Organic Metals; Mono- and 2,5-Di-substituted 7,7,8,8-tetracyano-p-quinodimethanes and Conductivities of their Charge-transfer Complexes

By **Jan R. Andersen** * and **Ole Jørgensen**, Chemistry Department, Risø National Laboratory, DK–4000 Roskilde, Denmark

The syntheses of the electron acceptors methyl-7,7,8,8-tetracyano-p-quinodimethane (MTCNQ) (10), 2,5-di-methyl-7,7,8,8-tetracyano-p-quinodimethane (DMTCNQ) (5a), and 2,5-diethyl-7,7,8,8-tetracyano-p-quinodi-methane (DETCNQ) (5b) from commercially available starting materials are described. Purification procedures utilizing multiple recrystallizations from CH_3CN, followed by gradient sublimation, yield high quality materials for the preparation of conducting organic charge-transfer complexes based on these acceptors. Field-ionization mass spectrometry was found to be a convenient means of monitoring the impurity contents during purification. Room-temperature conductivity data for selected donor–acceptor combinations are reported, together with the electro-chemical reduction potentials of the acceptors. The latter indicate that these have slightly poorer electron-accepting properties than unsubstituted TCNQ.

IN recent years much attention has been focused on organic solids with interesting electronic properties.[1,2] The charge-transfer complex between tetrathiafulvalene (TTF)[3] and tetracyanoquinodimethane (TCNQ)[4] is the prototype of such a class of compounds, and it is probably the best known and most investigated highly conducting organic material prepared so far.

In the search for compounds with improved properties, the chemistry leading to TTF–TCNQ was expanded to yield a wide variety of new systems; however, most of the successes in terms of highly conducting macro-crystalline materials were obtained from new donors of the TTF-type with unsubstituted TCNQ.[5] Although many substituted tetracyanoquinodimethanes have been prepared,[6,7] and some of them are known to make conducting solids,[8] only those resulting from three alkylated TCNQ derivatives have been treated in any detail in the literature and, what is more important, they are still of great current interest.

The three acceptors in question are methyl-TCNQ (MTCNQ),[6] 2,5-dimethyl-TCNQ (DMTCNQ),[6,7] and 2,5-diethyl-TCNQ (DETCNQ).[7] Their special importance is due to their ability to produce highly conducting macro-crystalline charge-transfer salts with selected donors,[9–13] and also because, as a result of their sub-stituents, they push apart the separated donor and acceptor stacks characteristic of these materials, thereby decreasing the important inter-stack interactions.[14] Furthermore, MTCNQ is being widely used as an acceptor-stack dopant in order to yield information about the roles of the individual stacks.[15,16]

Although alkylated TCNQ derivatives apparently give highly conducting macro-crystalline charge-transfer salts more readily than TCNQ derivatives with other substituents, not all donor–acceptor combinations result in conducting materials, as is seen in Table 1. These changes in conductivity reflect changes in the crystal structure. The conducting materials consist of segregated,[17] uniform stacks of donor and acceptor molecules, whereas the insulating ones, as judged by their electronic spectra,[18] have mixed stacks of donors and acceptors.

Synthetic routes leading to MTCNQ, DMTCNQ, and DETCNQ have been reported, but since they are rather

incomplete[6] (or lengthy with risks of the formation of carcinogenic by-products[7]) we give here procedures that we found to be convenient, time-saving and safe, yielding high-purity products from commercially available chemicals.

