

Tetramethyltetracyanoquinodimethane

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Synthesis of the title compound, description of its novel single wave, two-electron reduction, and preliminary data on the electrical switching of its copper salt are presented.

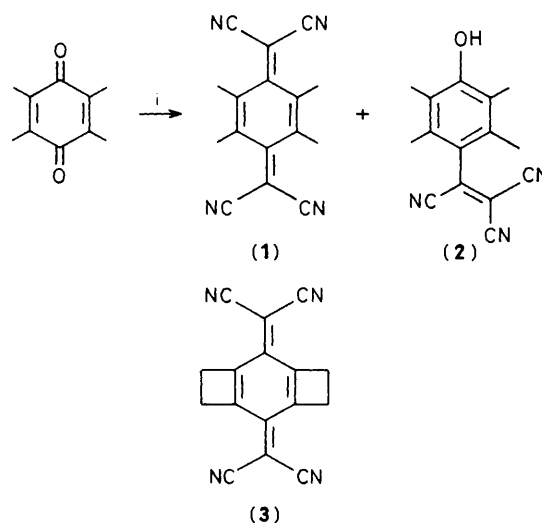
Substituent-effect induced tuning of the molecular and solid state properties of organic metals has been of interest to us as a part of our research programme.¹ For instance, methyl substitution on tetracyanoquinodimethane, TCNQ, affects electron affinities, such that band filling can be varied, as well as inter-stack interactions (because of the longer inter-stack distances), so that a nearly one-dimensional system can be obtained.

With the precedents of methyl-TCNQ^{2,4} and 2,5-dimethyl-TCNQ^{2,3,4} yielding conductive charge-transfer salts^{4,5} and copper or silver salts of 2,5-dimethyl-TCNQ favouring threshold type electrical switching phenomena,⁶ we have been pursuing the hitherto unknown tetramethyl-TCNQ (**1**), TMTCNQ, which in principle retains the full symmetry of TCNQ. Synthetic sequences that paralleled the DuPont workers' strategies^{2,3} had been unsuccessful earlier in this laboratory.⁷ We herein report the synthesis and properties of TMTCNQ and preliminary results on the electrical behaviour of the copper salt, Cu₂TMTCNQ.

The synthesis of TMTCNQ was achieved *via* the TiCl₄-mediated Knoevenagel condensation procedure of Lehnert,⁸ which was recently extended by Aumuller and Hunig⁹ for the synthesis of tetracyanoanthraquinodimethane, TCAQ, from 9,10-anthraquinone. In the absence of TiCl₄, quinones in general do not yield quinodimethanes. Formation of phenolic products and heterocyclic compounds arising from conjugate additions is well known.¹⁰ When we treated duroquinone with a mixture of TiCl₄ (2.5 equiv.), malononitrile (2.5 equiv.), and pyridine (5 equiv.) in methylene chloride at room temperature for 24 h,† TMTCNQ was obtained in *ca.* 55% yield, along with the phenolic product (**2**). The latter can be conveniently separated during workup by dilute alkali wash. Benzoquinone also reacted in a similar way. Our attempts (by varying molar ratios, temperatures, and solvents) to achieve the exclusive formation of TMTCNQ were unsuccessful.

TMTCNQ‡ appears to possess a nonplanar structure evidently owing to steric factors. Its u.v. spectrum [375 nm (ϵ 29 890), 265 (11 350), 260 (12 100)] is blue-shifted and weaker compared to TCNQ (393 nm), MeTCNQ (396 nm),² and 2,5-Me₂TCNQ (403 nm).²

Cyclic voltammetry of TMTCNQ (0.1 M Bu₄NBF₄-MeCN-Pt button) revealed only one redox wave at -0.405 V vs. Ag/AgNO₃ reference electrode. Anodic and cathodic peak separation of *ca.* 35 mV and coulometry established it to be a reversible, two-electron process. This is in sharp contrast to TCNQ, MeTCNQ, and 2,5-Me₂TCNQ, all of which exhibit two one-electron reductions (Table 1). The Meyers-Shain



i, CH₂(CN)₂, TiCl₄, pyridine, CH₂Cl₂, room temp., 24 h.

