$_3$ and 100% charge transfer in ØBP-TCNQ$_2$.

Introduction

The N,N′-dimethyl-4,4′-bipyridinium dication and its alkyl and aryl substituted congeners find use as redox indicators [1], as herbicides [2] and, also, as the active components of photochromic and electrochromic cells [3–5]. In solution the viologens are readily reduced to their highly coloured radical cations with polarographic reduction potentials of – 0.11 to – 0.69 V versus SCE (the saturated calomel electrode) [6]. In the solid state charge transfer occurs between oppositely charged ions. Evidence is provided by the fact that DMBP dichloride is colourless whereas the dibromide and diiodide are yellow and red respectively [7, 8]. The colour progression is in accordance with the decrease in electron affinity [9] from chlorine (3.61 eV) to bromine (3.36 eV) to iodine (3.06 eV). The dichloride shows no new absorption bands whereas the dibromide and diiodide show charge transfer bands at 395 and 450 nm respectively [10]. It is *partly* because of this observed back charge transfer and *partly* because the electron affinity of TCNQ (2.84 eV [11]) is slightly lower than that of iodine that the TCNQ salts of the N,N′-dimethyl-4,4′-bipyridinium cation were chosen for investigation. The lower electron affinity favours incomplete charge transfer and the effect on the solid state conduction process is of interest. If back charge transfer were substantial we would expect the conductivity of the simple ionic 1:2 salt to be enhanced [12]. The conductivity at 300 K is in fact five orders of magnitude lower than that of the 1:3 complex salt, which suggests that there is only limited charge transfer interaction between the TCNQ anions and the DMBP dication. Thermoelectric studies carried out on the 1:3 salt show approximately 8% back charge transfer.

Experimental

Synthesis of TCNQ Salts

Materials. N,N′-dimethyl-4,4′-dipyridinium diiodide (DMBP-I$_2$) was prepared by the method of Dunn et al. [13] and purified by recrystallisation from aqueous ethanol. N-phenyl-4-(4′-pyridyl)-pyridinium chloride (ØBP-Cl) was kindly provided by Mr. J. G. Allen of ICI Runcorn and used without further purification. 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) was purified successively by gradient sublimation and recrystallisation from acetonitrile until the crystals were orange-yellow. The acetonitrile was distilled before use from anhydrous potassium carbonate.

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* Present address: Institute of Chemistry, Pedagogical University of Opole, ul. Oleska 48, 45-052 Opole, Poland.

Reprint requests to Dr. G. J. Ashwell, Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, England.

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DMBP-TCNQ$_3$. The 1:3 radical anion salt was obtained when a hot acetonitrile solution (250 cm^3) of neutral TCNQ (0.3 g) and an aqueous solution (10 cm^3) of DMBP-I$_2$ (0.25 g) were mixed and the resultant solution allowed to cool slowly to ambient temperature. After 48 hours a product of black parallelpiped crystals was collected. The crystals were washed with toluene, until the washings were colourless, to remove unreacted TCNQ. The electronic absorption spectrum of the product, dissolved in acetonitrile, gave the peak height ratio $A_{395}/A_{842} = 1.4$, characteristic of a TCNQ$^-$ to TCNQ^0 ratio of 2:1 and thus a stoichiometry of 1:3. (Found: C, 72.11; H, 3.31; N, 24.63%; $\varepsilon_{395} = 1.0 \times 10^4$ m^2 mol^{-1}; $\varepsilon_{342} = 7.5 \times 10^3$ m^2 mol^{-1}. $C_{48}H_{26}N_{14}$ requires C, 72.18; H, 3.26; N, 24.56%.)

ØBP-TCNQ$_2$. The 1:2 salt was obtained when a hot acetonitrile solution (200 cm^3) of TCNQ (0.2 g) and LiTCNQ (0.2 g) was added to an aqueous solution (10 cm^3) of ØBP-Cl (0.3 g) and the resultant solution allowed to cool slowly. Attempts to obtain single crystals were unsuccessful and a product of fine matted hairs was obtained. The absorption spectrum gave the peak height ratio, $A_{395}/A_{842} = 2.0$, characteristic of a TCNQ$^-$ to TCNQ^0 ratio of 1:1 and thus a stoichiometry of 1:2. (Found: C, 74.97; H, 3.30; N, 21.92%. $C_{40}H_{21}N_{10}$ requires C, 74.88; H, 3.28; N, 21.84%.)