TABLE 1

Four probe room-temperature conductivities ($S\ cm^{-1}$) for charge-transfer complexes based on DMTCNQ, DETCNQ, and MTCNQ [a]

	DMTCNQ	DETCNQ	MTCNQ
TTF	1 [b]	500 [c,d]	500 [c,e]
DMTTF [f]	3 [b]	1 [b]	2 [b]
TMTTF [g]	1 [b]	1 [b]	5 [b]
TSF [h]	2 [b]	800 [c,i]	6 [b]
TMTSF [j]	500 [c,k]	10^{-9} [c]	10^{-5} [c]
HMTSF [l]	10^{-9} [c]	10^{-10} [c]	
NMP [m]	$<10^{-11}$ [b]	10^{-6} [b]	10^{-8} [c]

[a] Compactions of TTF–TCNQ normally give values of 1—3 $S\ cm^{-1}$. [b] Compactions. [c] Single crystals. [d] Data from ref. 11. [e] Data from ref. 12. [f] A. N. Bloch, J. P. Ferraris, D. O. Cowan, and T. O. Poehler, *Solid State Comm.*, 1973, **13**, 753. [g] J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, *Tetrahedron Letters*, 1973, 2553. [h] E. M. Engler and V. V. Patel, *J. Amer. Chem. Soc.*, 1974, **96**, 7376; E. M. Engler, B. A. Scott, S. Etemad, T. Penney, and V. V. Patel, *J. Amer. Chem. Soc.*, 1977, **99**, 5909. [i] Data from ref. 13. [j] K. Bechgaard, D. O. Cowan, and A. N. Bloch, *J.C.S. Chem. Comm.*, 1974, 937. [k] Data from ref. 9. [l] A. B. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle, R. H. Banks, and T. O. Poehler, *Phys. Rev. Letters*, 1975, **34**, 1561. [m] NMP is N-methylphenazinium.

RESULTS AND DISCUSSION

DMTCNQ and DETCNQ were prepared starting from 2,5-bis(ethoxycarbonyl)cyclohexane-1,4-dione (1) as out-lined in Scheme 1. Alternately, (1) can be synthesized by base-catalysed condensation of 2 mol of diethyl succinate;[19] if desired, the alkylation can be achieved by adding the appropriate alkyl iodide directly to the reaction mixture[9,13] to give (2), although in lower yields than when pure (1) is employed as starting material. We found that the alkylation of (1) proceeded most smoothly when the milder K_2CO_3–acetone–alkyl iodide reagent mixture was used. A mixture of two isomers is obtained in both cases [(2a) and (2b)], the ester groups probably being *cis* or *trans* with respect to the cyclo-hexane ring. After saponification and decarboxylation, no signs of isomerism are observed. The condensation of (3) with malononitrile is extremely sluggish when

compared to the analogous reaction of unsubstituted cyclohexane-1,4-dione, which takes place with an almost explosive violence; this is probably connected with the spatial extent of the alkyl groups, see below.

Scheme 2 shows the synthetic route followed to obtain MTCNQ starting from toluhydroquinone (6).[6] Again, Claisen conditions were chosen for the alkylation step because of their convenience and the purity of the product. A Birch reduction followed by treatment of acid gave the desired methylcyclohexane-1,4-dione (8), which in turn was converted to the TCNQ analogue in the usual manner. The indication of steric hindrance observed for the dialkylated TCNQ derivatives is corroborated by the finding that the condensation to give (9) proceeds in two steps: a very fast one yielding the intermediate 4-dicyanomethylene-2-methylcyclo-hexanone [as determined by field ionization (f.i.) mass spectrometry] followed by a much slower step giving (9).

As expected, the alkylated TCNQ derivatives are poorer acceptors, at least as judged by electrochemical measurements, than the unsubstituted parent compound. A comparison of their reduction potentials is given in Table 2. The ' anomalous ' value of the second reduction potential of MTCNQ may be due to a difference in solvation caused by the small, permanent dipole moment of this species.

