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PREPARATION, PROPERTIES AND X-RAY CRYSTAL STRUCTURES OF COMPLEXES OF 4,4-DIETHYLMORPHOLINIUM WITH 2,5-DIBROMO- AND 2,5-DICHLORO-7,7,8,8-TETRACYANO-p-QUINODIMETHANE : DEM$(TCNQBr_2)_2$ AND DEM-$TCNQCl_2$

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Abstract: 4,4-Diethylmorpholinium forms a 1:2 complex with 2,5-dibromo-TCNQ and a 1:1 complex with 2,5-dichloro-TCNQ; both are insulators at room temperature, and their single crystal X-ray structures have been determined at 293 K.

Since the discovery of high electrical conductivity in the complex of the electron donor tetrathiafulvalene with the acceptor tetracyano-p-quinodimethane (TTF-TCNQ) there has been unabated interest in the synthesis, properties and structures of related organic charge-transfer complexes.[1] Of the new quasi-one-dimensional materials much attention is currently focussed on alkyl morpholinium-TCNQ salts.[2] In particular several phase transitions are accompanied by striking changes in crystal structure, optical, magnetic and electrical properties, our understanding of which have been considerably assisted by recent structural studies on a range of complexes in which the donor has been varied. Thus, 4-ethyl-,[3] 4,4-dimethyl,[4] 4,4-ethylmethyl-(MEM)[5] and 4,4-diethyl-morpholinium (DEM)[6] cations all form 1:2 complexes with TCNQ. Most attention has been paid to the complexes MEM$(TCNQ)_2$ and DEM$(TCNQ)_2$ whose various phases (conducting, semi-conducting and insulating) span almost all the typical properties of TCNQ salts.

The key role of electron distribution on the acceptor stack is now well established[2,7] and it has become clear that valuable information could be gained by varying the acceptor. In spite of subtle variations on the TCNQ skeleton afforded by 2,5-dibromo- and 2,5-dichloro-TCNQ their relative inaccessibility has inhibited many studies of their complexes. The TTF complexes are known,[8] but the only X-ray structural study is on the 1:1 complex of $TCNQCl_2$ with dibenzo-TTF.[9] We now report on the complexes of DEM with $TCNQBr_2$ and $TCNQCl_2$.

Dark violet crystals of DEM$(TCNQBr_2)_2$ (1) and DEM-$TCNQCl_2$ (2) were grown from equimolar mixtures of DEM iodide with $TCNQBr_2$ and $TCNQCl_2$, respectively, in hot acetonitrile.[≠] This provides the first example of a 1:1 alkyl morpholinium-TCNQ salt.[10]

The structure of (1)[†] consists of stacked $TCNQBr_2$ molecules whose mean planes lie almost parallel to b (Figure 1) and the cavities so formed between these columns are occupied by the DEM ions. The interplanar spacings along the columns alternate, 3.28 and 3.42 Å; this is similar to the observed structure of DEM$(TCNQ)_2$.[6] Ring-external bond overlap typical of TCNQ complexes[11] occurs between the planes 3.28 Å apart. Peculiar to (1) is the interdimer (3.42 Å) twisted (15°) ring-ring overlap (Figure 2); molecular models show the observed intrastack "mirror image flip" and twisting of the TCNQBr$_2$ molecules efficiently minimises steric repulsions between the bulky bromine atoms.

Structure (2) shows a similar stacking of TCNQCl$_2$ molecules lying almost perpendicular to a, again with alternating interplanar spacings of 3.28 and 3.38 Å but with a more involved arrangement of DEM ions (Figure 3). In any column of TCNQCl$_2$ molecules there is no ring-ring overlap but a ring slippage (Figure 4) relating the molecules in pairs similar to that observed previously,[9] and thus clearly differing from the TCNQBr$_2$ molecules in structure (1). There is unfortunately a positional disorder observed in the TCNQCl$_2$ molecules such that the two possible *ortho* sites (2,5 or 3,6) are occupied in the ratio 60:40 and 93:7 in the two independent molecules. In both complexes all DEM ions adopt the normal chair conformation, and no unusual molecular parameters are observed with TCNQX$_2$ molecules.

Both (1) and (2) are insulators at 293 K (single crystal resistivities > 10^6 Ω cm); this is consistent with the proposal[5c] that a regular, and not a dimerised, acceptor stack may be necessary for high conductivity. Experiments are in progress to establish the nature of phase transitions in these new complexes.

