11,11,12,12-Tetracyano-2,6-anthraquinodimethane (TANT) as a Novel Extensive Electron Acceptor

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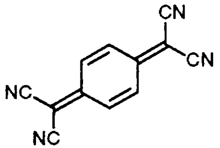
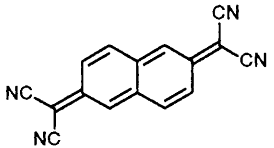
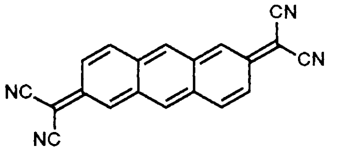
The title compound is prepared as a higher homologue in an extensively conjugated series of TCNQ (7,7,8,8-tetracyanoquinodimethane) and TNAP (9,9,10,10-tetracyano-2,6-naphthoquinodimethane); its complexes with TTT (tetrathiatetracene) and HMTTeF (hexamethylenetetratellurafulvalene) are electrically highly conductive.

Recent efforts to develop novel organic metals have been focused primarily on the design of extensively conjugated electron donors and acceptors with reduced on-site coulombic repulsion.[1] Garito and Heeger first noted its importance by comparing three electron acceptors, tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 9,9,10,10-tetracyano-2,6-naphthoquinodimethane (TNAP).[2] The small acceptor TCNE possesses nearly the same accepting ability as TCNQ and TNAP, but formed no electrically conductive complex. On the other hand, the large acceptors TCNQ and TNAP are able to form a variety of conductive complexes including TTF (tetrathiafulvalene) complexes. The reduced on-site coulombic repulsion is thus realized by insertion of an extensive conjugated quinoid system as a building block between two electron-withdrawing dicyanomethylene groups. In this regard, the further higher homologues of TCNQ and TNAP[3] are more interesting. 11,11,12,12-Tetracyano-2,6-anthraquinodimethane (TANT) is one such compound, until now unknown. The two isomeric 11,11,12,12-tetracyano-9,10-anthraquinodimethane (9,10-TCAQ)[4,5] and 1,4-anthraquinodimethane (1,4-TCAQ)[4] have been previously reported, but cannot behave as good electron


TCNQ


TNAP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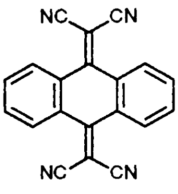
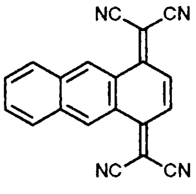
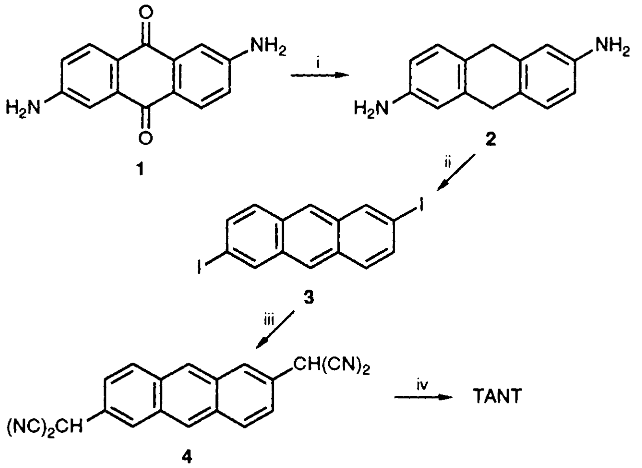

9,10-TCAQ


1,4-TCAQ



Scheme 1 *Reagents and conditions*: i, Zn, aq. NH_4OH, 90 °C, 64 h; ii, $NaNO_2$, conc. HCl, −3 °C, 10 min, then KI, 100 °C, 1 h; iii, $Pd(PPh_3)_4$, NaH, $CH_2(CN)_2$, THF, reflux, 20 h, then 10% HCl; iv, DDQ, MeCN, room temp., 1 h

Table 1 Electronic absorption data and half-wave redox potentials of TCNQ, TNAP and TANT[a,b]

Compound	λ_{max}/nm	log ε	$E_{1/2}(1)$/V	$E_{1/2}(2)$/V	ΔE/V
TCNQ	400	4.81	+0.20	−0.43	0.63
TNAP	479.5	4.97	+0.23	−0.21	0.44
TANT	576.5	4.89	+0.20	−0.12	0.32

[a] Electronic absorption spectra were measured in dichloromethane. [b] Cyclic voltammetry was carried out in benzonitrile containing 0.1 mol dm^{-3} Bu_4NClO_4 with a platinum electrode and an Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1}.

acceptors owing to nonplanarity or weak electron-accepting ability. In this paper, we report the synthesis and some properties of TANT as a novel extensive electron acceptor.

The synthesis of TANT was carried out according to Scheme 1. Reduction of commercially available 2,6-diaminoanthraquinone **1** with active zinc gave 2,6-diamino-9,10-dihydroanthracene **2** in 94% yield. The Sandmeyer reaction of **2** was accompanied by dehydrogenation to give 2,6-diiodoanthracene **3** in 20% yield. The nucleophilic substitution of **3** with dicyanomethanide in the presence of tetrakis(triphenylphosphine)palladium[6] gave 2,6-bis(dicyanomethyl)anthracene **4** in 65% yield, which was readily dehydrogenated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to afford TANT in 98% yield.

TANT is a stable, deep-green material with a melting point above 300 °C and is poorly soluble in common solvents. The infrared absorption spectrum shows nitrile vibrational frequencies at 2217 and 2208 cm^{-1}. The electronic absorption spectrum shows a strong transition at 576.5 nm, which is shifted to a much longer wavelength as compared with those of TCNQ and TNAP, reflecting further extensive conjugation of TANT (Table 1). The cyclic voltammogram of TANT shows two reversible redox waves. The first half-wave reduction potential (+0.20 V) is almost the same as the corresponding ones of TCNQ and TNAP, but the second one (−0.12 V) is higher, demonstrating the potential of TANT as a powerful electron acceptor with effective reduction of one-site coulombic repulsion. In fact, it formed deep-purple 1 : 1 complexes with tetrathiatetracene (TTT) and with hexamethylenetetratellurafulvalene (HMTTeF), both of which are highly conductive; TTT complex: 7.0 S cm^{-1}, ν_{CN} 2193 and 2179 cm^{-1}; HMTTeF complex: 11.5 S cm^{-1}, ν_{CN} 2195 cm^{-1}.†

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† Conductivities were measured on compressed pellets by a four-probe method at room temperature.