It has been argued that the purity of the constituents may have important consequences for the properties of the resulting charge-transfer complexes,[20] hence a careful purification of the substituted TCNQ derivatives is necessary. Multiple recrystallizations from CH$_3$CN
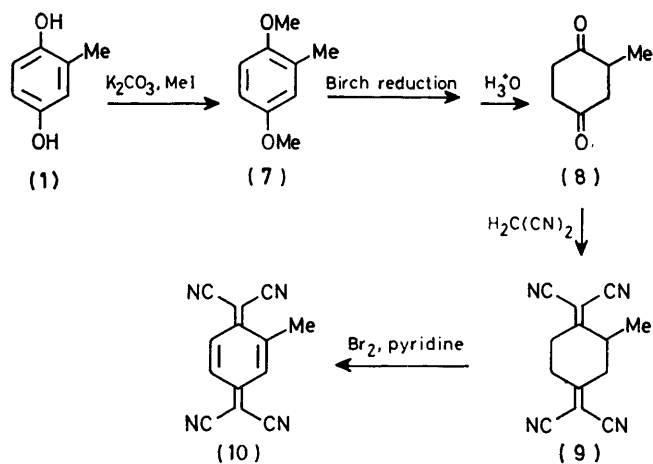
SCHEME 1

(until no increase in m.p. is observed), followed by one or more gradient sublimations [21] onto an inert material such as Teflon or Kapton, brings the impurity level below the detection limit of electron impact (e.i.) mass spectrometry, which in our experience is the most sensitive method for observing impurities in these acceptors,* as only few and rather low-intensity frag-

* E.i. mass spectrometry was also used in ref. 7 for determining the nature of impurities in TCNQ derivatives.
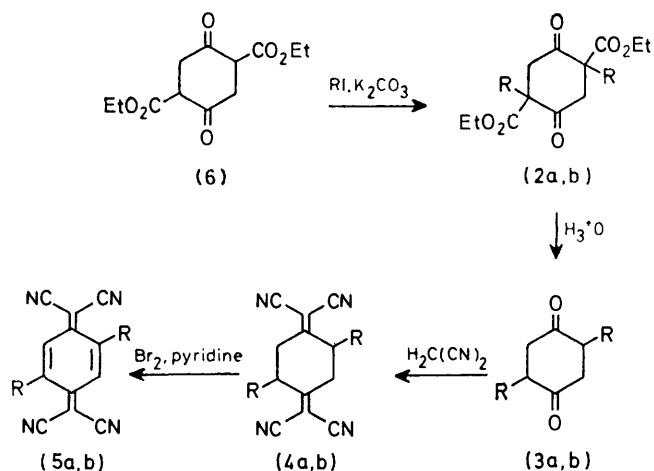
SCHEME 2

ment ions are observed in their spectra.† During the clean-up procedure, f.i. mass spectrometry provides a convenient means of monitoring impurities, since it gives directly the molecular ions of all substances in the sample without any fragmentation.[22]

TABLE 2

Half-wave reduction potentials (V vs. the s.c.e.) as deter-mined by cyclic voltammetry at a Pt-button electrode in CH$_3$CN–[Bu$^n_4$N][BF$_4$] (0.1M)

	TCNQ	MTCNQ	DMTCNQ	DETCNQ
$E_{\frac{1}{2}}^1$	0.190	0.170	0.110	0.120
$E_{\frac{1}{2}}^2$	−0.350	−0.340	−0.350	−0.365

EXPERIMENTAL

The mass spectra (m.s.) were measured with a Varian MAT CH-5 instrument equipped with a combined e.i., f.i., and field desorption ion source. The samples were intro-duced in gold crucibles by the direct inlet system. The conditions for e.i. were electron voltage 70 eV, ionizing current 100 μA, ion source temperature 200 °C, probe temperature 20—150 °C, resolution approximately 1 000. The f.i. spectra were recorded using a 10 μm tungsten wire activated in benzonitrile vapour as emitter.

