Synthesis and Electrochemical Properties of 15,15,16,16-Tetracyano-6,13-pentacenequinodimethane (TCPQ)

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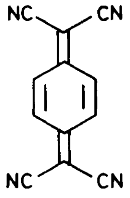
The title compound TCPQ (**3**) has been synthesized from the corresponding 6,13-pentacenequinone (**10**) and malononitrile; cyclic voltammetric studies reveal two reduction potentials.

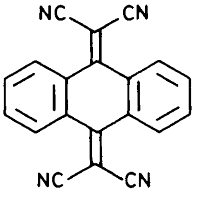
Tetracyanoquinodimethane (TCNQ) (**1**) has been widely used as an acceptor molecule to form highly conducting charge transfer complexes.[1] Although many TCNQ-derivatives have been prepared, TCNQ analogues fused with aromatic rings have received less attention.[2] The extension of the π-system has been shown to lead to a reduction of the intramolecular Coulomb repulsion. Compared to the corresponding TCNQ-complexes enhanced electrical conductivity was observed for some tetracyanonaphthoquinodimethane (TNAP) complexes.[3] Hence, there is competitive interest to synthesize such ring-fused TCNQ derivatives[4—7] and study their electrical properties in charge transfer complexes.

Recently, the syntheses and electrochemical properties of 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) (**2**), as the first example in which the TCNQ (**1**) molecule is fused with two benzene rings, were published simultaneously by different authors.[4—7] Some of the reported procedures to obtain TCAQ (**2**) describe complicated multistep syntheses, some of them having low yields.[4,7]

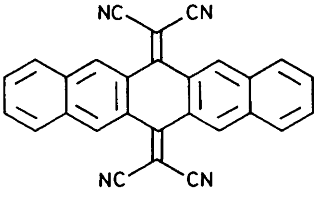
We now report the synthesis and electrochemical properties of the TCNQ-analogue, 15,15,16,16-tetracyano-6,13-pentacenequinodimethane (TCPQ) (**3**). The synthesis of (**3**) was first attempted by a direct reaction of *ortho*-quinodimethane (**5**), which can be favourably generated *in situ* from the sultine (**4**)[8] to form the bis-adduct (**6**) in one step. Dehydrogenation of (**6**) should lead to (**3**) (Scheme 1). Refluxing TCNQ (**1**) with



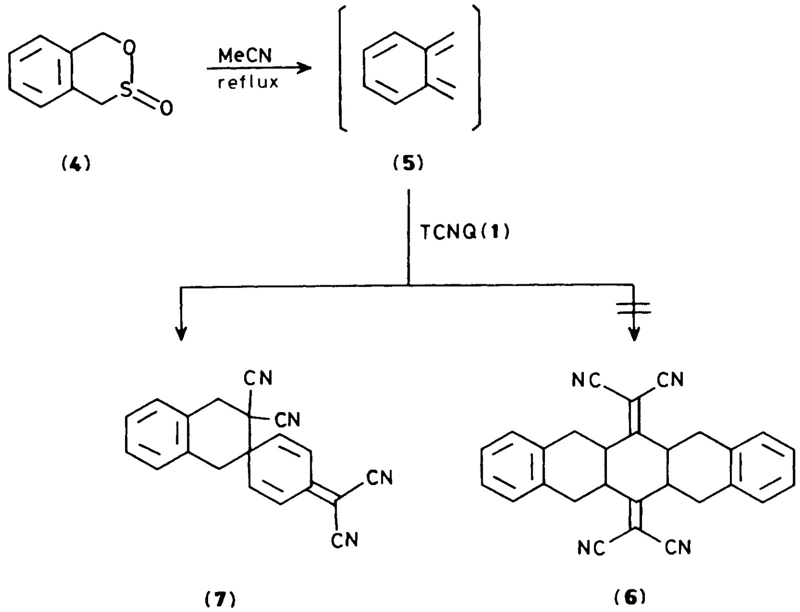
TCNQ (**1**)



