1106 *Chem. Mater.* **1994,** *6,* 1106-1108

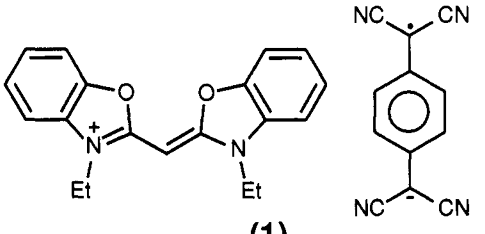
1:1 Imidazolium 7,7′,8,8′-Tetracyano-*p*-quinodimethanide ($[\text{TCNQ}]^{\bullet-}$) Salts: Substituent Control of Solid-State Architecture

Martin C. Grossel,[*,†] Peter B. Hitchcock,[‡]
Kenneth R. Seddon,[§] Thomas Welton,[⊥] and
Simon C. Weston[†]

Department of Chemistry, University of Southampton
Highfield, Southampton, SO9 5NH, U.K.
School of Chemistry and Molecular Sciences
University of Sussex, Falmer
Brighton, BN1 9QJ, U.K.

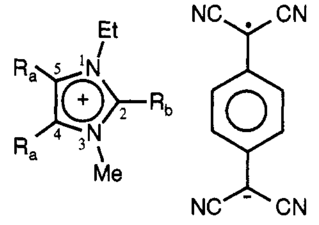
Received February 8, 1994
Revised Manuscript Received May 2, 1994

The solid-state properties of 7,7′,8,8′-tetracyano-*p*-quinodimethanide ($[\text{TCNQ}]^{\bullet-}$) salts are particularly sensitive to the nature of the cation.[1] Despite suggestions to the contrary,[2] direct interaction with a counterion is common. In 1:1 stoichiometry alkali metal $\text{TCNQ}^{\bullet-}$ salts, metal ions coordinate directly to the nitrile groups of the anion but where direct interaction is not possible, e.g., with organic cations, aromatic face-to-face stacking is normally observed unless the cation prefers to stack with itself (as in TTF/TCNQ).[1] When direct interaction is inhibited, by for example crown ether encapsulation of the metal cation, structural reorganization occurs in which the TCNQ stack is replaced by isolated $\{[\text{TCNQ}]^{\bullet-}\}_2$ dimers but the overall structure is such that coordination to the cation is maintained.[3,4] 3,3′-Diethyloxacyaninium tetracyano-*p*-quinodimethanide, **1**, forms columns in which pairs of cations and anions alternate and are stacked face-to-face ($D^+D^+A^-A^-D^+D^+$, where D is the electron donor and A is the electron acceptor).[5] A number of structures have also been observed in which the $[\text{TCNQ}]^{\bullet-}$ anion enters into hydrogen-bonding interactions with N–H hydrogen-bond donors.[6]



(1)

We have now studied the solid-state behavior of three (1:1) imidazolium TCNQ salts **2** in which the substitution pattern about the cation is varied. All the ring protons of substituted imidazolium cations have been shown to act as excellent C–H hydrogen-bond donors.[7] Such cations may also enter into aromatic-stacking interactions.[8] In this communication, we demonstrate that both types of interaction can occur in these salts **2**, depending on the substitution pattern, and that they can be used to control the architecture of the TCNQ salt.



(2)

a $R_a = R_b = H$ [emim][TCNQ]
b $R_a = H$, $R_b = Me$ [edmim][TCNQ]
c $R_a = R_b = Me$ [etmim][TCNQ]

The three alkylated imidazolium tetracyanoquinodimethanides **2a–c** were prepared by the metathesis reaction of Li[TCNQ] with the appropriate imidazolium

---

[†] University of Southampton.

[‡] University of Sussex.

[§] Current address: School of Chemistry, David Keir Building, The Queen's University of Belfast, Belfast, BT9 5AG, Northern Ireland.

[⊥] Current address: Department of Chemistry, Imperial College, London, SW7 2AY, U.K.

(1) Endres, H. *Extended Linear Chain Compounds: Salts of 7,7,8,8-Tetracyano-p-quinodimethane with Simple and Complex Metal Cations*; Miller, J. S., Ed.; Plenum Press: New York, 1980; Vol. 3, Chapter 5.

(2) Ballester, L.; Barral, M. C.; Gutierrez, A.; Jimenez-Aparico, R.; Martinez-Muyo, J. M.; Perpinan, M. F.; Monge, M. A.; Ruiz-Valero, C. *J. Chem. Soc., Chem. Commun.* **1991**, 1396–1397.

(3) Grossel, M. C.; Weston, S. C. *J. Phys. Org. Chem.* **1992**, *5*, 533–539.

