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COMPLEXES OF 4,4-DIETHYLMORPHOLINIUM WITH 2,5-DIBROMO-7,7,8,8-TETRACYANO-p-QUINODIMETHANE : $(DEM)_x(TCNQBr_2)_y$

Martin R. Bryce[a] and Judith A.K. Howard[b]

[a] Department of Chemistry, University of Durham, South Road, Durham
DH1 3LE, U.K.

[b] School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.

Abstract : 4,4-Diethylmorpholinium forms four complexes with 2,5-dibromo-TCNQ of stoichiometries 1:1, 1:2, 2:3 and 3:4, two of which are semiconductors at high temperature; the single crystal X-ray structure of the 1:1 complex has been determined at 293 K.

Morpholinium-TCNQ charge transfer salts are currently receiving much attention largely due to their interesting structural, electrical, optical and magnetic properties in the solid state.[1] We have recently reported X-ray structural studies on complexes of 4,4-diethylmorpholinium (DEM) with 2,5-dibromo- and 2,5-dichloro-TCNQ, the latter providing the first example of a 1:1 salt in this series.[2] We now find that DEM and $TCNQBr_2$ yield four complexes; in addition to the 1:2 complex,[2] salts of stoichiometry 1:1, 2:3, and 3:4 have been isolated and characterised.[≠] The formation of such a range of complexes is remarkable and provides a unique chance for studying the effects of structure on properties within the same donor-acceptor pair.

The maximum yield of 1:1 salt (85%) was obtained on cooling a hot acetonitrile solution of $TCNQBr_2$ and a three fold molar excess of DEM iodide. The 2:3 and 3:4 complexes were similarly obtained (30 and 25%) from DEM^+I^- and $TCNQBr_2$ in molar ratios 2:3 and 3:4 respectively. The 1:2 salt was obtained as described previously[2] or in higher overall yield (35%) by recrystallisation of the 1:1 salt from acetonitrile containing an equimolar amount of added $TCNQBr_2$. The success of this method, new to morpholinium-TCNQ complexes, suggests the possibility of doping the acceptor stack.[3] The combination of equimolar amounts of $Li^+TCNQBr_2^-$, neutral $TCNQBr_2$ and DEM^+I^- also gave the 1:2 salt but in variable yield.

All four complexes are insulators at 293 K [single crystal conductivity, $\sigma > 10^{-6}$ $(\Omega\ cm)^{-1}$] and the 1:1 complex remains so over the range 135-450 K, whereas for the 1:2 and 2:3 complexes the conductivity rises steadily to that of a semiconductor at 450 K [σ 2 x 10^{-3} and 2 x 10^{-4} $(\Omega\ cm)^{-1}$ respectively]. Cracking of the crystals precludes high temperature measurements on the 3:4 complex. The characterisation of more than one complex of the same donor and acceptor is unusual, but cases are well documented of enhanced conductivity of "complex" salts relative to their 1:1 counterparts.[4] In contrast to many morpholinium-TCNQ complexes no definite phase transitions could be detected by differential scanning calorimetry.

We have determined the X-ray crystal structure of the 1:1 salt (1) at 293 K. In particular this provides the first chance for detailed structural comparison of a 1:1 alkylmorpholinium salt with its 1:2 analogue.

The structure of (1)[†] consists of dimerised stacks of $TCNQBr_2$ molecules whose mean planes lie almost perpendicular to <u>a</u> (i.e. the stacks extend along the direction of needle growth) (Figure 1). The intra- and inter-dimer separations are 3.20 and 3.59 Å, in contrast to those of 3.28 and 3.42 Å in DEM-$(TCNQBr_2)_2$, and 3.28 and 3.38 Å in DEM-$TCNQCl_2$.[2] The overlap pattern within the dimer of (1) (Figure 2) is similar to that found in the analogous $TCNQCl_2$ complex (slipped ring-ring overlap). However, the bromine atoms in (1) are staggered with respect to one another within the dimer and eclipsed across the larger separations; this differs from both DEM-$(TCNQBr_2)_2$ and DEM-$TCNQCl_2$.[2] Unfortunately there is similar disorder of the bromine atoms in (1) to that found for the chlorines in the $TCNQCl_2$ complex,[2] namely the two independent <u>ortho</u> sites (2,5 or 3,6) are occupied in the ratio 91:9 in both $TCNQBr_2$ molecules of the asymmetric unit of (1) (omitted from Figures for clarity). The DEM molecules in structure (1) adopt the normal chair conformation, and within the estimated errors there are no unusual molecular parameters in the $TCNQBr_2$ molecules.

