N,7,7-Tricyanoquinomethaneimines:† New Electron Acceptors for Organic Metals

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Four derivatives of the title system, which is a new class of electron acceptor, have been synthesised; cyclic voltammetric data show that these compounds undergo one- and two-electron reductions.

The study of new electron acceptors remains central to the development of organic metals,[1] and derivatives and analogues of the 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (**1**)[2] and *N*,*N'*-dicyano-*p*-quinonediimine (DCNQI) (**2**) systems are of considerable current interest. The DCNQI system (**2**) forms organic metals that do not undergo a Peierls distortion even at very low temperatures,[3] *e.g.* the copper salt of 2,5-dimethyl-DCNQI (**2a**) (1:2 stoicheiometry)[3a] has conductivity σ (3.5 K) = 5×10^5 S cm^{-1}. We now describe the first examples of the title system, TCNQI; these acceptors (**5a—c**) and (**6**) can be considered as hybrids of the TCNQ (**1**) and DCNQI (**2**) systems.††

Table 1. Cyclic voltammetric and u.v. spectroscopic data.

Compound	$E^1_{\frac{1}{2}}$	$E^2_{\frac{1}{2}}$	ΔE/V	$\lambda_{max.}$/nm[f]
(**5a**)[a]	+0.11	−0.43	0.54	387.0
(**5b**)[a]	+0.07	−0.41	0.48	387.5
(**5c**)[a]	−0.03	−0.23	0.20	358.5
(**6**)[b]	−0.43			342.0, 278.0
TMTCNQ[c]	−0.40(2e)			375[g]
TCAQ[d]	−0.29(2e)			347, 305, 283
TMDCNQI[e]	+0.05	−0.39	0.44	346
DCAQI[e]	−0.11	−0.46	0.35	322, 351

[a] This work; *vs.* Ag/AgCl, electrolyte 2×10^{-2} M $Bu_4N^+ClO_4^-$; solvent MeCN; Pt working electrode, scan rate 100 mV s^{-1}. [b] As footnote a except solvent CH_2Cl_2; scan rate 50 mV s^{-1}. [c] Ref. 2a; *vs.* Ag/$AgNO_3$ in MeCN. [d] Ref. 2c; *vs.* Ag/$AgNO_3$ in MeCN. [e] Ref. 3c; *vs.* Ag/AgCl in CH_2Cl_2. [f] Solvent: (**5a—c**), (**6**) and TCAQ,[2c] CH_2Cl_2; TMDCNQI and DCAQI, MeCN;[3b] TMTCNQ, solvent not given.[2a] [g] *Cf.* TCNQ, $\lambda_{max.}$ 393 nm; 2,5-dimethyl-TCNQ, $\lambda_{max.}$ 396 nm.[2a]

Acceptors (**5a—c**) and (**6**) are prepared in two steps from the corresponding quinone. Titanium tetrachloride-mediated Knoevenagel condensation of quinone with malononitrile‡ introduced one dicyanomethylene group affording compounds (**3**) and (**4**).[4] The cyanoimine group was then introduced by reaction of (**3**) and (**4**) with bis(trimethylsilyl)carbodiimide in the presence of titanium tetrachloride.§ Compounds (**5a—c**) and (**6**) were isolated as air-stable, orange, crystalline solids.

Table 1 compares cyclic voltammetric data and u.v. spectroscopic data for the title compounds with analogues from the TCNQ (**1**) and DCNQI (**2**) series.¶ For alkyl-TCNQI derivatives (**5a—c**) the first reduction wave was reversible for each compound (anodic–cathodic peak separation of *ca.* 60 mV established a one-electron process) while the second reduction wave was fully reversible only for compound (**5c**). The difference, ΔE, between the first and second reduction

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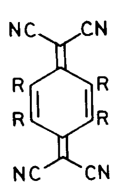
† *N*-Cyano-4-dicyanomethylenecyclohexa-2,5-dienylideneamine.

†† *Note added in proof:* Japanese workers have also now reported some derivatives of the title system (S. Iwatsuki, T. Itoh, and H. Itoh, *Chem. Lett.*, 1988, 1187).