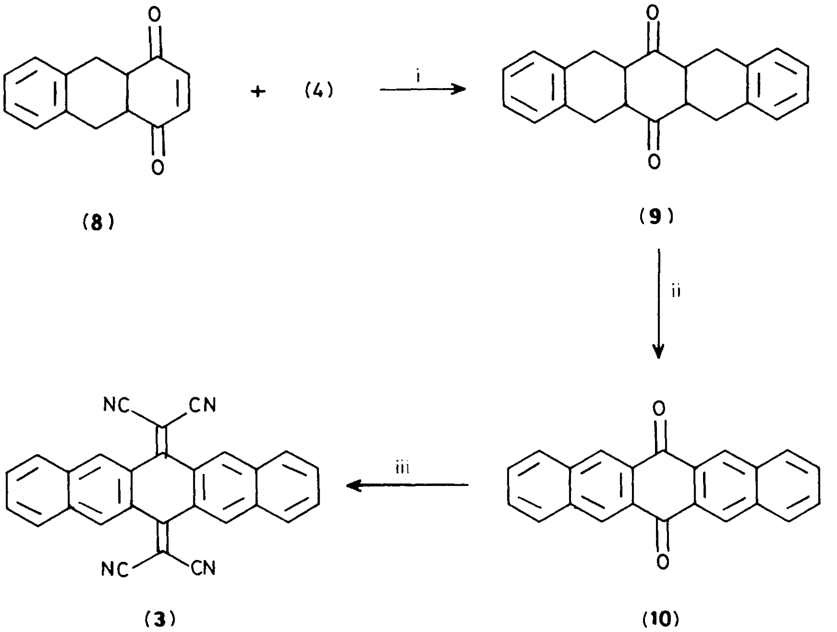
TCAQ (**2**)



TCPQ (**3**)



Scheme 1



Scheme 2. *Reagents*: i, C_6H_6, reflux; ii, Br_2–pyridine, DMF; iii, $CH_2(CN)_2$, $TiCl_4$, pyridine.

the sultine (**4**) in acetonitrile under nitrogen atmosphere afforded a solid product. From the spectroscopic data,† it was evident, however, that the intermediate *ortho*-quinodimethane (**5**) had not reacted with TCNQ (**1**) to form (**6**), but had undergone addition to the more electron-poor double bond in (**1**) with exclusive formation of the spiro compound (**7**) (Scheme 1).

To the best of our knowledge, only the reaction of 1-cyclopropylbutadiene with the exocyclic double bond in TCNQ (**1**) to form the corresponding Diels–Alder adduct has been reported.[9] Cowan and Gerson[7] claim to have obtained a partially saturated TCAQ (**2**) from the reaction of butadiene with TCNQ (**1**) as an intermediate which however was not spectroscopically identified.

6,13-Pentacenequinone (**10**), which can be obtained from phthaldialdehyde and cyclohexane-1,4-dione,[10] was then chosen as a suitable precursor for (**3**). Quinone (**10**) was synthesized by the *ortho*-quinodimethane route as given in Scheme 2. The conjugated diketone (**8**) starting material was easily prepared as reported[11] by the reaction of *ortho*-quinodimethane (**5**) with *p*-benzoquinone. The diketone (**8**) reacted with an excess of (**5**) [formed from (**4**)] to lead to octahydropentacene-6,13-dione (**9**) in 51% yield.† The dione (**9**) was converted to (**10**) by bromination and dehydrobromination in hot pyridine and dimethylformamide (DMF). The crude 6,13-pentacenequinone (**10**) was formed in 78% yield and was then condensed with malononitrile in the presence of $TiCl_4$ as catalyst[5,6] by refluxing in pyridine to give TCPQ (**3**) in 54% yield.†

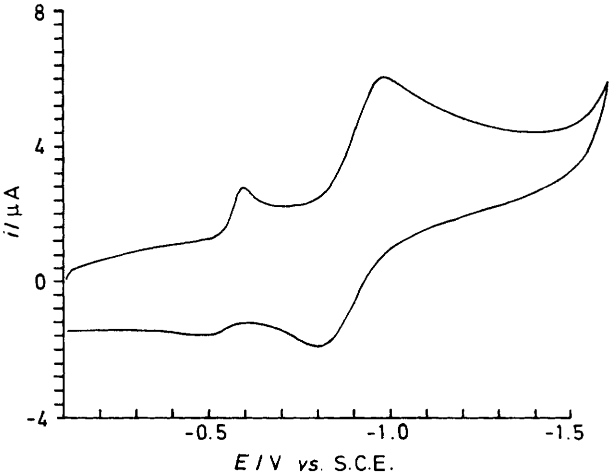


Figure 1. Cyclic voltammogram of TCPQ (**3**). Scan rate 100 mV s^{-1}.