Results and Discussion

Electrical Conductivity

The electrical properties of DMBP-TCNQ$_3$ are anomalous. Along the stacking direction it has a moderate conductivity of 1 S cm^{-1} at 300 K, a value more frequently associated with the quasi-one-dimensional salts TEA-TCNQ$_2$ [14] and DBzPE-TCNQ$_5$ [15]. In DMBP-TCNQ$_3$ the TCNQ molecules do not form continuous stacks but, instead, are arranged in stoichiometric groups of three with a favourable exocyclic bond to quinonoid ring overlap and a short interplanar spacing of 3.16 Å within each group. Between groups there is no direct plane-to-plane overlap but there are close carbon-carbon contacts of 3.333 Å. It is interesting to compare the properties of [1,4-bis(1-quinolinium methyl)benzene]$^{2+}$(TCNQ)$_3^{2-}$, which exhibits a similar packing arrangement [16]. Within the stoichiometric unit the inter-TCNQ spacing are slightly shorter at 3.07 Å (cf. 3.16 Å in DMBP-TCNQ$_3$) whereas between non-overlapping triads all contacts are greater than the sum of the van der Waals radii. The conductivity at 300 K of the quinolinium salt is a factor of 5000 smaller and this is attributed to a weaker interaction between the stoichiometric TCNQ groups. Full details of the crystal structure of DMBP-TCNQ$_3$ have been published separately [17].

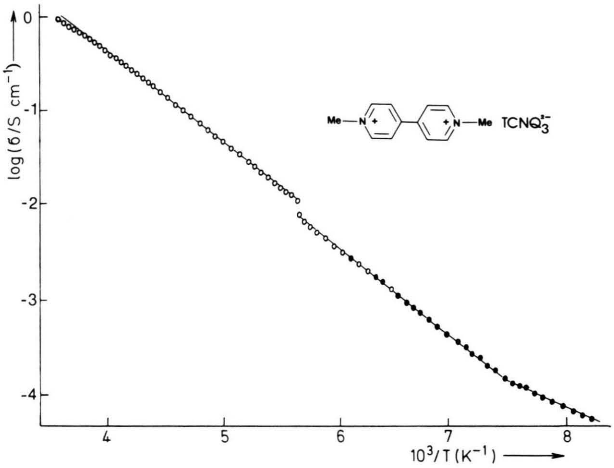

Fig. 1. Conductivity temperature dependence of single crystal (○) and compacted pellet (●) samples of DMBP-TCNQ$_3$. The crystals were mounted along the needle axis.

The conductivity temperature dependence of DMBP-TCNQ$_3$ is shown in Figure 1. Above 135 K the conductivity varies as $\sigma = \sigma_0 \exp(-E_a/kT)$, where $\sigma_{300\,K} = 1$ S cm^{-1} and $E_a = 0.18$ eV, whereas below 135 K the activation energy is 0.13 eV. The transition may be attributed to the onset of extrinsic behaviour as below this temperature the thermoelectric e.m.f. changes from n-type to p-type. An interesting feature of Fig. 1 is the small but abrupt decreases in conductivity at 170 K. The transition, reproducible for five crystals investigated, may be attributed to a phase change. Tentative evidence of the phase transition has been obtained from a DSC trace which shows an endotherm upon heating at 170 K, but anomalously not all samples investigated by differential scanning calorimetry showed this transition.

The microwave Hall mobility of DMBP-TCNQ$_3$, investigated at room temperature by Eley and Lockhart on one of our samples, was found to be below the detectable limit of 0.3 cm^2 V^{-1} s^{-1} whereas the mobility of the 1:4 salt, DMBP-TCNQ$_4$, is

2.3 cm^2 V^{-1} s^{-1} [18]. The properties of the 1:4 salt are adequately described by band theory, and the microwave Hall mobility is in reasonable agreement with the value obtained by combining the conductivity and thermoelectric data [19]. The low mobility of DMBP-TCNQ$_3$ does not correspond to a meaningful mean free path, and band theory is not applicable. The mean free path (λ) may be calculated from the expression

$$\lambda = \frac{3\mu(2\pi m_e^* k_B T)^{1/2}}{4e}, \qquad (1)$$

where μ is the mobility, m_e^* the effective mass, k_B the Boltzmann constant and e the electron charge. At $T = 300$ K the upper limit of the mean free path is given by $\lambda = 0.22\,(m_e^*/m_e)^{1/2}$Å for $\mu = 0.3$ cm^{2}V^{-1} · s^{-1}. Bright et al. have found for TTF-TCNQ that $m_e^* = 5m_e$ [20]. If this relationship is appropriate here the upper limit of the mean free path of DMBP-TCNQ$_3$ is 0.5 Å whereas for DMBP-TCNQ$_4$ $\lambda = 3.8$ Å. Clearly the value obtained for the 1:3 salt is smaller than the lattice spacing and band theory is not applicable. The results are in general agreement with the thermoelectric data which show a temperature independent e.m.f. of $-20\,\mu$V K^{-1} in the high temperature region characteristic of hopping and which may be described by the Chaikin and Beni model. The properties of the 1:3 and 1:4 salts are summarised in Table 1.