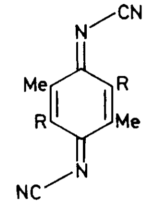
‡ Reaction conditions are essentially those described by Cowan *et al.*[2a] for the preparation of tetramethyl-TCNQ from duroquinone: *viz.* quinone, $TiCl_4$, malononitrile, and pyridine in the molar ratio 1:2.5:2.5:5 in dry CH_2Cl_2 at 20 °C under nitrogen for 24 h. Yields of compounds (**3a—c**) were 25—40% after purification by chromatography (silica column; eluent toluene). Compound (**4**) was obtained by this method, at reflux, in 10% yield.[4]

§ Reaction conditions are based on the route to DCNQIs:[3b] *viz.* compounds (**3**) or (**4**), $TiCl_4$, bis(trimethylsilyl)carbodiimide in the molar ratio 1:1.25:1.25 in dry CH_2Cl_2 at 20 °C under nitrogen for 40 h. Yields of compounds (**5a—c**) were *ca.* 80% and compound (**6**) (35%) after purification by chromatography [silica column; eluent CH_2Cl_2 for compounds (**5a—c**), eluent toluene for compound (**6**)]. Satisfactory analytical data for (**5a—c**) and (**6**) were obtained. Spectroscopic data for compound (**5b**) are representative: $\nu_{max.}$ (KBr) 2220, 2160, and 1540 cm^{-1}; δ_H ($CDCl_3$) 7.45 (1H, s), 2.58 (3H, s), 2.55 (3H, s), and 2.30 (3H, s); $\lambda_{max.}$ (CH_2Cl_2) 387.5 nm.

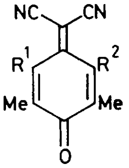
¶ 2,6-Dimethyl-TCNQ and 2,3,5-trimethyl-TCNQ are not known compounds.



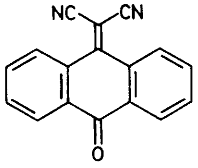
(1) a; R = H, TCNQ
b; R = Me, TMTCNQ



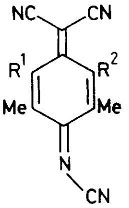
(2) a; R = H, DCNQI
b; R = Me, TMDCNQI



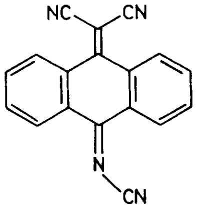
(3) a; $R^1 = R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = R^2 = Me$



(4)



(5) a; $R^1 = R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = R^2 = Me$



(6)

potentials for the tetramethyl derivative (**5c**) (0.20 V) is significantly reduced relative to dimethyl- and trimethyl-derivatives, (**5a**) and (**5b**), respectively. This behaviour for (**5c**) is intermediate between that of TMTCNQ (**1b**) (ΔE = 0.0 V)[2a] and TMDCNQI (**2b**) (ΔE = 0.44 V).[3c] This supports Cowan's assertion that the coalescence of the two reduction waves of TMTCNQ (**1b**) occurs for steric, rather than electronic, reasons: *i.e.* to relieve severe crowding in neutral (**1b**) which has a severely distorted ring skeleton.[2f] The NCN group is smaller than the $C(CN)_2$ group so steric hindrance decreases progressively along the series (**1b**), (**5c**), (**2b**), with an associated increase in the value of ΔE.

Within the alkyl-TCNQI series (**5a—c**) there is a predictable lowering of electron affinity with successive methyl substitution, and compound (**6**) is a considerably weaker acceptor than derivatives (**5a—c**). The cyclic voltammetric behaviour of (**6**) contrasts markedly with that of both the TCNQ analogue (10,10,11,11-tetracyanoanthraquinodimethane, TCAQ) and the DCNQI analogue (*N,N'*-dicyanoanthraquinonediimine, DCAQI); compound (**6**) undergoes a reversible one-electron reduction and we do not detect the dianion of (**6**), whereas, for both TCAQ[2b] and DCAQI,[3c] dianion formation is clearly observed. As yet, we do not understand this anomalous behaviour of compound (**6**).

The u.v. spectra of compounds (**5c**) and (**6**) are strikingly blue-shifted and weaker compared to compounds (**5a**) and (**5b**). This is clearly indicative of non-planar structures for (**5c**) and (**6**), but with less deviation from planarity than the respective TCNQ analogues (**1b**)[2a] and TCAQ,[2b,c] (Table 1).

We have established that the title system is suitable for the formation of crystalline charge transfer salts. Immersion of copper wire into an acetonitrile solution of acceptor (**5a**) at 20 °C under nitrogen affords a dark purple copper salt ($\nu_{max.}$ C≡N, 2210, 2150 cm^{-1}) for which analytical data fit the stoicheiometry 4 : 3 [copper : acceptor (**5a**)]. The conductivity of this salt (compressed pellet, two-probe measurement) is $\sigma_{rt} = 10^{-5}$ S cm^{-1}.

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