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Tcaq (11,11,12,12-Tetracyano-9,10-Ahthraqu Inod Imethane): A Novel Electron Acceptor

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TCAQ (11,11,12,12-TETRACYANO-9,10-ANTHRAQUINODIMETHANE): A NOVEL ELECTRON ACCEPTOR

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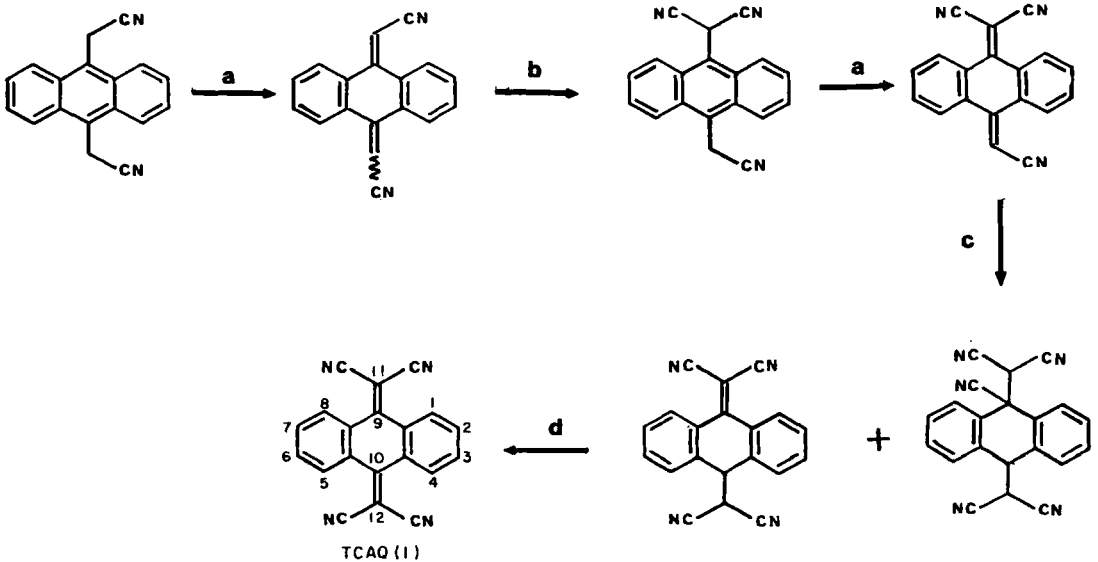
Abstract A new synthesis of TCAQ starting with 9,10-bis(cyanomethyl) anthracene is reviewed. Electrochemical studies reveal that TCAQ undergoes a reversible two-electron reduction [$E_{1/2}$ = - 0.285 V, CH_3CN, Et_4NBF_4, Ag/AgCl ref.].

In the search for organic conducting salts derived from TCNQ and related acceptors, considerable attention has been directed towards the synthesis and study of acceptors with extended π-networks.[1] These investigations are predicted on the notion that the enlargement of the π-framework leads to reduced intramolecular coulomb interactions.[2] Recently, several groups have developed different synthetic routes for the preparation of dibenzoTCNQ (TCAQ).[3,4,5]

Our strategy to synthesize TCAQ, which may be applicable to other cyanocarbons with extended π-systems, begins with 9,10-bis(cyanomethyl)anthracene and proceeds via the dicyano and tricyano analogs of TCAQ (Scheme I). The substantially blue-shifted UV absorption characteristics of TCAQ (343 nm) compared to TCNQ (393 nm) and benzoTCNQ (404 nm) indicate that TCAQ is not planar. A recent X-ray structural study shows that TCAQ in the solid state has a boat-like structure.[6]



SCHEME I

a. Br_2, $ClCH_2CH_2Cl$, Reflux, 1 h, (72%)

b. NaCN, dioxane/95% EtOH (7:3), reflux, 24 h, (100%)

c. NaCN, DMF, 100°, 5 hr, (70–80%)

d. Br_2, Et_3N, CH_3CN, room temp. (92%)