Cyclic voltammetry of TCPQ (**3**) (Figure 1) revealed two one-electron reduction waves at −0.57 and −0.91 V [in acetonitrile/Bu_4NClO_4 *vs.* standard calomel electrode (SCE)]. These values are not in agreement with the two-electron single-wave reduction of TCAQ (**2**)‡ in the same solvent ($E_{\frac{1}{2}}$ −0.285 V).[5,7] The *X*-ray structure of TCAQ (**2**)[12] showed a highly distorted structure with the central ring in a boat form

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† All new compounds gave satisfactory microanalyses. Compound (**7**): 40% yield; m.p.: 213—215 °C (decomp.) (MeCN); i.r. (KBr): 2232, 2222, 1657, 1645, 1542, 1496, 1455, 1433, 836, 816, 749 cm^{-1}; ^1H n.m.r. (400 MHz, CD_3SOCD_3) δ: 7.32—7.20 (m, 4H, ArH), 7.17 (d, 2H, =C–H, *J* 10 Hz), 6.93 (d, 2H, =C–H, *J* 10 Hz), 3.88 (s, 2H, CH_2), 3.18 (s, 2H, CH_2); ^{13}C n.m.r. (100 MHz, CD_3SOCD_3) δ: 153.6, 143.6, 129.3, 129.2, 128.9, 127.7, 127.5, 127.3, 126.0, 113.6, 112.2, 80.2, 45.1, 39.2, 34.6, 33.7; *m/z*: 308 (100%, M^+), 281 (82, M^+−HCN), 254 (12, M^+ −2HCN), 243 (92), 216 (32), 178 (34).

Compound (**9**): m.p. 233—235 °C [DMF or tetrahydrofuran-(THF)]; i.r. (KBr): 1705, 1500, 1170, 965, 790, 755, 750 cm^{-1}; ^1H n.m.r. (90 MHz, $CDCl_3$) δ: 7.11 (br. s, 8H, ArH), 3.23—2.90 (m, 12H, CH_2, CH); *m/z*: 316 (16%, M^+), 298 (6), 280 (6), 157 (7), 142 (100), 129 (40), 115 (12).

Compound (**3**): m.p. >320 °C (DMF): u.v. ($\lambda_{max.}$ in $CHCl_3$): 249, 322, 415 nm; i.r. (KBr): 2228, 2222, 1575, 1559, 1552, 1506, 1490, 1447, 1394, 1290, 917, 785, 753 cm^{-1}; ^1H n.m.r. (400 MHz, CD_3SOCD_3) δ: 8.86 (s, 4H, ArH), 8.23—8.21 (m, 4H, ArH), 7.84—7.81 (m, 4H, ArH); ^{13}C n.m.r. (100 MHz, CD_3SOCD_3) δ: 161.56, 132.62, 130.18, 129.13, 128.35, 126.70, 114.29, 82.11; *m/z*: 404 (100%, M^+), 377 (18, M^+ −HCN), 350 (8, M^+ −2HCN), 323 (5, M^+ −3HCN).

‡ Two one-electron reduction waves ($E_{\frac{1}{2}}^1$ −0.46; $E_{\frac{1}{2}}^2$ −0.65 V) in acetonitrile have also been reported for TCAQ.[4]

and the two benzene rings in a non-coplanar position. This severe deformation from planarity was assumed to be responsible for its electrochemical behaviour;[6] it exhibits a single-wave, two-electron reduction to the dianion.

Cyclic voltammetric studies of TCPQ (**3**) indicate that it is a poorer electron-acceptor than TCNQ (**1**) ($E_{\frac{1}{2}}^1$ 00.8; $E_{\frac{1}{2}}^2$ −0.48 V)[4] and TCAQ (**2**).[7] However, the smaller difference between the midpoint potential§ for the first and second reduction of TCPQ (**3**) ($E_{\frac{1}{2}}^1 - E_{\frac{1}{2}}^2$ 0.34 V) compared with that for TCNQ (**1**) (0.56 V) suggests that the intramolecular Coulomb repulsion is reduced in TCPQ (**3**) owing to the extension of the π-system. Accordingly attempts to prepare charge transfer complexes with the electron-donor tetrathiafulvalene (TTF) have not yet succeeded. The reaction of other even stronger electron-donors with TCPQ is under investigation.

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§ As illustrated in Figure 1, the redox potential of TCPQ deviates from a typical completely reversible one-electron transfer wave.

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