Segregated Stack Crystal Structure of an Ion-radical Salt based on 7,7,8,8-Tetracyanoquinodimethane

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Variation of the organic cation skeleton in an anion-radical salt of the simple salt series based on 7,7,8,8-tetracyanoquinodimethane results in improved conducting properties; the *X*-ray structure of a complex ion-radical salt containing acetonitrile is described.

Among the different types of non-bonded interactions, hydrogen bonding can play an important role in the formation of segregated stack crystal structures[1] which are necessary for good electrical conductivity in organic compounds. Intermolecular forces like this are of special importance in conducting 1:1 ion-radical salts of nitrogen heterocyclic monocations[2] with 7,7,8,8-tetracyanoquinodimethane (TCNQ) because a mixed stack arrangement with alternating cations and anions should optimize electrostatic interactions.

Thus, we introduced a flexible bonded hydroxy group to different quinoline derivatives (**1**)—(**7**) (Table 1) and prepared the corresponding radical anion salts based on TCNQ.[3]

In contrast to the 2-methylquinoline educt and several examples known in the literature,[3] the complex synthesis by means of durohydroquinone and TCNQ only affords the simple salts (**1**) and (**2**), even if an excess of TCNQ is employed. Interestingly, the conductivity of the simple salt (**1**)

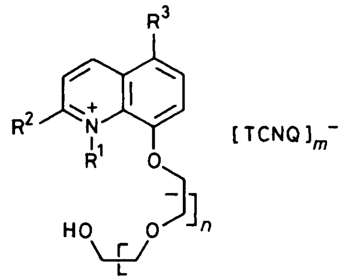

Table 1. Room temperature conductivity data for the radical-anion salts (**1**)—(**7**).

Compound[a]	R^1	R^2	R^3	n	m	$\sigma/(\Omega^{-1}\,cm^{-1})$[b]
(**1**)	H	H	H	0	1	1.7×10^{-2}
(**2**)	H	H	Cl	0	1	3.7×10^{-6}
(**3**)	H	Me	H	0	2	1.8×10^{-3}
(**4**)	Me	H	H	0	1	4.6×10^{-7}
(**5**)	Me	H	H	0	2	1.7×10^{-4}
(**6**)	Me	H	H	1	2	2.9×10^{-1} [c]
(**7**)	Me	H	Cl	0	2	1.2×10^{-4}
(**7**)·MeCN	Me	H	Cl	0	2	7.4×10^{-2}

[a] Satisfactory elemental analyses (C,H,N) were obtained. [b] Two-probe measurements on polycrystalline compactions unless otherwise noted. [c] Four-probe measurement.

is as high as the usual conductivity of complex salts, thus indicating a segregated stack crystal structure. Normally, 1 : 1 TCNQ salts of planar closed-shell nitrogen heterocyclic monocations are insulators. There are only a few exceptions.[2—4] Unfortunately, (**1**) could be obtained only as microcrystalline needles so that no single-crystal measurement or structure analysis could be performed. We determined the crystal structure (at −85 °C) of (**7**)·MeCN instead, to examine the influence of the 2-hydroxyethoxy group. In addition, we were interested in the structure of this compound because it appears to clathrate acetonitrile, the solvent of crystallization.[5] Interestingly, the conductivity of (**7**)·MeCN decreases to $1.2 \times 10^{-4}\ \Omega^{-1}\,cm^{-1}$ upon removing acetonitrile at 70 °C in high vacuum without changing its outer appearance.

The complex salt (**7**)·MeCN forms hard, black, irregular platelets with a metallic sheen. *Crystal data:* $(C_{12}H_{13}ClNO_2)^+(C_{12}H_4N_4)_2^-\cdot CH_3CN$, $M = 688.13$, triclinic, space group $P\bar{1}$, $a = 804.1(5)$, $b = 1376.5(3)$, $c = 1546.7(4)$ pm, $\alpha = 95.74(2)$, $\beta = 92.63(3)$, $\gamma = 103.33(3)°$, $U = 1.635$ nm^3, $Z = 2$, $D_c = 1.39$ g/cm^3, final $R = 0.058$ for 3354 unique reflexions (Figure 1).

The structure was solved by direct methods (MULTAN 80[8]) (500 E's, $6.38 > E > 1.40$, 7 628 triplets). The refinement was carried out by the block-diagonal least-squares method (SHELX 76[9]) with anisotropic temperature factors for the C, O, N, and Cl atoms. The H atoms were constrained to a C–H