(4) Grossel, M. C.; Evans, F. A.; Hriljac, J. A.; Morton, J. R.; LePage, Y.; Preston, K. F.; Sutcliffe, L. H.; Williams, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 439–442.

(5) Grossel, M. C.; Evans, F. A.; Hriljac, J. A.; Prout, K.; Weston, S. C. *J. Chem. Soc., Chem. Commun.* **1990**, 1494–1495.

(6) For example: Kobayashi, H. *Acta Crystallogr., Sect. B* **1978**, *34*, 2818–2825. Strzelecka, H.; Veber, M.; Zinsou, A. T.; Bassoul, P.; Petit, P.; Bieber, A.; Andre, J. J. *J. Mater. Chem.* **1993**, *3*, 59–65. Truong, K. D.; Bandrauk, A. D.; Ishii, K.; Carlone, C.; Jandl, S. *Mol. Cryst. Liq. Cryst.* **1985**, *120*, 105–110.

(7) Hitchcock, P. B.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans.*, in press.

(8) Avent, A. G.; Chaloner, P. A.; Day, M. P.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans.*, in press.

(9) Crystals of the moisture-sensitive salts were prepared by crystallization from solutions in dry ethanol; acceptable combustion analyses were obtained for all three samples. The crystals were isolated, dried, and mounted in Lindemann capillary tubes for structural analysis. In each case data were collected using monochromated Mo Kα radiation, $\lambda = 71.069$ Å, $\mu = 0.7$ cm^{-1}, on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with a scan width of $(0.8 + 0.35 \tan \theta)°$ and a maximum scan time of 1 min. There was no crystal decay in any case, and no corrections were made for absorption. The structures were solved by direct methods and non-hydrogen atoms refined, with anisotropic thermal parameters by full-matrix least squares. In all three cases hydrogen atoms were located on a difference map and held at idealized positions, with $U_{\text{iso}} = 1.3U_{\text{eq}}$ for the parent atom. [Emim][TCNQ] **2a**: $C_{18}H_{15}N_6$, M = 315.4, monoclinic space group $P2_1/c$, $a = 8.045(2)$, $b = 14.704(2)$, $c = 14.289(2)$ Å, $\beta = 91.77(2)°$, $U = 168.96$ Å^3, $Z = 4$, $D_{\text{calc}} = 1.24$ g cm^{-3}, $F(000) = 660$. Data were collected using a crystal of 0.3 × 0.1 × 0.05 mm. A total of 3093 unique reflections were measured for $2 < \theta < 25°$ and $+h+kl$, and 844 reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$, were used in the refinement. With a weighting scheme of $\omega = 1/\sigma^2(F)$, the refinement converged to give $R = 0.039$, $R' = 0.042$, 217 variables, $S = 1.4$, $(\Delta/\sigma)_{\text{max}} = 0.03$, $(\Delta\rho)_{\text{max,min}} = +0.12, -0.21$ e Å^{-3} on a final difference map. [Edmim][TCNQ] **2b**: $C_{19}H_{17}N_6$, M = 329.4, triclinic space group $P(-1)$ (No. 2), $a = 8.504(3)$, $b = 10.019(2)$, $c = 11.016(2)$ Å, $\alpha = 85.91(1)$, $\beta = 91.77(2)$, $\gamma = 84.93(2)°$, $U = 888.3$ Å^3, $Z = 2$, $D_{\text{calc}} = 1.23$ g cm^{-3}, $F(000) = 346$. Data were collected using a crystal of 0.5 × 0.2 × 0.15 mm. A total of 3108 unique reflections were measured for $2 < \theta < 25°$ and $+hkl$, and 1372 reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F\%) = \{\sigma^2(I) + (0.04\ I)^2\}^{1/2}/Lp$, were used in the refinement. With a weighting scheme of $\theta = 1/\sigma^2(F)$, the refinement converged to give $R = 0.053$, $R' = 0.066$, 226 variables, $S = 1.9$, $(\Delta/\sigma)_{\text{max}} = 0.01$, $(\Delta\rho)_{\text{max,min}} = +0.20, -0.20$ e Å^{-3} on a final difference map. [Etmim][TCNQ] **2c**: $C_{21}H_{21}N_6$, $M = 359.4$, orthorhombic space group *Pbca* (No. 61), $a = 10.318(4)$, $b = 14.379(2)$, $c = 26.398(2)$ Å, $U = 3916.3$ Å^3, $Z = 8$, $D_{\text{calc}} = 1.21$ g cm^{-3}, $F(000) = 1512$. Data were collected using a crystal of 0.5 × 0.2 × 0.08 mm. A total of 3888 unique reflections were measured for $2 < \theta < 25°$ and $+h+k+l$, and 866 reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$, were used in the refinement. With a weighting scheme of $\omega = 1/\sigma^2(F)$, the refinement converged to give $R = 0.049$, $R' = 0.056$, 244 variables, $S = 1.9$, $(\Delta/\sigma)_{\text{max}} = 0.02$, $(\Delta\rho)_{\text{max,min}} = +0.17, -0.30$ e Å^{-3} on a final difference map. Atomic coordinates, bond lengths, and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