Thermoelectric Properties

The thermoelectric data of DMBP-TCNQ$_3$ are shown in Figure 2. They also reflect the two transitions and, in Table 2, the properties are summarised for the three temperature ranges. These are separated by the extrinsic transition at 135 K and the phase transition at 170 K. In the low-temperature region the thermoelectric e.m.f. changes from p-type to n-type and reaches a minimum with $dS/dT < 0$ below 135 K and $dS/dT > 0$ above. In the intermediate period the thermoelectric e.m.f. at first rises steeply and then saturates to a temperature independent value of $-20\,\mu$VK^{-1} in the high temperature region. The phase transition is less obvious than the extrinsic transition although DSC studies have provided evidence of the change. There is only a gradual change to the temperature independent thermoelectric e.m.f.

The thermoelectric properties of the conductive TCNQ salts, including those with a small activation energy, frequently give a good fit to the Chaikin and Beni model [21]: For a system of carriers with a strong on-site Coulomb repulsion the thermoelectric e.m.f., associated with the spin degrees of freedom, may be represented by the expression

$$S = -(k_B/e)\ln[2(1-\varrho)/\varrho], \qquad (2)$$

where ϱ is the mean charge on the TCNQ lattice sites. The equation predicts a temperature indepen-

Table 1. Comparison of the properties of the 1:3 and 1:4 TCNQ salts of DMBP.

Salt	Electrical properties			Magnetic properties		Refs.
	$\sigma_{300\,K}$/S cm^{-1}	E_a/eV	$\mu_{300\,K}$/cm^2 V^{-1} s^{-1}	$\chi_{300\,K}$/emu mol^{-1}	J/eV*	
DMBP-TCNQ$_3$	1	0.18	< 0.3	0.8×10^{-3}	0.028	this work
DMBP-TCNQ$_4$	0.1	0.21	2.3	1.1×10^{-3}	0.035	[19]

* From the empirical relation $\chi T = C_0 \exp(-J/kT)$.

Table 2. Summary of the properties of DMBP-TCNQ$_3$ in the regions separated by the extrinsic transition at 135 K (T_{ex}) and the phase change at 170 K (T_p).

	Low-temperature region	T_{ex}	Intermediate region	T_p	High-temperature region
DSC				170 K	
Conductivity	$E_a = 0.13$ eV	135 K	$E_a = 0.18$ eV	170 K	$E_a = 0.18$ eV
Thermopower	$dS/dT < 0$	135 K	$dS/dT > 0$	?	$dS/dT = 0$

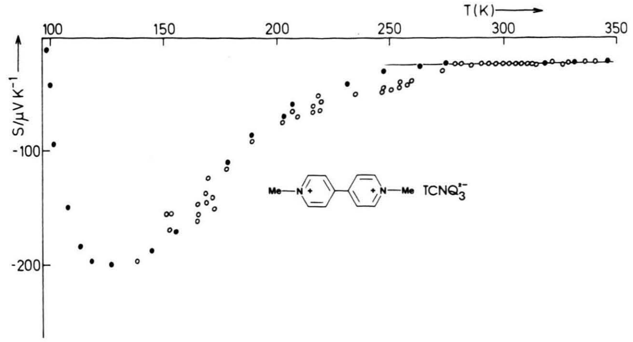

Fig. 2. Temperature dependence of the thermoelectric e.m.f. of single crystal (○) and compacted pellet (●) samples of DMBP-TCNQ$_3$. The horizontal line corresponds to the theoretical value obtained by substituting $\varrho = 0.61$ into (2). The crystals were mounted along the needle axis.

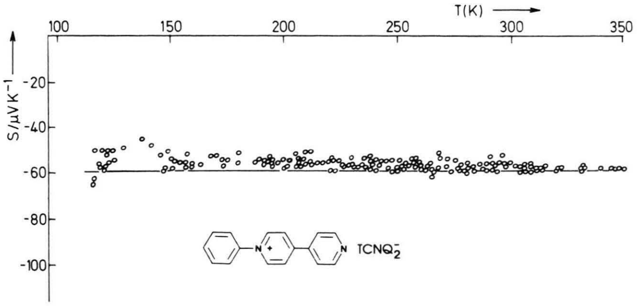

Fig. 3. Temperature dependence of the thermoelectric e.m.f. of a compacted pellet sample of ØBP-TCNQ$_2$. The horizontal line corresponds to the theoretical value obtained by substituting $\varrho = 0.5$ into (2).

