JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 1, 275–280 (1988)

2,3:5,6-BIS(ETHYLENEDITHIO)- AND BIS(TRIMETHYLENEDITHIO)-N,N′-DICYANOQUINONEDIIMINES AS NEW ELECTRON ACCEPTORS

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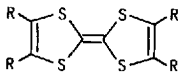
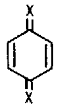
ABSTRACT

In order to examine the substituent effect of ethylenedithio and trimethylenedithio groups on electron acceptors, the two title compounds were prepared in one step from the corresponding quinones. These species behave as weak π-electron acceptors owing to the electronic and sterical effects of the fused groups. Only the bis(ethylenedithio) derivative formed a charge-transfer complex with tetrathiotetracene, which showed a moderate electric conductivity of $2\cdot0 \times 10^{-2}$ S cm^{-1}. In addition, both species oxidized copper, sodium, and potassium iodides to give the corresponding deeply colored metal salts, most of which were semiconductive. The naphtho analogs were similarly studied, but hardly served as electron acceptors.

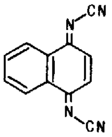
The discovery of a highly conducting charge-transfer complex of 1,1′,3,3′-tetrathiafulvalene (TTF) (**1**) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) (**3**) has led to the dramatic development of new electron donors and acceptors which behave similarly. Of them, 4,5:4′,5′-bis(ethylenedithio)-1,1′,3,3′-tetrathiafulvalene (BEDT-TTF) (**2**) has been a topical donor since the appearance of superconductivity in some of its radical cation salts.[1] The superior conductivity is mainly attributable to intermolecular sulfur-sulfur interactions of the fused ethylenedithio groups in the crystal structures. This has stimulated us to study a similar molecular modification on typical acceptors such as TCNQ and N,N′-dicyano-1,4-benzoquinonediimine (DCNQI) (**4**). DCNQI and its naphtho analog (**5**) were recently developed by Aumüller and Hünig and have aroused wide interest because they formed extraordinarily conductive complexes.[2,3,4]



1, R = H
2, R,R = SCH_2CH_2S



3, X = $C(CN)_2$
4, X = N–CN



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0894–3230/88/050275–06$05.00
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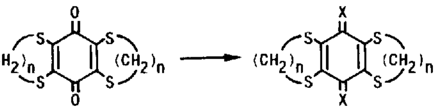
Received 25 February 1988
Revised 14 March 1988

RESULTS AND DISCUSSION

We have first designed the synthesis of 2,3:5,6-bis(ethylenedithio)-7,7,8,8-tetracyanoquinodimethane (**8**) using a modern synthetic method of TCNQ.[5] However, a direct condensation of 2,3:5,6-bis(ethylenedithio)-1,4-benzoquinone and malononitrile induced by $TiCl_4$ was unsuccesful. On the other hand, a similar treatment of 2,3-(ethylenedithio)-1,4-naphthoquinone (**11**) led to the formation of 2,3-(ethylenedithio)-11,12-tetracyano-1,4-naphthoquinodimethane (**13**) in 22% yield together with half-substituted compound (**16**) in 30% yield. The non-formation of **8** as well as the low yield of **13** are attributable to steric hindrance accompanied by the introduction of the dicyanomethylene function. In sharp contrast, the introduction of the less bulky cyanoimine function is very favorable.

Scheme 1

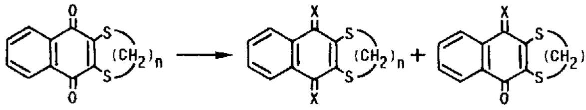


6, n = 2
7, n = 3

8, n = 2, X = C(CN)$_2$ 0%
9, n = 2, X = N–CN 85%
10, n = 3, X = N–CN 28%

2,3:5,6-Bis(ethylenedithio)-N.N′-dicyano-1,4-benzoquinonediimine (BEDT–DCNQI) (**9**) and 2,3-(ethylenedithio)-N,N′-dicyano-1,4-naphthoquinonediimine (**14**) like the parent compounds **4** and **5** were thus obtained in excellent yields from quinones **6** and **11**, respectively. In addition, 2,3:5,6-bis(trimethylenedithio)-N,N′-dicyano-1,4-benzoquinonediimne (BTDT–DCNQI) (**10**) and its naphtho analog (**15**) were similarly prepared. The low yield (28%) of **10** from **7** seems to reflect another sterical problem of the more bulky trimethylenedithio group than the ethylenedithio group. Very small amounts of the half-substituted compounds **17** and **18** were also isolated as by-products of **14** and **15**, respectively.