0897-4756/94/2806-1106$04.50/0

chloride salt. They were structurally characterized,[9] and their single-crystal solid-state EPR properties were investigated.

[Emim][TCNQ] **2a** (where $[emim]^+$ is the 1-ethyl-3-methylimidazolium cation) has previously been shown to be a semiconductor.[10] In the solid state it forms segregated, infinite stacks of adjacent $[TCNQ]^{\bullet-}$ and $[emim]^+$ ions (Figure 1a,b). Within the $[emim]^+$ stack, the cations are dimerized with the imidazolium rings antiparallel and the ethyl groups external to the dimer. The $[TCNQ]^{\bullet-}$ anion exhibits a distorted boat conformation, as seen for Rb[TCNQ].[11] Within the $[TCNQ]^{\bullet-}$ stack, the anions are dimerized, the intradimer overlap being long-axis slipped (see Table 1); the interdimer overlap is also considerably long-axis slipped (Figure 1a and Table 1), but in the reverse direction. This is quite unlike the usual "staircase" formation found in the $[TCNQ]^{\bullet-}$ dimer stacks of simple metal TCNQ salts.[12] It would appear that this distortion is caused by the presence of hydrogen-bond-type interactions[13] (A and B in Figure 1c; for A, C–H···N = 2.33, C···N = 3.19 Å; for B, C–H···N = 2.52, C···N = 3.29 Å) A being between one of the $[TCNQ]^{\bullet-}$ nitrile groups and H-2 of the imidazolium ring and B between the neighboring nitrile group and the methyl protons of the cation. The center of symmetry within the $[TCNQ]^{\bullet-}$ dimer leads to the pairs of hydrogen-bonds being *trans* disposed (Figure 1c). The consequence of this arrangement is that while one of the $[TCNQ]^{\bullet-}$ anions is pulled into the "staircase" the other is pulled out of it (Figure 1a,c). This is the first recorded observation of an interaction of $[TCNQ]^{\bullet-}$ with a C–H hydrogen-bond donor. It is quite remarkable that such an interaction, which would at first sight be expected to be weak, should have such a dramatic effect on the solid-state structure of this salt.

In the solid-state EPR spectrum of **2a**, there is a sharp central line which is both orientation and temperature independent: this signal arises from a doublet species. Above 50 °C, a second orientation-independent, but temperature-dependent, resonance appears overlapping with the doublet species: this arises from a migrating triplet exciton. Such behavior is typical of salts with infinite chains of $[TCNQ]^{\bullet-}$ anions.[14]

[Edmim][TCNQ] **2b** (where $[edmim]^+$ is the 1-ethyl-2,3-dimethylimidazolium cation) was prepared in order to investigate the consequence of blocking the hydrogen-bonding site (C-2) of the imidazolium ring. In this case the solid-state architecture adopts a pattern in which stacks of cations and anions alternate (i.e., $D^+D^+A^-A^-D^+D^+$) in a manner similar to that observed for **1**.[3] Within the $\{[TCNQ]^{\bullet-}\}_2$ dimer, the overlap is short-axis slipped (Table 1), each anion having a distorted boat conformation. The $[edmim]^+$ cation dimers adopt an antiparallel arrangement, in which the ethyl groups are internal to the dimer (Figure 2). No hydrogen-bonding interactions are evident (shortest C···N = 3.38 Å). The solid-state EPR spectrum