The ^{1}H n.m.r. spectra were recorded for CDCl$_3$ solutions with a JEOL PMX 60 instrument using tetramethylsilane as internal standard. The compounds (4a, b), (5a, b), (9), and (10) were too insoluble for an n.m.r. spectrum to be obtained. M.p.s were measured on a Büchi SMP 20 and are uncorrected. All compounds gave satisfactory ele-mental analysis (±0.3% for C, H, and N), which are given in Supplementary Publication SUP 22580 (2 pp.).‡

2,5-Bis(ethoxycarbonyl)-2,5-dimethylcyclohexane-1,4-dione (2a).—A slurry of 2,5-bis(ethoxycarbonyl)cyclohexane-1,4-dione (1) (0.125 mol) (Fluka-Buchs, Switzerland), finely divided anhydrous K$_2$CO$_3$ (0.18 mol), methyl iodide (0.30

† The mass spectra of TCNQ, MTCNQ, DMTCNQ, and DETCNQ have been deposited with the Mass Spectrometry Data Centre, UKCIS, The University, Nottingham N67 2RD.
‡ For details see Notice to Authors No. 7, J.C.S. Perkin I, 1978, Index issue.

mol), and dry acetone (150 ml) was refluxed for 20 h. The reaction mixture was then allowed to cool, filtered, and evaporated to dryness. The residue was redissolved in $CHCl_3$ (100 ml), washed with water (2 × 100 ml), dried (Na_2SO_4), concentrated *in vacuo*, and the resulting oil was treated with hexane–ether (3 : 1) at 0 °C and the solid formed filtered off. Recrystallization from hexane gave (2a) (isomer (1) as colourless prisms in 30% yield, m.p. 71—72 °C; δ 4.16 (q, 2 H, *J* 7 Hz), 3.15 and 2.76 (AB quartet, 2 H, *J* 15 Hz), 1.40 (s, 3 H), and 1.25 (t, 3 H, *J* 7 Hz).

The second isomer was separated from the remaining oil by t.l.c. [silica, benzene–ethyl acetate (9 : 1)] to give a 20% yield of a colourless oil; δ 4.19 (q, 2 H, *J* 7 Hz), 3.47 and 2.60 (AB quartet, 2 H, *J* 15 Hz), 1.40 (s, 3 H), and 1.25 (t, 3 H, *J* 7 Hz); the mass spectra of the isomers were identical; *m/e* 284 (26%), 238 (29), 211 (47), 210 (48), 164 (100), 142 (27), 137 (48), 114 (42), 113 (52), 87 (22), 86 (28), and 69 (98).

2,5-Bis(ethoxycarbonyl)-2,5-diethylcyclohexane-1,4-dione (2b).—The alkylation reagent was ethyl iodide, but otherwise the same procedure as above was followed. Methylcyclohexane was employed for the trituration and recrystallization; yield 35%, colourless needles, m.p. 68—70 °C (mixture of isomers). When (2b) was prepared by base-catalysed condensation of diethyl succinate followed by direct alkylation of the crude product,[13,19] only one isomer was obtained after work-up, yield 10%, m.p. 80—81 °C; δ 4.18 (q, 2 H, *J* 7 Hz), 3.15 and 2.70 (AB quartet, 2 H, *J* 15 Hz), 1.97 (multiplet, 2 H), 1.24 (t, 3 H, *J* 7 Hz), and 0.90 (t, 3 H, *J* 7 Hz).

By subtracting the spectrum of the pure isomer from that of the mixture melting at 68—70 °C, the n.m.r. data of the other isomer was obtained: δ 4.15 (q, 2 H, *J* 7 Hz), 3.27 and 2.58 (AB quartet, 2 H, *J* 15 Hz), 1.97 (multiplet, 2 H), 1.24 (t, 3 H, *J* 7 Hz), and 0.90 (t, 3 H, *J* 7 Hz); the mass spectra of the two isomers were identical; *m/e* 312 (21%), 239 (34), 238 (44), 192 (100), 165 (28), 164 (25), 155 (17), 128 (18), 127 (33), 100 (17), 83 (46), and 55 (61).

