

## 4,8-BIS(DICYANOMETHYLENE)-4,8-DIHYDROBENZO[1,2-c:4,5-c']DITHIOPHENE.

## A NEW ELECTRON ACCEPTOR

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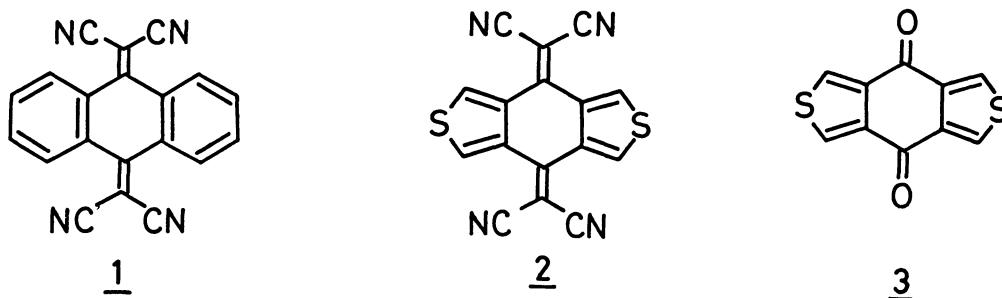
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The title compound was designed as a new acceptor and was synthesized from the corresponding quinone and malononitrile. Electrochemical studies suggested that the molecule is not so much distorted as tetracyanoanthraquinodimethane.

The design and synthesis of new donors and acceptors for conductive charge-transfer complexes are of great current interest. A variety of acceptor species have been searched for. Among those, tetracyanoanthraquinodimethane (1), being recently reported from several laboratories,<sup>1-3)</sup> is an interesting structural modification of TCNQ in terms of  $\pi$ -system extension. We now describe the synthesis and some properties of a new acceptor, 4,8-bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-c:4,5-c']dithiophene (2), which is endowed with an isoelectronic structure with 1 but is designed to increase the inter-stack interactions by the incorporation of sulfur atoms within the molecular framework.<sup>4)</sup> This design strategy is anticipated to suppress the Peiers transitions, hence to bring about the stable metallic state.

The synthesis of 2 is based on the procedure described by Hünig for 1.<sup>1)</sup> To a solution of 4,8-dihydrobenzo[1,2-c:4,5-c']dithiophene-4,8-dione (3),<sup>5)</sup> malononitrile (20 equiv.), and pyridine (40 equiv.) in chloroform was added  $\text{TiCl}_4$  (2 equiv.) and the mixture was refluxed for 5 h. The crude product was recrystallized from acetonitrile to afford 2 in 24% yield as bright yellow needles with absorption maxima at 360 and 278 nm (in  $\text{CH}_3\text{CN}$ ).  $\text{Mp} > 270^\circ\text{C}$ .  $^1\text{H-NMR}(\text{CDCl}_3)$   $\delta$  8.81.  $^{13}\text{C-NMR}(\text{DMSO}-d_6)$   $\delta$  76.03, 114.42, 131.27, 132.78, 150.03. IR(nujol)  $2225\text{ cm}^{-1}$ . Found: C, 60.68; H, 1.44; N, 17.83; S, 20.58%. Calcd for  $\text{C}_{16}\text{H}_4\text{N}_4\text{S}_2$ : C, 60.75; H, 1.27; N, 17.71; S, 20.27%.

As shown in Fig. 1, the cyclic voltammetry of 2 (0.1 M  $n\text{-Bu}_4\text{NClO}_4$ , in DMF, Pt-electrode) revealed two reversible one-electron reduction waves at -0.49 and



-0.73 V *vs.* SCE. The first reduction potential is comparable to the second one of TCNQ.<sup>3a)</sup> The difference between halfwave potentials for the first and second reductions of 2 is apparently small as compared with that of TCNQ,<sup>3a)</sup> indicating that the intramolecular Coulomb repulsion is considerably reduced in 2.

Very recently it has been reported that tetracyanoanthraquinodimethane (1) exhibits a single-wave, two-electron reduction to the dianion,<sup>1,2)</sup> which has been attributed to a highly distorted structure of 1 with central ring existing in a boat form. Thus, the observation of two one-electron reduction waves in 2, in contrast to 1, suggests that 2 is more planar than 1.

It is interesting to note that the anion radical produced upon the first wave reduction is represented by valence formulas involving tetravalent sulfur as the uncharged resonance contributors. A few examples of such nonclassical condensed thiophenes have been reported,<sup>6)</sup> including benzo[1,2-c:4,5-c']dithiophene ring system.<sup>7)</sup>

The evidence for the complexation with TTF was observed by color change and electronic spectra. The isolations of charge-transfer complexes with various donors are under current investigation.

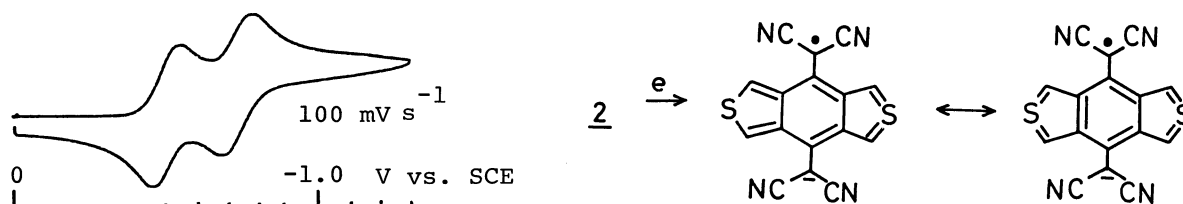


Fig. 1. CV of 2.

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