'Organic Metals' with Asymmetric Acceptors: The Monofluorotetracyanoquinodimethane Anion

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Summary The synthesis and properties of monofluorotetracyanoquinodimethane (FTCNQ) and several of its tetrathia- and tetraselena-fulvalene complexes are described.

The discovery of metallic conductivity in TTF–TCNQ (tetrathiafulvalene–tetracyanoquinodimethane) has generated substantial interest in the synthesis and characterization of related organic charge-transfer complexes.[1] Much of the present knowledge of the transport properties of the parent system has been gained by exploiting the extensive derivative chemistry of the donor unit, TTF, while retaining the acceptor, TCNQ, unchanged. These materials generally display anisotropic transport and optical phenomena since their crystal structures allow significant orbital overlap solely along the stack axis. It is well recognized, however, that the lower dimensionality and narrow bands of this type of system make the achievement of the metallic state complicated. In fact, the majority of the TCNQ-based salts exhibit either low room temperature conductivity or metallic properties over a limited temperature range.

In an attempt to stabilize the metallic state, we have prepared monofluorotetracyanoquinodimethane (FTCNQ), an acceptor for which a stronger electron affinity than TCNQ is expected without a significant increase in the molecule's physical size.† This latter point is critical for maintenance of a favourable intrastack distance in the complexes. The use of alloys should then allow control over the degree of band filling.‡ In addition, the high electronegativity of fluorine imparts an electronic perturbation to the acceptor ion which is both asymmetric§ and

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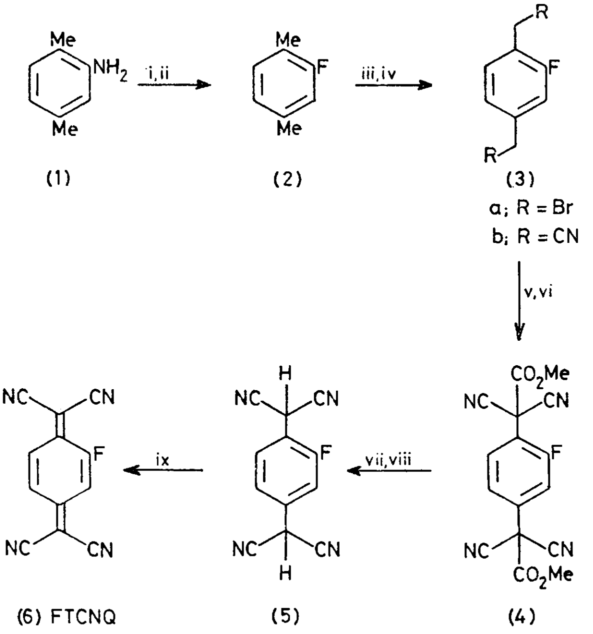
† Van der Waals radii for typical substituents on TCNQ: r_{H}, 1·20; r_{F}, 1·35; r_{Cl}, 1·80; r_{Br}, 1·95; r_{Me}, 2·0 Å. We recognize, however that the polarizability gain of Cl or Br substituents (heavy atom effect) will be unavailable to FTCNQ.

‡ Merely increasing the electron affinity indiscriminately does nothing to stabilize the metallic state. One of the strongest acceptors, $\mathrm{TCNQF_4}$ (E_{A} = 3·22 eV) invariably affords insulating complexes because significant charge density is drawn into the ring thus enhancing coulombic effects.

§ The aperiodic potential from randomly oriented FTCNQ ions is expected to suppress the Peierls distortion in a manner similar to the fluctuating dipoles in NMP–TCNQ.

substantive.¶ Finally, the possibility that the asymmetric acceptor could impose its periodicity into the donor stack of 'disordered' complexes with dipolar cations [*e.g.* *N*-methylphenazinium (NMP), quinolinium] by local electrostatic interactions should not be overlooked.



Scheme. Reagents: i, $NaNO_2$, HCl; ii, HBF_4, heat; iii, Br_2, *h*ν; iv, KCN, tetrahydrofuran–H_2O–EtOH; v, $MeOCO_2Me$, NaOMe; vi, CNCl; vii, KOH–H_2O; viii, HCl–H_2O; ix, Br_2–H_2O.