2,5-Dimethylcyclohexane-1,4-dione (3a) *and* *2,5-Diethylcyclohexane-1,4-dione* (3b).—(2a) or (2b) (0.1 mol) was treated with a mixture of 4M H_2SO_4 (500 ml) and ethanol (50 ml) at reflux for 48 h. When cold, the reaction mixture was extracted with ether (2 × 100 ml), and the combined extracts were washed with water (2 × 100 ml), dried (Na_2SO_4), and evaporated to dryness. Recrystallization afforded the pure products. (3a), yield 60%, colourless needles, m.p. 92—93 °C (H_2O); δ 2.66 (m, 1 H) and 1.12 (d, 1 H, *J* 6 Hz); *m/e* 141 (8%), 140 (96), 125 (51), 71 (27), 70 (51), 69 (45), 56 (18), 55 (45), 43 (14), 42 (100), 41 (39), and 39 (24). (3b), yield 90%, colourless prisms, m.p. 49—50 °C (hexane); δ 2.63 (m, 3 H), 1.70 (m, 2 H), and 0.97 (t, 3 H, *J* 7 Hz); *m/e* 168 (42%), 140 (33), 139 (100), 111 (11), 85 (10), 84 (8), 83 (30), 69 (10), 56 (40), 55 (63), 41 (28), and 39 (10).

1,4-Bis(dicyanomethylene)-2,5-dimethylcyclohexane (4a) *and* *1,4-Bis(dicyanomethylene)-2,5-diethylcyclohexane* (4b).—(3a) or (3b) (50 mmol) was mixed with malononitrile (0.1 mol), water (15 ml), and β-alanine (0.2 g), and then heated to 110 °C for 12 h with stirring. The resulting thick slurry was allowed to cool to ambient and was washed with water and ether. Filtration and drying *in vacuo* gave the crude products as off-white powders in 100% yield, purified by recrystallization to constant melting point; (4a), yield 75%, colourless prisms, m.p. 250—253 °C (DMF) (lit.,[6] 180—

235 °C); *m/e* 236 (30%), 235 (18), 221 (28), 208 (13), 194 (16), 171 (16), 145 (100), 131 (30), 119 (16), 118 (25), 78 (14), and 39 (14). F.i.–m.s. indicated no impurities above the detection limit (*ca.* 0.1%). (4b), yield 85%, colourless prisms, m.p. 214—216 °C [DMF–H_2O (4 : 1)]; *m/e* 264 (56%), 249 (39), 236 (37), 235 (59), 233 (37), 208 (33), 173 (100), 146 (44), 145 (89), 132 (38), 131 (58), and 42 (56). F.i.–m.s. indicated a content of *ca.* 1% of a mono-ethylated species.

DMTCNQ (5a) *and* *DETCNQ* (5b).—(4a) or (4b) (25 mmol) was suspended in CH_3CN (100 ml), and Br_2 (50 mmol) was added. The suspension was cooled with ice, and a solution of pyridine (0.1 mol) in CH_3CN (10 ml) was slowly added. The cooling agent was removed, and the reaction was then stirred for 18 h. Ice-cold water (150 ml) was then slowly added and stirring was continued for 3 h, after which the precipitate was filtered off and washed with water followed by ether. The crude products were purified by multiple recrystallizations from CH_3CN followed by gradient sublimation onto Kapton. The latter purification step was necessary as f.i.–m.s. indicated that a common impurity (the dihydro-TCNQ derivative) cannot be removed by crystallization. After a typical purification procedure of four recrystallizations and two gradient sublimations, the yields were 30—50% of pale yellow crystals with a pink sheen. DMTCNQ, m.p. 283—284 °C (lit., 265—267,[6] 277—279 °C[7]); *m/e* 233 (17%), 232 (100), 231 (14), 206 (14), 205 (88), 204 (16), 179 (9), 178 (39), 165 (11), 151 (11), 89 (6), and 39 (7). DETCNQ, m.p. 176—177 °C (lit.,[7] 174—175 °C); *m/e* 260 (100%), 232 (49), 231 (88), 206 (74), 205 (41), 193 (21), 179 (51), 178 (41), 166 (26), 164 (21), 153 (20), and 140 (24).