dent thermopower and with $\varrho = \frac{2}{3}e$, commensurate with the formula, the theoretical themoelectric e.m.f. of the 1:3 salt is $S = 0$. This is inconsistent with the experimental data for DMBP-TCNQ$_3$, which show a temperatrure independent value of $-20\,\mu\mathrm{V\,K^{-1}}$ in the high temperature region. The data may still be interpreted by the Chaikin and Beni model in which case the discrepancy may be attributed to slight back charge transfer from TCNQ$^-$ to the dication. Macfarlane and Williams [10] have provided evidence of charge transfer interaction between oppositely charged ions in the DMBP halometallate salts, and Mahmoud and Wallwork [22] have shown that DMBP diiodide forms a ternary charge transfer salt with quinol in which the dication and quinol alternate in columns. In fact DMBP is a relatively strong acceptor and in aqueous solution its polarographic half-wave reduction potential is -0.69 V versus SCE [6]. This supports our claim and makes the interpretation of the thermoelectric data acceptable. Thus, if the Chaikin and Beni model is in deed applicable and if charge transfer is a valid explanation, the mean charge density on the TCNQ lattice sites may be calculated by substituting $S = -20\,\mu\mathrm{V\,K^{-1}}$ into (2). This gives $\varrho = 0.61\,e$, which corresponds to 92% charge transfer from the cation to the TCNQ moieties.

The thermoelectric properties of the monoquaternised salt, ØBP-TCNQ$_2$, may also be interpreted by the Chaikin and Beni model. The thermoelectric e.m.f., shown in Fig. 3, is independent of temperature throughout the temperature range investigated and has a mean value of $-55 \pm 5\,\mu\mathrm{V\,K^{-1}}$. In the absence of back charge transfer the theoretical value, obtained by substituting $\lambda = 0.5\,e$ into (2), is $-59.8\,\mu\mathrm{V\,K^{-1}}$. Thus, there is excellent agreement between the experimental and theoretical data and this is consistent with the fact that the monoquaternised cation is less readily reduced than DMBP. In this case charge transfer is complete whereas in DMBP-TCNQ$_3$ there is approximately 8% back charge transfer from the TCNQ moieties to the dication.

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[1] L. Michaelis and E. S. Hill, J. Amer. Chem. Soc. **55,** 1481 (1933).
[2] W. R. Boon, Outlook Agric. **4,** 163 (1964).
[3] H. Sato and T. Tamamura, J. Appl. Polym. Sci. **24,** 2075 (1979).
[4] R. C. Cieslinski and N. R. Armstrong, J. Electrochem. Soc. **127,** 2605 (1980).
[5] N. Kumar, C. P. Sharma, R. K. Sarna, S. Chandra, and V. G. Bhide, Indian J. Pure Appl. Phys. **22,** 471 (1984).
[6] G. J. Ashwell, J. G. Allen, E. P. Goodings, and I. W. Nowell, Phys. Stat. Sol. (a) **82,** 301 (1984).
[7] J. H. Russel and S. C. Wallwork, Acta Cryst. **B 28,** 1527 (1972).

[8] A. Nakahara and J. H. Wang, J. Phys. Chem. **67,** 496 (1963).
[9] Handbook of Chemistry and Physics, 60th ed., R. C. Weast (ed.), CRC Press (1980).
[10] A. J. Macfarlane and R. J. P. Williams, J. Chem. Soc. **A** 1517 (1969).
[11] E. C. M. Chen and W. E. Wentworth, J. Chem. Phys. **63,** 3183 (1975).
[12] J. B. Torrance, Acc. Chem Res. **12,** 79 (1979).
[13] M. J. Dunn, R. J. Martin, N. L. Roberts, P. Slade, H. Standen, and P. Walker, J. Chem. Soc. **C** 1468 (1966).
[14] H. Kobayashi, Y. Ohashi, F. Marumo, and Y. Saito, Acta Cryst. **B 26,** 459 (1970).
[15] G. J. Ashwell, D. D. Eley, A. Harper, A. C. Torrance, S. C. Wallwork, and M. R. Willis, Acta Cryst. **B 33,** 2258 (1977).
[16] G. J. Ashwell, D. D. Eley, S. C. Wallwork, M. R. Willis, G. F. Peachey, and D. B. Wilkos, Acta Cryst. **B 33,** 843 (1977).
[17] G. J. Ashwell and S. C. Wallwork, Acta Cryst. **B 35,** 1648 (1979).
[18] D. D. Eley and N. C. Lockhart, J. Phys. **E 16,** 47 (1983).
[19] G. J. Ashwell, D. D. Eley, M. R. Willis, and J. Woodward, JCS Faraday Trans. II **71,** 1785 (1975).
[20] A. A. Bright, A. F. Garito, and A. J. Heeger, Phys. Rev. **B 10,** 1328 (1974).
[21] P. M. Chaikin and G. Beni, Phys. Rev. **B 13,** 647 (1976).
[22] M. M. Mahmoud and S. C. Wallwork, Acta Cryst. **B 32,** 440 (1976).