Scheme 2



11, n = 2
12, n = 3

13, n = 2, X = C(CN)$_2$ 22%
14, n = 2, X = N–CN 86%
15, n = 3, X = N–CN 77%

16, n = 2, X = C(CN)$_2$ 30%
17, n = 2, X = N–CN 2%
18, n = 3, X = N–CN trace

DCNQI (**4**) can take two configurations of *syn* and *anti* as to the mutual orientation of the cyano group,[2] while N,N′-dicyano-1,4-naphthoquinonediimine (**5**) takes only one *syn* configuration, where both cyano groups are directed to the opposite site of the *peri* hydrogens.[3,6] The present symmetrical compounds **9** and **10** presumably maintain the same stereochemistry as **4**, though there is no evidence for it. Unsymmetrical compounds **14** and **15** like **5** favor a *syn* configuration, but the cyano groups are directed to the *peri* hydrogen rather than the sulfur sites. This was confirmed by observation of an anisotropic effect of the cyano group on the *peri*-hydrogen signals (δ 9·01 of **14** and δ 8·84 of **15**) in their NMR spectra as compared to that (δ 8·34) of **5**.

The cyclic voltammograms of all the present DCNQI acceptors exhibit two reversible redox waves. As shown in Table 1, the first half-wave reduction potentials of **9** and **10** relative to DCNQI **4** are rather lower, but the second one higher. This is also the case for **14** and **15** relative to **5**. The ethylenedithio and trimethylenedithio groups apparently exert an electron releasing effect as opposed to the substituent effect in BEDT–TTF,[7] so as to retard the first reductions. On the other hand, the steric effects prompt the second reductions because the resulting dianions can be strain-free. The severe sterical requirement of the dicyanomethylene group of **13** especially favors the formation of dianion, causing a coalescence of the first and second reduction waves.

Table 1. Half-wave redox potentials[a]

Acceptor	$E_{1/2}$ (1)/V	$E_{1/2}$ (2)/V
3	+0·25	−0·47
4	+0·30	−0·35
5	+0·13	−0·43
9	+0·19	−0·23
10	+0·22	−0·20
13	0·0	
14	+0·05	−0·36
15	+0·02	−0·36

[a] vs. Ag/AgCl in dichloromethane.

In addition to the decreasing electron affinity and the increasing steric hindrance, the less solubilities of the present DCNQI derivatives tend to make their π-complexation difficult. They, unlike parent DCNQI (**4**) and naphtho analog (**5**), formed no crystalline complexes with TTF. Only BEDT–DCNQI (**9**) could form a 1:2 charge-transfer complex with a stronger donor, tetrathiotetracene (TTT), whose electric conductivity was relatively high, 2·0 × 10^{-2} S cm^{-1} (Table 2). On the other hand, both BEDT–DCNQI (**9**) and BTDT–DCNQI (**10**) could readily oxidize copper(I) iodide to form the black copper salts consisting of 1:1 composition of copper and acceptor, whose conductivities were, however, low. Both species also reacted with sodium iodide and potassium iodide to give deeply colored complexes which were semi-conductive or nearly insulating. Only the Na and K salts of BEDT-DCNQI (**9**) were characterized to take 1:1 composition. All the naphtho compounds (**13**), (**14**), and (**15**) have too weak electron affinities to oxidize such metal iodides. Thus, treatments of **14** and **15** with copper(I) iodide precipitated black semi-conductive materials, which corresponded to simply co-ordinated complexes with compositions of **14**·Cu_2Cl_2 and **15**·Cu_2Cl_2 respectively.

EXPERIMENTAL

NMR spectra were determined on a JEOL PMX-60 or FX-90A spectrometer, MS spectra on a Shimazu QP-1000A spectrometer at 70 eV, and IR spectra on a Hitachi 260-30

Table 2. Complexation of acceptors **9**, **10**, **14**, and **15**

Complex	Appearance	D.P. /°C	Found (Calculated)/% C	H	N	$\nu_{C\equiv N}$ /cm^{-1}	Conductivity[a] /S cm^{-1}
9·(TTT)$_2$	greenish black powder	>300	55·01 (55·36)	2·30 (2·32)	5·15 (5·38)	2095	$2{\cdot}0 \times 10^{-2}$
9·Cu	black powder	238	35·69 (36·03)	2·20 (2·20)	13·53 (14·01)	2140	$9{\cdot}7 \times 10^{-7}$
10·Cu	black powder	>300	40·37 (39·19)	2·89 (2·82)	10·75 (13·06)	2129	$6{\cdot}4 \times 10^{-10}$
14·Cu$_2$I$_2$	black powder[b]	>300	25·12 (25·62)	1·25 (0·92)	8·10 (8·53)	2149	$1{\cdot}8 \times 10^{-5}$
15·Cu$_2$I$_2$	black powder[b]	222	27·61 (26·33)	1·51 (1·47)	7·28 (8·19)	2120	$3{\cdot}0 \times 10^{-7}$
9·Na	pale brown powder	117	40·40 (40·10)	3·31 (2·24)	14·88 (15·59)	2136	$3{\cdot}8 \times 10^{-8}$
9·K	pale brown powder	197	37·72 (38·38)	2·29 (2·15)	14·25 (14·92)	2135	$3{\cdot}5 \times 10^{-6}$

[a] The electric conductivities of all complexes except **9**·(TTT)$_2$ were measured on a compressed pellet by a two probe method at room temperature. The conductivity of **9**·(TTT)$_2$ was determined by use of a four probe method.
[b] Beilstein test was positive.

spectrophotometer. Cyclic voltammetry was made at 100 mV s^{-1} scan rate in 2 mol m^{-3} dichloromethane solution with tetrabutylammonium perchlorate as supporting electrolyte by a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator using a Ag/AgCl reference electrode, a glassy carbon working electrode, and a platinum counter electrode.