A cyclic voltammogram of TCAQ, depicted in Figure 1, shows redox waves at potentials $E_{1/2}$ of - 0.285 V (2e, reversible), - 2.06 V (1e, reversible), and - 2.58 V (1e, irreversible). These are assigned to the processes described in Equations (1), (3) and (4), respectively. That the redox wave at $E_{1/2}$ = - 0.285 V is a two-electron reduction was deduced from the peak potential separation of 30 mV between cathodic and anodic waves and was confirmed by coulometry. However, when TCAQ was reduced electrolytically or chemically (potassium, 1:1 THF/1,2-dimethoxyethane), ESR and ENDOR spectra attributable to $TCAQ^{\bar{\bullet}}$ could be obtained. Also, UV-Vis-Near IR spectral monitoring of TCAQ during electrochemical reduction revealed a weak absorption at 1060 nm which attained its maximum intensity at ca. one equivalent of charge added and then disappeared after consumption of two equivalents of charge. These findings strongly imply a coproportionation pathway to $TCAQ^{\bar{\bullet}}$, as in Equation (2).

$$TCAQ + 2e \rightleftharpoons TCAQ^{2-} \quad (1)$$

$$TCAQ + TCAQ^{2-} \rightleftharpoons 2\ TCAQ^{\bar{\bullet}} \quad (2)$$

$$TCAQ^{2-} + e \rightleftharpoons TCAQ^{3\bar{\bullet}} \quad (3)$$

$$TCAQ^{3\bar{\bullet}} + e \longrightarrow TCAQ^{4-} \quad (4)$$

The redox waves at $E_{1/2}$ = - 2.06 V and - 2.58 V are due to the addition of electrons to the anthracene moiety of $TCAQ^{2-}$. This was clearly established by comparison to the cyclic voltammogram of anthracene under the same conditions (Figure 1).

Preliminary experiments to form charge-transfer salts with various donors and metallic copper have been unsuccessful so far, perhaps not a surprising observation considering the electrochemical data. However, copper-electron acceptor salts can also be formed thermally and we are currently exploring these possibilities.

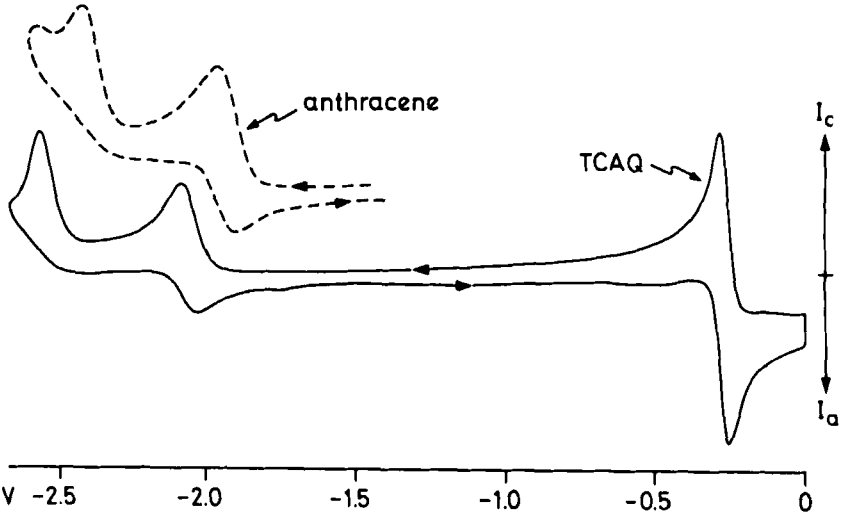


FIGURE 1 Cyclic voltammograms of TCAQ and anthracene. Solvent, acetonitrile; supporting electrolyte, $Et_4N^+BF_4^-$; reference electrode, Ag/AgCl/KCl 3M: sweep, 200 mV/s.

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