FTCNQ was obtained as an orange-red solid, by modification of the method of Wheland and Martin[2] in *ca.* 20% overall yield (Scheme).** It has the following properties: m.p. (uncorrected) 215—216 °C; u.v. (MeCN), λ_{max} 389 (ϵ 5·11 × 10^4), 370 sh (3·35 × 10^4) nm; i.r. (KBr): 3071m, 2020s, 1619m, 1549s, 1392m, 1208s, 1109m, 881s, and 812m cm^{-1}; n.m.r.: ^1H [$(CD_3)_2CO$; Me_4Si] δ 7·25—7·58, m; mass spectrum: *m/e* 222 (M^+, 100%), 223 ($M^+ + 1$, 14·2%, calc: 14·9%). The electron affinity for FTCNQ may be estimated from the solution charge-transfer bands of its hexamethylbenzene and pyrene complexes. E_A for FTCNQ at 2·95 eV is 0·11 eV higher than that for TCNQ.[3] This value compares favourably with the cyclic voltammetry results which exhibit two reversible one-electron reduction waves at $E_{\frac{1}{2}}^{1} = 0{\cdot}260$ and $E_{\frac{1}{2}}^{2} = -0{\cdot}185$ V (*vs.* SCE; 0·1 M $LiClO_4$; MeCN; Pt electrode; 25 °C). Under the same conditions, TCNQ reveals $E_{\frac{1}{2}}^{red}$ waves at 0·139 and −0·287 V respectively (lit.,[4] 0·127 and −0·291 V). The $\Delta E_{\frac{1}{2}}$ values for FTCNQ and TCNQ determined here are essentially identical, suggesting that although the degree of charge transfer in the FTCNQ complexes will be substantially altered compared to respective TCNQ salts, their electronic double occupancy states should be no more difficult to achieve than those of $TCNQ^{2-}$.

Mixing equimolar solutions of gradient-sublimed FTCNQ and TTF in acetonitrile quantitatively precipitates the 1 : 1 complex as black microcrystals. The four-probe d.c. conductivity properties at room temperature on compressed pellets for this and the FTCNQ complexes of tetramethyltetralthiafulvalene (TMTTF), tetramethyltetraselenafulvalene (TMTSF), hexamethylenetetralthiafulvalene (HMTTF), and hexamethylenetetraselenafulvalene (HMTSF) and the position of their near i.r. absorption bands taken in KBr were determined. The observed λ_{max} values were all > *ca.* 2·5 μm, a value usually taken as a necessary but insufficient criterion for high conductivity.

Although compaction studies mask the intrinsic activation energies and temperature dependencies of the transport process, the magnitude of the conductivities at 300 K for the FTCNQ complexes compare favourably with their TCNQ counterparts. Our inability to date to obtain single crystals suitable for four-probe measurements under extensive variation of concentration and solvent parameters suggests that considerable disorder has been introduced into the acceptor stack.†† The introduction of FTCNQ as a low level dopant should enjoy greater success.

We acknowledge the Robert A. Welch Foundation and Research Corporation for support of this work.

(*Received*, 8*th August* 1978; *Com.* 871.)

¶ This is to be contrasted with the methyl group of MTCNQ which imparts only a weak electronic perturbation to the anion. Hence even very low doping levels of FTCNQ are expected to produce significant changes in the solid state properties of the unadulterated complexes.

** All compounds were characterized spectroscopically and satisfactory elemental analyses (Galbraith Laboratories, Knoxville, Tenn.) were obtained for new compounds with the exception of (**4**), whose reactivity precluded adequate purification without partial decomposition.

†† Preliminary voltage-shorted-compaction measurements (L. B. Coleman, *Rev. Sci. Instrum.*, 1978, **49**, 58) show no obvious metal to insulator transitions above 77 K for these samples but final proof of their suppression must await future single crystal studies. Static magnetic susceptibility measurements are currently being conducted.

[1] 'Organic Conductors and Semiconductors,' eds. L. Pal, G. Grüner, A. Janossy, and J. Solyom, Springer-Verlag, Berlin, 1977.
[2] R. C. Wheland and E. L. Martin, *J. Org. Chem.*, 1975, **40**, 3101.
[3] E. C. M. Chen and W. E. Wentworth, *J. Chem. Phys.*, 1975, **63**, 3183.
[4] D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, 1962, **84**, 3370.