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‡ Satisfactory analytical data were obtained for both complexes.
Complex (1): i.r. (nujol) 2182, 1560, 1275, 1128, 990, 900, 867, 790 cm^{-1}; e.s.r. (powder) strong singlet, g 2.0021.
Complex (2): i.r. (nujol) 2182, 1563, 1270, 1130, 1083, 1005, 900, 826 cm^{-1}; e.s.r. (powder) strong singlet, g 2.0020.

† Crystal data: For both complexes diffracted intensities were recorded at room temperature on a Nicolet P2$_1$/m four-circle diffractometer (ω scans), Mo-Kα (λ = 0.71069 Å).
Complex (1): $C_8H_{14}NO$: $(C_{12}H_2N_4Br_2)_2$, M 863.3, orthorhombic, space group Pca2$_1$, a = 14.116(3), b = 8.137(6), c = 28.757(17) Å, U = 3303 Å^3, Z = 4, F(000) 1683.6, μ = 48.7 cm^{-1}, R 0.047 (R' 0.052) for 1880 reflections 2θ ≤ 50°.
Complex (2): $C_8H_{14}NO$: $C_{12}H_2N_4Cl_2$, M = 417.1, monoclinic, space group P2$_1$/n, a = 13.608(12), b = 14.312(5), c = 21.649(11) Å, β = 106.03(5)°, U = 4052(4) Å^3, Z = 8, F(000) 1657.7, μ = 3.4 cm^{-1}, R 0.067 (R′ 0.085) for 1400 reflections 2θ ≤ 40°.

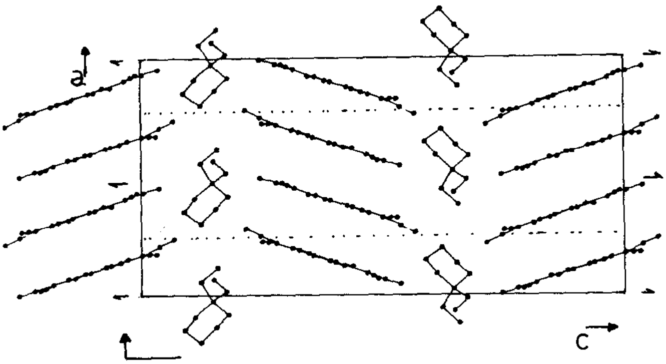

Figure 1

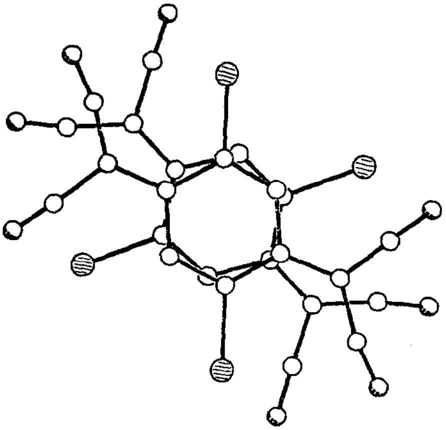

Figure 2

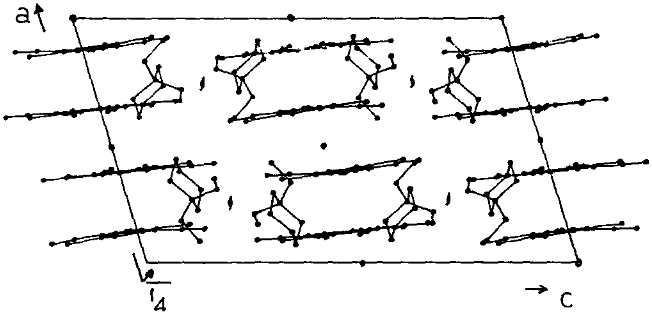

Figure 3

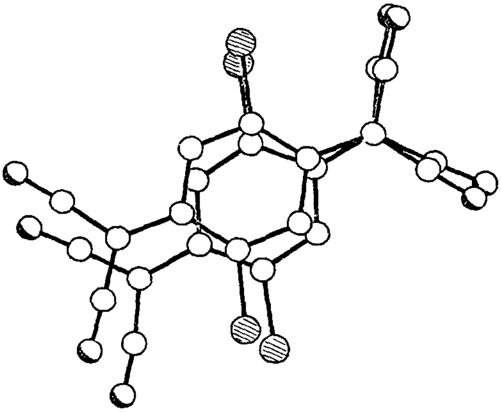

Figure 4

Figure 1. Crystal structure of (1).

Figure 2. $TCNQBr_2$ overlap in (1) (3.42 Å spacing).

Figure 3. Crystal structure of (2).

Figure 4. $TCNQCl_2$ overlap in (2) (3.28 Å spacing).

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