

## **Difluorotetracyanoquinodimethane: Electron Affinity Cut-off for 'Metallic' Behaviour in a Tetrathiafulvalene Salt**

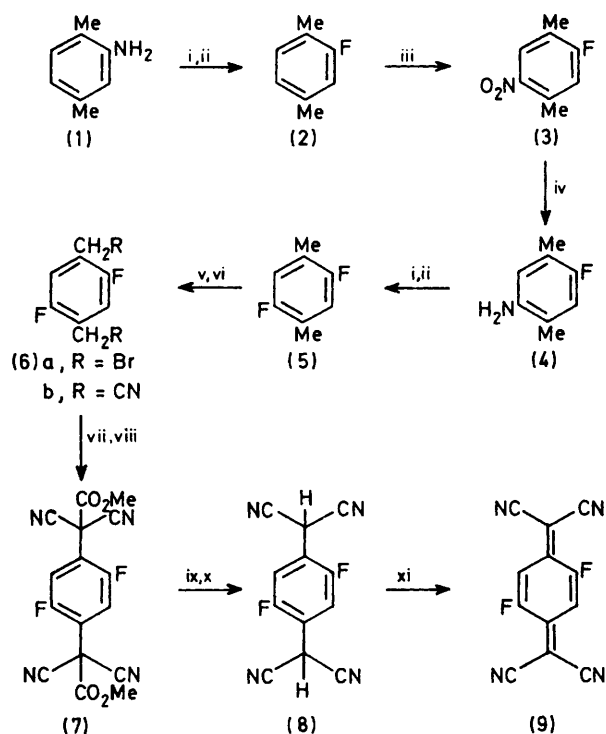
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**Summary** The synthesis and properties of 2,5-difluoro-tetracyanoquinodimethane and its tetrathiafulvalene salt

whose electrical conductivity is limited by the enhanced acceptor electron affinity are described.

MANY studies on TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) and its derivatives and analogues have produced some discernment of the variation in solid state properties with changes in crystal structure, dimensionality, and degree of charge transfer.<sup>1</sup> We sought to investigate the metal-to-insulator transition by alteration of the electron affinity of the acceptor while keeping structural perturbations to a minimum. The monotonic introduction of fluorine substituents onto TCNQ seemed the ideal choice since the van der Waals' radii of F and H are comparable while the electronic perturbation imparted by each successive fluorine would be substantive. TCNQ affords 'organic metals' while TCNQF<sub>4</sub> invariably forms insulating salts with fulvalene donors even when these systems are essentially isostructural with their TCNQ counterparts.



SCHEME. i, NaNO<sub>2</sub>, HCl; ii, HBF<sub>4</sub>, heat; iii, fuming HNO<sub>3</sub>; iv, SnCl<sub>2</sub>, HCl; v, *N*-bromosuccinimide; vi, KCN, tetrahydrofuran-H<sub>2</sub>O-EtOH; vii, MeOCO<sub>2</sub>Me, NaOMe; viii, CNCl; ix, KOH-H<sub>2</sub>O; x, HCl-H<sub>2</sub>O; xi, Br<sub>2</sub>-H<sub>2</sub>O.

In a previous communication<sup>2</sup> we reported the synthesis and 'metallic' properties of salts based on monofluoro-tetracyanoquinodimethane (FTCNQ), an acceptor with an asymmetric electronic distribution and enhanced electron affinity compared to TCNQ. We now describe the syn-

thesis and properties of a new TCNQ derivative, 2,5-difluorotetracyanoquinodimethane (F<sub>2</sub>TCNQ), (9), whose symmetry is C<sub>2h</sub>. (Scheme)

The fluoroxylene obtained by thermal decomposition of the fluoroborate salt of *p*-xylylidine was treated with fuming nitric acid to give (3) as a pale yellow solid, m.p. 61.5 °C (lit.<sup>3</sup> 49–50 °C) in 50% yield. <sup>1</sup>H n.m.r.: (CDCl<sub>3</sub>, Me<sub>4</sub>Si) δ 2.30 (s, 3H), 2.56 (s, 3H), 6.91 [d, 1H, *J*<sub>F-H(ortho)</sub> 17 Hz] and 7.85 [d, 1H, *J*<sub>F-H(meta)</sub> 12 Hz]. The nitro group was reduced smoothly with stannous chloride in concentrated HCl to give (4) as a white solid, m.p. 80.0–80.5 °C in 82% yield. <sup>1</sup>H n.m.r.: (CDCl<sub>3</sub>, Me<sub>4</sub>Si) δ 2.11 (s, 3H), 2.18 (s, 3H), 3.22 (br, 2H), 6.41 [d, 1H, *J*<sub>F-H(meta)</sub> 10 Hz], and 6.66 [d, 1H, *J*<sub>F-H(ortho)</sub> 17 Hz]. Compound (4) was converted into 2,5-difluoro-*p*-xylene (5), m.p. 39.0–40.0 °C, in 39% yield by a procedure analogous to the initial step. <sup>1</sup>H n.m.r.: (CDCl<sub>3</sub>, Me<sub>4</sub>Si) δ 2.20 (s, 6H), 6.64, 6.77, and 6.90 (2H). Bromination with *N*-bromosuccinimide affords (6a), m.p. 107–108 °C (lit.<sup>4</sup> 53–55 °C)† which was directly converted into the dinitrile (6b), m.p. 88–92 °C. The remainder of the synthesis is essentially the procedure of Wheland and Martin.<sup>5</sup>