Evidence for dimerised acceptor stacks in the 2:3 and 3:4 complexes comes from solid state electronic spectra which bear close resemblance to those of the $TCNQBr_2^-$ dimer in solution.[5] There is 0.24 V difference in electron affinity between TCNQ and $TCNQBr_2$[6] and it seems that in all these $TCNQBr_2$ complexes charge transfer from donor to acceptor is complete, and Coulombic repulsions on the acceptor stack limit the conductivity and prevent the metallic behaviour observed at high temperatures in $MEM(TCNQ)_2$.[7]

[≠] Satisfactory elemental analyses (0.3 for C, H, N and 0.4 for Br), i.r. u.v., and e.s.r. data were obtained for all the new complexes.

[†] Crystal data : $C_8H_{14}NO : C_{12}H_2N_4Br_2$, M = 502.2, monoclinic, space group $P2_1/n$, <u>a</u> 6.918(9), <u>b</u> 27.373(10), <u>c</u> 22.210(7) Å, β = 94.97(4)°, <u>U</u> = 4190(3) $Å^3$. F(000) 1943.5, μ(Mo-Kα) 38.5 cm^{-1}, <u>Z</u> = 8, ρ_{calc} = 1.56 gcm^{-3}, R(R′) 0.060(0.062) for 1462 independent (absorption corrected) intensities recorded on a Nicolet P3m four-circle automated diffractometer (ω: 2θ scans, $2\theta \leq 40°$, Mo(Kα), λ = 0.71069 Å).

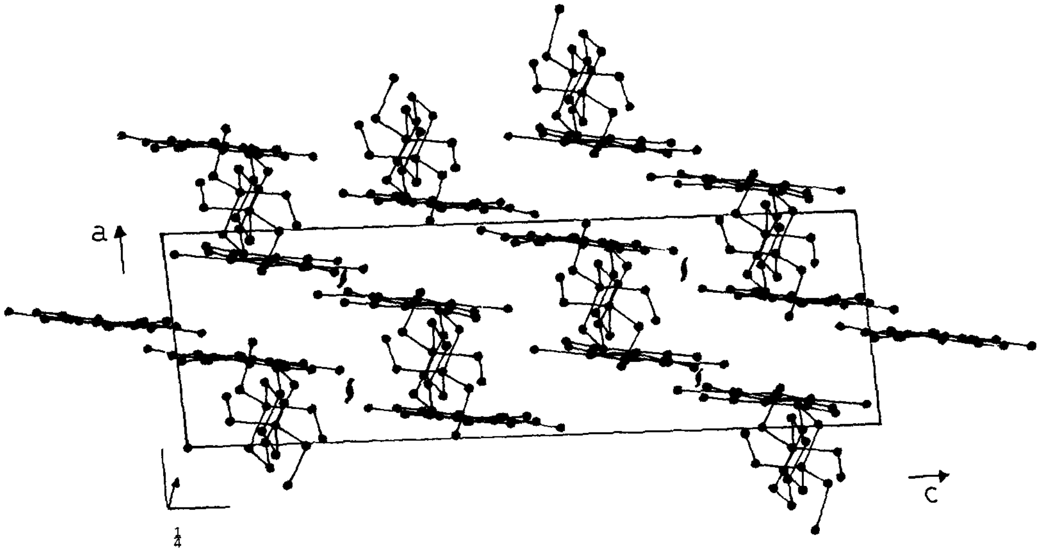

Figure 1. Contents of unit cell viewed down b towards the origin.

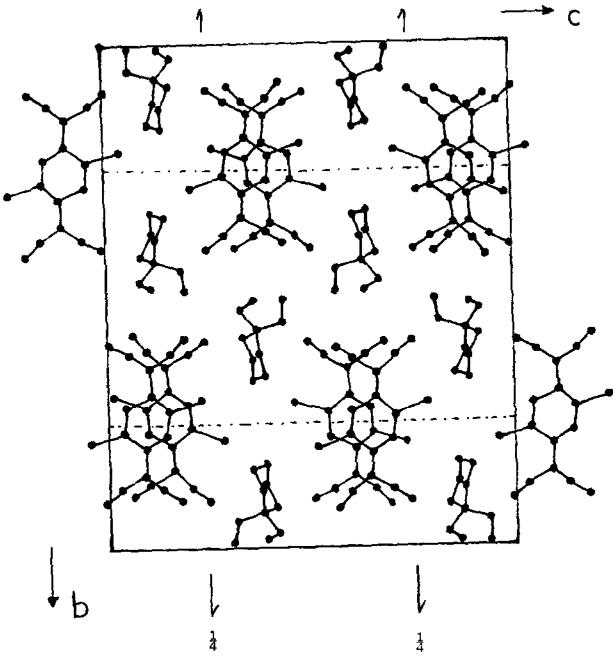

Figure 2. Contents of unit cell viewed in projection down a towards the origin.

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