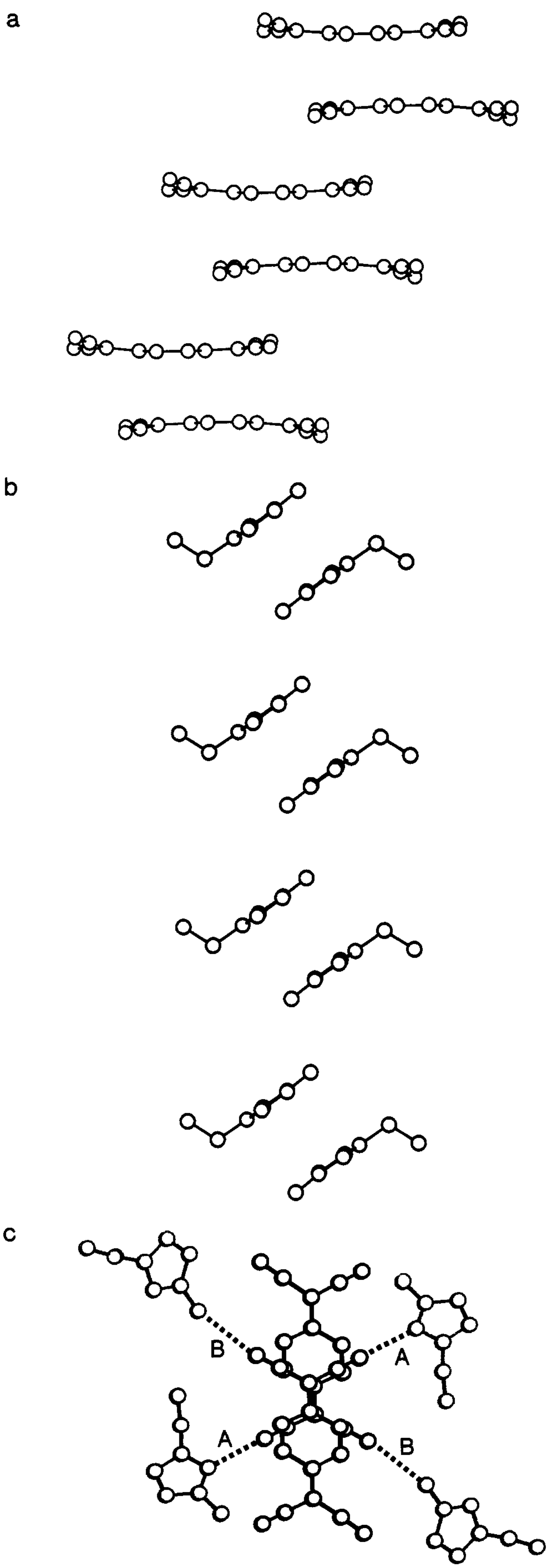


Figure 1. Views of the solid-state structure of **2a** showing (a) the $TCNQ^{\bullet-}$ stack, (b) the $[emim]^+$ cation stack, and (c) the close C–H···N contacts.

---

(10) Sorm, M.; Nespurek, S.; Prochazka, M.; Koropecky, I. *Coll. Czech. Chem. Commun.* **1993**, *48*, 103–111.

(11) Hoekstra, A.; Spoedler, T.; Vos, A. *Acta Crystallogr., Sect. B* **1972**, *28*, 14–25.

(12) Pope, M.; Swenberg, C. E. *Monographs on the Physics and Chemistry of Materials. 39: Electronic Processes in Organic Crystals*; Oxford University Press: Oxford, 1982; pp 581–641.

(13) C–H···X interactions have significant electrostatic content and direct comparison with van der Waals forces may be misleading since the former will fall off more slowly with distance; see: Desiraju, G. R. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 63–74.

(14) Tanaka, J.; Tanaka, M.; Takabe, T.; Maki, O. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2358–2373.

Table 1. Comparison of TCNQ$^{\bullet-}$ Dimer Geometries in 2a–c

compound	vertical π–π separation (Å)	short-axis slip deg	short-axis slip Å	long-axis slip deg	long-axis slip Å
2a (intradimer)	3.11	3.9	0.21	35	2.17
2a (interdimer)	3.7	12.2	0.8	59.7	6.34
2b	3.25	4.8	0.27	0.8	0.05
2c	3.19	15.3	0.87	0.8	0.04

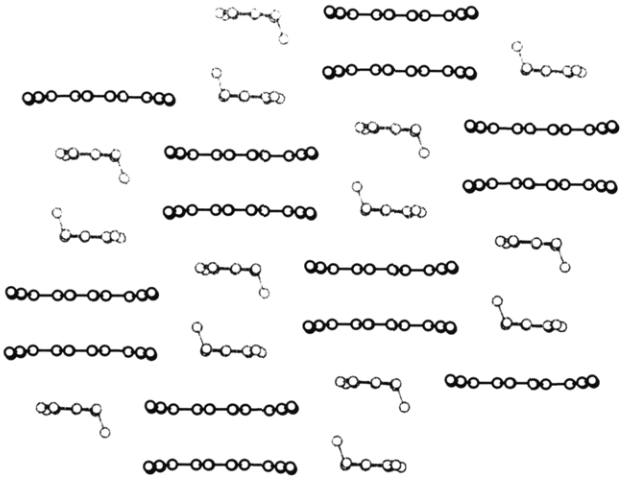


Figure 2. Side view of packing in **2b**, showing the columns of alternation of 1-ethyl-2,3-dimethylimidazolium cation and {[TCNQ]$^{\bullet-}$}$_2$ dimers.