Compound (9) is obtained as a golden-brown solid after purification by multiple gradient sublimation in a 2% overall yield from (1), [m.p. (uncorrected) 259.0–260.0 °C; u.v.: (MeCN) λ<sub>max</sub> 392 (ε 4.1 × 10<sup>4</sup>), 372 (2.7 × 10<sup>4</sup>) nm; i.r.: (KBr) 3066 s, 2235 m, 1575 s, 1551 m, 1391 s, 1199 s, 1138 m, 908 m, and 789 s cm<sup>-1</sup>; mass spectrum: *m/e* 240 (M<sup>+</sup>, 100%), 241 (M<sup>+</sup> + 1, 15.5%, calc 14.9%)]. The cyclic voltammogram displays two reversible one-electron reduction waves at E<sub>1</sub><sup>‡</sup> = 0.300 and E<sub>2</sub><sup>‡</sup> = -0.144 V (vs. standard calomel electrode, 0.1 M LiClO<sub>4</sub>, MeCN, Pt electrode, 25 °C). This yields an electron affinity of 3.00 eV, in excellent agreement with that estimated from the solution charge transfer bands of F<sub>2</sub>TCNQ with pyrene or hexamethylbenzene [3.02 eV using E<sub>A</sub>(TCNQ) = 2.84 eV].<sup>6</sup>

Plots of the E<sub>1</sub><sup>‡</sup> values for the series F<sub>*n*</sub>TCNQ (*F* = 0, 1,<sup>1</sup> 2,4<sup>7</sup>) vs. Hammett σ values<sup>8</sup> show the following linear correlations:† E<sub>1</sub><sup>‡</sup> = 0.214 Σσ + 0.134 (r = 0.995) and E<sub>2</sub><sup>‡</sup> = 0.170 Σσ - 0.273 (r = 0.99). Furthermore, the E<sub>1</sub><sup>‡</sup> and E<sub>2</sub><sup>‡</sup> values are linearly related with E<sub>2</sub><sup>‡</sup> = 0.831E<sub>1</sub><sup>‡</sup> - 0.400 (r = 0.9995) indicating that there should be virtually no enhanced coulomb repulsive forces operating in the doubly charged states of any fluorinated member in the series.§

Unlike the FTCNQ salts which fail to produce large crystals,<sup>2</sup> single crystals of TTF-2,5-F<sub>2</sub>TCNQ typically 3.0 × 0.1 × 0.1 mm<sup>3</sup> are readily obtained by slow cooling of acetonitrile solutions. Four-probe d.c. conductivity measurements on 5 samples give an average conductivity of ca. 2 × 10<sup>-5</sup> ohm<sup>-1</sup> cm<sup>-1</sup> with E<sub>act</sub> ca. 0.36 eV.

The exact degree of charge transfer in TTF-F<sub>2</sub>TCNQ will have to await future ESCA and/or X-ray studies but the low electrical conductivity implies that it is probably

† The reported low m.p. suggests the inclusion of significant amounts of mono- and/or tri-bromide impurities.

‡ Plots of E<sub>1</sub><sup>‡</sup> vs. (σ<sub>m</sub> + σ<sub>p</sub>)/2 proposed by Wheland and Gillson, *J. Amer. Chem. Soc.*, 1976, **98**, 916 are also linear (slope 0.474 and 0.423, and intercept 0.141, -0.069 for E<sub>1</sub><sup>‡</sup> and E<sub>2</sub><sup>‡</sup>, respectively). This correlation in a series of TCNQ and *p*-benzoquinone derivatives as well as other π-acceptors will be discussed elsewhere. (G. Saito, unpublished results).

§ This is at variance with theories initially offered (ref. 7) to explain the insulating character of F<sub>4</sub>TCNQ salts but is consistent with current views (A. N. Bloch, W. A. Bryden, D. O. Cowan, M. E. Hawley, T. J. Kistenmacher, T. O. Poehler, and J. P. Stokes, Abstracts, ACS/CSJ Chemical Congress, April, 1979, Honolulu).

close to 1.00 as in  $F_4TCNQ$  salts. Assuming similar crystal structures, it is unlikely that symmetry perturbations available to the (yet unsynthesized) 2,3- and 2,6- $F_2TCNQ$  isomers can outweigh the large ionization potential-electron affinity difference.

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<sup>8</sup>  $\sigma$  Values for phenols ( $\sigma_o = 0.54$ ,  $\sigma_m = 0.34$ ) were used. H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191; A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 1961, 388.