Synthesis of 13,13,14,14-tetracyanopyreno-2,7-quinodimethane, an Electron Acceptor for Organic Metals

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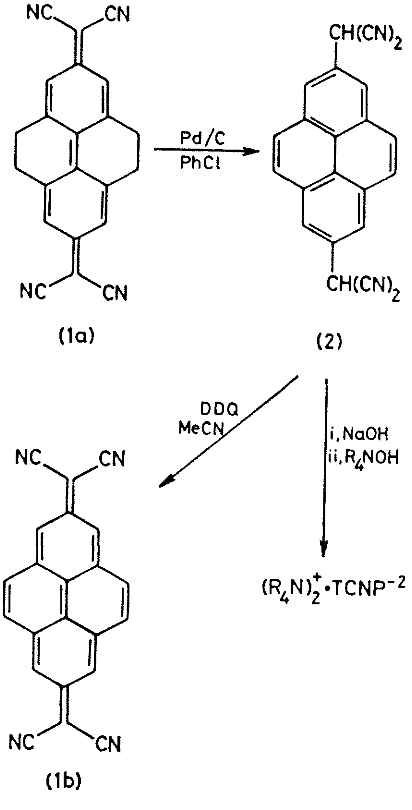
Summary The title compound (**1b**) and its bistetra-alkylammonium salts can be prepared from the dehydrogenation product of 13,13,14,14-tetracyano-4,5,9,10-tetrahydropyrenoquinodimethane.



Charge transfer salt organic conductors consist of segregated stacks of electron donors and electron acceptors, one or both of which is capable of existing in multiple oxidation states. The overlapping p_z orbitals form nearly one-dimensional energy bands a few hundred meV in width. Highly conducting donor–acceptor combinations are characterized by a charge transfer ranging from 0·5 to 0·8 per formula unit. The typical structural features[1] are planarity with extended π-molecular orbitals, high symmetry, and a widely spaced charge and spin distribution. In order to obtain partial charge transfer for a given organic donor of ionization potential IP_1, the first electron affinity of the acceptor, EA_1, must be large enough to effect reaction, yet small enough to avoid the complete charge transfer characteristic of a Mott–Hubbard insulator.[2]

We have sought to provide an acceptor compatible with the larger and less reactive π-donors by synthesizing 13,13,14,14-tetracyanopyreno-2,7-quinodimethane (TCNP), the pyrene analogue of tetracyanoquinodimethane (TCNQ). It has D_{2h} symmetry with the terminal methylene groups spaced *ca.* 9·5 Å apart. According to half-wave potentials obtained from cyclic voltammetry of its dianion,[3] the EA_1 is 2·90 V, 60 meV higher than that of TCNQ, yet well below the threshold between conductor and insulator established by Ferraris.[4] Its $\Delta E_{\frac{1}{2}}$, indicative of the relative intramolecular Coulomb repulsion in similar compounds, is 0·304 V under the same electrochemical conditions used to measure about 0·640 V for many substituted TCNQ acceptors.

Neutral TCNP is prepared by catalytic dehydrogenation of the tetrahydro-derivative (TCNTP)[5] followed by treatment of the resulting pyrene-2,7-dimalononitrile (**2**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Refluxing a solution of TCNTP in chlorobenzene with 10% palladium on carbon yields (**2**) (80%), m.p. > 360 °C, ν_{max} (KBr) 3025, 2250, 1605, 1442, 1403, and 1312 cm^{-1}; λ_{max} (MeCN) 260 (log ϵ 3·97), 272 (40·5), 305 (3·95), 323 (40·00), and 338 nm (4·08). The mass spectrum of (**2**) obtained by direct exposure methods[6] has major fragments at *m/e* 330 (M^+), 266 ($M^+ - C_3N_2$), 240 ($M^+ - C_4N_3$), 202 ($M^+ - C_6N_4$), and 101 ($M^{2+} - C_6N_4$). A large excess of DDQ is added to a refluxing solution of (**2**) in acetonitrile to yield (*ca.* 90%) TCNP, m.p. > 360 °C, ν_{max} (KBr) 2205, 1595, 1401, 1372, and 1312 cm^{-1}; λ_{max} (butyronitrile) 243 (log ϵ 4·60), 340 (3·31), and 557 nm (4·12). Low solubility of TCNP in common solvents prevented further characterization by cyclic voltammetry.

Tetra-alkylammonium salts of TCNP are prepared by taking (**2**) up in aqueous sodium hydroxide and precipitating bistetraethyl- or tetrabutyl-ammonium salts of TCNP by addition of the ammonium hydroxide. The tetraethylammonium salt exhibits ^{1}H n.m.r. (CD_3CN) signals at δ (from Me_4Si) 7·80 (8H, br s, Ar-H), 3·42 (16H, q, *J* 7 Hz, NC–H), and 1·45 (24H, t, *J* 7 Hz, CH_3). Bis(tetrabutylammonium) TCNP, somewhat less sensitive to air oxidation, has electronic absorption maxima at 292 (log ϵ 3·91), 312 (4·08), 327 (4·52), 341 (4·26), and 371 (4·36), ν_{max} (KBr) 2160, 2120, 1604, 1450, and 1315 cm^{-1}. The absorptions at 2160 and 2120 cm^{-1} are sharp, equally intense, and presumably due to two asymmetric modes involving the C–N vibration. Its cyclic voltammogram in butyronitrile with 0·1 M tetrabutylammonium tetrafluoroborate has anodic current peaks at $E^1_{Pa} = -0{\cdot}278$ V and $E^2_{Pa} = +0{\cdot}026$ *vs.* an $Ag/AgNO_3$ standard electrode. The first oxidation is reversible, but the second is largely irreversible owing to the insolubility of neutral TCNP. Oxidation of $TCNP^{2-}$ at $-0{\cdot}02$ V results in the appearance of electronic absorbances at 910, 1124, and 1350 nm predicted for $TCNP^{\cdot -}$. Similarly reduction of a solution of neutral TCNP at $-0{\cdot}15$ V results in the emergence of the near-i.r. bands and disappearance of the visible band at 557 nm.

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