† Reaction conditions (quinone, TiCl₄, malononitrile, and pyridine in the molar ratio 1:2:20:40 in refluxing CHCl₃) described by Aumuller and Hunig (ref. 9) for TCAQ resulted in a dark, intractable polymeric material.

‡ TMTCNQ: m.p. 240–242 °C (decomp.); i.r.(KBr) 2218 cm⁻¹; ¹H-n.m.r. (CDCl₃) δ 2.38(s); ¹³C-n.m.r. (CDCl₃) δ 160.32 (s, C-1,4), 137.047 (s, C-2,3,5,6), 112.921 (s, CN), 83.394 (s, C-7,8), 18.016 (q, *J* 130.6 Hz, Me); mass spectrum, (100, M⁺); satisfactory elemental analyses were obtained.

Table 1. Cyclic voltammetric data.^a

	$E_{1/2}^{\circ}$ (1)	$E_{1/2}^{\circ}$ (2)	ΔE°
TCNQ	-0.14	-0.69	0.55
	0.08 ^b	-0.48 ^b	0.56 ^b
MeTCNQ ^c	-0.17	-0.68	0.51
Me ₂ TCNQ	-0.23	-0.71	0.48
TMTCNQ		-0.405(2e)	0.03 ^d
(3) ^b	0.04	-0.49	0.53

^a This work, vs. Ag/AgNO₃, MeCN/0.1 M Bu₄NBF₄/Pt button. ^b Ref. 14, vs. standard calomel electrode (s.c.e.), MeCN/0.1 M Et₄NBF₄/glassy carbon electrode. ^c Ref. 4, reported values vs. s.c.e., MeCN/0.1 M Bu₄NBF₄/Pt button were standardized to Ag/AgNO₃. ^d ΔE° , according to the analysis of Meyers and Shain (ref. 11).

analysis¹¹ of the cyclic voltammogram of TMTCNQ yields a value of 30 mV for $\Delta E^{\circ}(=E_1^{\circ} - E_2^{\circ})$, implying closely spaced first and second reductions, indiscernible by cyclic voltammetry. From the ΔE° , K_{SEM} was deduced to be 0.3, suggesting the presence of detectable amounts of TMTCNQ^{•-} during the reduction of TMTCNQ.¹² A weak, transient absorption band at 1080 nm appears during the electrochemical reduction after one equivalent of charge is consumed and then disappears upon complete reduction. The situation is analogous to that of TCAQ,¹³ another TCNQ derivative displaying a single wave, two-electron reduction. Furthermore, that the redox characteristics of TMTCNQ are the result of steric rather than the electronic effects of methyl substitution is borne out by a comparison with bis(ethano)TCNQ (3),¹⁴ which undergoes two single-electron reductions at potentials comparable to that of TCNQ (Table 1).

Attempts to prepare charge-transfer salts of TMTCNQ with tetrathiafulvalene, tetramethyltetrathiafulvalene, and tetramethyltetraselenafulvalene so far have been unsuccessful, indicative of its weak π -acidity. However, metallic copper reacted slowly with TMTCNQ in warm acetonitrile solution to form a dark blue film of composition Cu₂TMTCNQ. § This, to

our knowledge, is the first transition metal-TCNQ salt of a 2:1 composition formed by a spontaneous redox reaction.

Electrical contacts were made on the Cu₂TMTCNQ film following the procedure outlined earlier.⁶ Two-probe current-voltage experiments were then performed under constant current conditions. The films exhibited I - V curves characteristic of a current controlled negative resistance device with memory. Resistances ranged from 10⁷-10⁸ ohms in the high-resistance state to 10-10² ohms in the low-resistance state. Samples returned to the high-resistance state with heating. The threshold voltage was dependent upon the history of the device.

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§ Determined by elemental analysis and ESCA.