of **2b** consists of a sharp central line which is both orientation and temperature independent, arising from a doublet species, in addition to a thermally activated static triplet exciton [activation energy J = 0.58(6) eV]. This behavior is typical of salts with isolated {[TCNQ]$^{\bullet-}$}$_2$ dimers.[3–5]

In [etmim][TCNQ] **2c** (where [etmim]$^+$ is the 1-ethyl-2,3,4,5-tetramethylimidazolium cation) the presence of the additional methyl groups prevents close face-to-face contact of imidazolium rings. In this case, the solid-state structure consists of isolated {[TCNQ]$^{\bullet-}$}$_2$ dimers encapsulated by coplanar pairs of [etmim]$^+$ cations forming $(D^+)_2A^-A^-(D^+)_2$ columns (Figure 3). The {[TCNQ]$^{\bullet-}$}$_2$ dimer is short-axis slipped (see Table 1), typical behavior in the absence of coordination,[3] and each [TCNQ]$^{\bullet-}$ anion adopts a distorted boat conformation. Each of the imidazolium rings is situated above a methine carbon of the [TCNQ]$^{\bullet-}$ anion rather than above the [TCNQ]$^{\bullet-}$ ring. The ethyl groups interlock about the {[TCNQ]$^{\bullet-}$}$_2$ dimers, thereby facilitating the closest possible packing of the structure, and result in adjacent columns being displaced. No triplet exciton behavior was observed in the solid-state EPR spectrum of **2c**. This unexpected result is still under investigation.

The structures of [TCNQ]$^{\bullet-}$ salts are extremely sensitive to changes in the cation. In the presence of a suitable hydrogen-bond donor (e.g., the [emim]$^+$ cation), interactions with the nitrile groups of the TCNQ anion control the structure. In the absence of such interactions, aromatic stacking effects, anion–anion, cation–cation, and cation–anion, dominate as seen in [edmim][TCNQ] **2b**. When aromatic stacking interactions of the cation are prevented, as in [etmim][TCNQ] **2c**, the structure is determined by aromatic stacking of the anion ([TCNQ]$^{\bullet-}$) and electrostatic attraction between C(CN)$_2$ moieties of the anion and the cation. The dramatic structural effects of such relatively small changes in the substitution pattern about the imidazolium ring are also reflected in the triplet exciton behavior of the salts **2a–c**. Indeed these salts show the complete range of thermally activated triplet exciton phenomena ranging from mobile excitons in **2a** through static exciton in **2b**, to no exciton behavior for **2c**. More detailed EPR studies are in progress to elucidate the cause–effect relationship between the structures and properties observed.

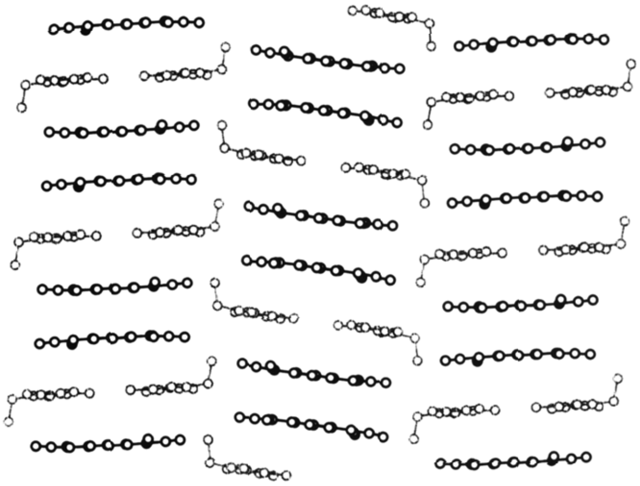


Figure 3. Side view of packing in **2c**, showing the isolated {[TCNQ]$^{\bullet-}$}$_2$ dimers.

Acknowledgment. We thank C. Dunn (University of Southampton) for help with EPR measurements, the SERC for a studentship and postdoctoral fellowship to SCW, and BP Venture Research for their funding (TW).

Supplementary Material Available: Additional figures showing the asymmetric units and crystallographic numbering schemes used for each of **2a–c**, together with tables of fractional atomic coordinates of all atoms, intramolecular distances and angles, and anisotropic thermal parameters for all non-hydrogen atoms (33 pages); listing of calculated and observed structure factors for each structure (15 pages). Ordering information is given on any current masthead page.