1,4-Dimethoxy-2-methylbenzene (7).—Toluhydroquinone (6) (0.1 mol), finely divided anhydrous K_2CO_3 (1.0 mol), and methyl iodide (1.0 mol) were refluxed in dry acetone (100 ml) for 24 h, after which the reaction mixture was filtered. The acetone was evaporated off and the crude product redissolved in ether (200 ml) and washed with 2M NaOH (200 ml portions) until the water phase was colourless. The organic phase was dried (Na_2SO_4) and the solvent evaporated. Distillation (0.8 mmHg, 56—58 °C) gave (7), 80% yield, as a slightly yellow oil; δ 6.74 (s, 1 H), 3.76 (s, 1 H), 3.74 (s, 1 H), and 2.30 (s, 1 H).

2-Methylcyclohexane-1,4-dione (8).—(7) (0.16 mol) was dissolved in a mixture of absolute ethanol (60 ml), dry ether (80 ml), and liquid NH_3 (600 ml). Sodium (1.0 mol) was cautiously added in small lumps over a period of 20 min. When the blue colour disappeared, NH_4Cl (1.5 mol) was added, and the ammonia was then allowed to evaporate. The residue was treated with boiling 4M HCl (500 ml) for 1 h, cooled to ambient temperature, and extracted with $CHCl_3$ (3 × 100 ml). The $CHCl_3$ phase was dried (Na_2SO_4) and the solvent evaporated to yield the crude product as an off-white solid, which was recrystallized from pentane–ether (4 : 1) to give (8) as colourless flakes, 60% yield, m.p. 48—49 °C; δ 2.79 (s, 6 H), 2.72 (d, 1 H, *J* 6 Hz), and 1.20 (d, 3 H, *J* 6 Hz); *m/e* 127 (8%), 126 (100), 111 (46), 83 (11), 71 (10), 69 (21), 56 (91), 55 (28), 43 (15), 42 (46), 41 (25), and 39 (19).

1,4-Bis(dicyanomethylene)methylcyclohexane (9).—The same procedure was used as for (4), but with only 1 h reaction time. The crude product was purified by recrystallization from DMF–H_2O (1 : 1) to give colourless needles, m.p. 199—201 °C (lit.,[6] 185—194 °C), yield 80%; *m/e* 222 (9%), 221 (11), 207 (9), 195 (7), 194 (11), 157 (14), 132 (11), 131 (100), 130 (10), 104 (9), 77 (8), and 39 (8).

F.i.–m.s. showed a low content (*ca.* 0.5%) of 4-dicyano-methylene-2-methylcyclohexanone.

MTCNQ (10).—To a suspension of (9) (0.1 mol) in CH_3CN (350 ml) was added Br_2 (0.2 mol). The mixture was cooled to −15 °C, pyridine (0.4 mol) was added over 20 min, and the reaction mixture was then stirred at ambient temperature for 24 h. Ice-cold water (200 ml) was added and the precipitate filtered off, washed with water and ether, and dried *in vacuo*. The crude yellow-green powder was purified by multiple recrystallizations from CH_3CN, followed by gradient sublimation onto Kapton, to yield pure MTCNQ, pale yellow chunks, m.p. 201—202 °C (lit.,[6] 200—201 °C for a sublimed sample); *m/e* 219 (10%), 218 (63), 192 (14), 191 (100), 190 (8), 165 (8), 164 (38), 163 (5), 137 (5), 87 (5), 75 (6), and 63 (5).

In some preparations the crude material obtained failed to dissolve in CH_3CN. For some unknown reason, the preparation resulted in a probably polymeric analogue of MTCNQ. However, this material could be cracked by boiling in *o*-dichlorobenzene to give monomeric MTCNQ, which was then purified as described above.

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