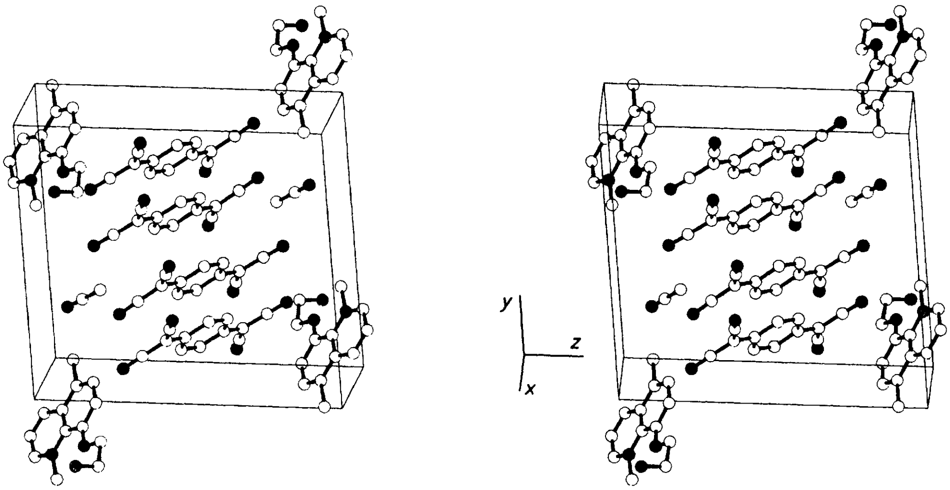

Figure 1. Stereoscopic view of the unit cell of (**7**)·MeCN. Hydrogen atoms are omitted for clarity; nitrogen and oxygen shaded.

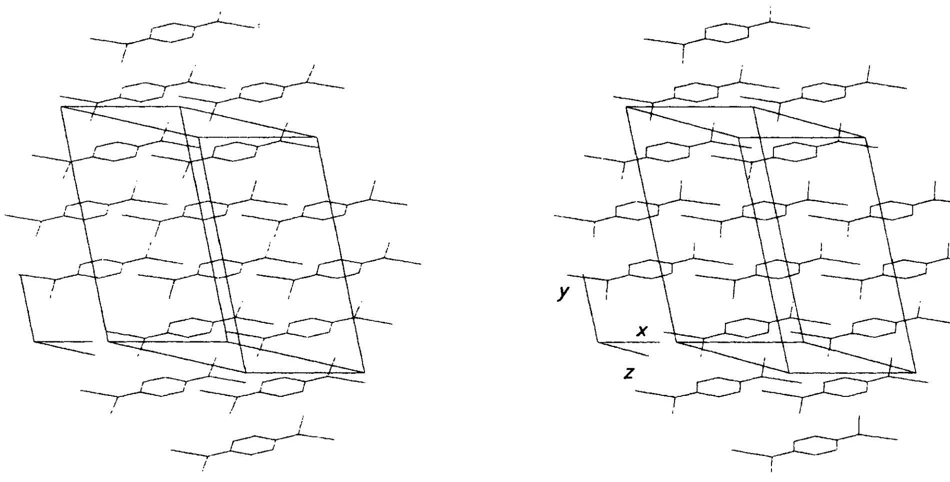

Figure 2. Illustration of infinite segregated stacks of TCNQ layers.

distance of 108 pm; only four common isotropic temperature factors were refined.†

As can be deduced from the conducting properties, the TCNQ moiety of (**7**)·MeCN crystallizes in segregated stacks. The stacks are subdivided into tetrads and arranged in a layer structure in which the planes of all the TCNQ molecules are parallel (Figure 2). Layers of TCNQ stacks alternate with layers of the cation. The cation molecules are sandwiched between layers of TCNQ stacks and do not form columnar structures as found in quinolinium(TCNQ)$_2$.[6]

The interplanar distances of TCNQ within the tetrads are identical (318 pm), and neighbouring molecules are superimposed characteristically with a shift of 1/4 molecular length relative to one another, such that the quinoid six-membered rings are opposite the quinoid terminal double bond (Figure 3a).

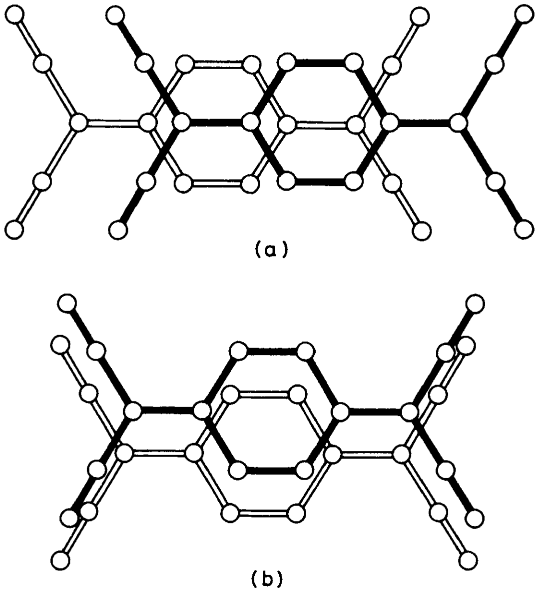

Figure 3. Superpositioning of neighbouring TCNQ molecules: (a) optimal overlap within the tetrads; (b) lateral shift between the tetrads.

The distance between neighbouring TCNQ molecules from different tetrads is 341 pm and the molecules are superimposed in a way which differs from optimal overlap (Figure 3b), thus limiting conductivity along the stacks.[1b] There are two different kinds of TCNQ molecule. For both, the distribution of bond lengths is intermediate between values reported for TCNQ and TCNQ$^-$.[7] The more negatively charged TCNQ molecules are positioned at the top and the bottom of the tetrads. At the border between cation and anion layers, the solvent molecules are included just on the plane between TCNQ tetrads.

Though the position of the hydrogen atom in the hydroxy groups could not be exactly determined, it is assumed from the small distance between the oxygen atom of the terminal hydroxy group and the acetonitrile nitrogen atom (298 pm) that the solvent molecules are fixed by hydrogen bonds.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.