Quinones 6, 7, 11, and 12.

The preparations of these quinones were carried out by a modification of the synthetic method of **11** reported by Hahn and Wojciechowski.[8]

2,3:5,6-Bis(ethylenedithio)-1,4-benzoquinone (**6**) was obtained by refluxing a mixture of chloranil (7·38 g, 30 mmol), sodium carbonate (12·19 g, 115 mmol), and 1,2-ethanedithiol (7·1 cm^3, 75 mmol) in ethanol (550 cm^3) for 5 h. The mixture was concentrated in vacuo, and the residue was extracted with dichloromethane using a Soxhlet extractor. After evaporation, the extract was recrystallized from chlorobenzene to give green fine crystals of **6**, yield 4·33 g (50%), mp>300°C (lit.,[9] mp 314–315°C); ^{1}H-NMR (CDCl$_3$) δ = 3·24 (s); IR (KBr) 1620 cm^{-1} (C=0); MS *m/z* 288 (M$^+$). Calculated for $C_{10}H_8O_2S_4$: C, 41·65; H, 2·80%. Found:C, 41·63; H, 2·78%.

2,3:5,6-Bis(trimethylenedithio)-1,4-benzoquinone (**7**) was similarly obtained by treatment of chloranil with 1,3-propanedithiol, yield 80%, green needles from chlorobenzene, mp>300°C; ^{1}H-NMR (CDCl$_3$) δ = 2·11 (4H, quint, J = 6·0 Hz), 3·55 (8H, t, J = 6·0 Hz); IR (KBr) 1624 cm^{-1} (C=O). Calculated for $C_{12}H_{12}O_2S_4$: C, 45·54; H, 3·82%. Found: C, 45·51; H, 3·80%.

2,3-(Ethylenedithio) and 2,3-(trimethylenedithio)-1,4-naphthoquinones (**11**) and (**12**) were obtained by a similar treatment of 2,3-dichloro-1,4-naphthoquinone (85 mmol) with the corresponding alkanedithiol (163 mmol) in refluxing butanol (700 cm^3) containing potassium carbonate (163 mmol). **11**: yield 92%, dark red needles from butanol, mp 241–242°C (lit.,[8] mp 241–241·5°C); ^{1}H-NMR ($CDCl_3$) δ = 3·27 (4H, s), 7·51–7·81 (2H, m), 7·87–8·17 (2H, m); IR (KBr) 1642 cm^{-1} (C═O). Calculated for $C_{12}H_8O_2S_2$: C, 58·04; H, 3·25%. Found: C, 58·00; H, 3·17%. **12**: yield 83%, reddish brown needles from ethanol, mp 148°C; ^{1}H-NMR ($CDCl_3$) δ = 2·16 (2H, quint, J = 6·6 Hz), 3·63 (4H, t, J = 6·6 Hz), 7·53–7·81 (2H, m), 7·93–8·16 (2H, m); IR (KBr) 1653 cm^{-1} (C═O); MS *m/z* 229 (M^+). Calculated for $C_{13}H_{10}O_2S_2$: C, 59·52; H, 3·84%. Found: C, 59·62; H, 3·81%.

Dicyanoquinonediimines 9, 10, 14, and 15.

Titanium tetrachloride (1·8 cm^3, 16·4 mmol) and bis(trimethylsilyl)carbodiimide (2·33 g, 12·5 mmol) were successively added into a stirred suspension of quinone **6** (0·15 q, 0·50 mmol) in dry dichloromethane (240 cm^3) under nitrogen. The mixture was allowed to react at room temperature for 4 days, quenched with water, and extracted with a large amount of dichloromethane. The extract was dried ($MgSO_4$), concentrated, and recrystallized from chlorobenzene to give copper-colored crystals of 2,3:5,6-bis(ethylenedithio)-N,N′-dicyano-1,4-benzoquinonediimine (**9**), yield 85%. mp>300°C; ^{1}H-NMR ($CDCl_3$) δ = 3·347 (s); IR (KBr) 2136 cm^{-1} (CN). Calculated for $C_{12}H_8N_4S_4$: C, 42·84; H, 2·40; N, 16·65%. Found: C, 42·85; H, 2·33; N, 16·63%.

2,3:5,6-Bis(trimethylenedithio)-N,N′-dicyano-1,4-benzoquinonediimine (**10**) was similarly prepared from quinone **7**, yield 28%, copper-colored crystals from acetonitrile, mp>300°C; ^{1}H-NMR ($CDCl_3$) δ = 2·167 (4H, quint. J = 6·0 Hz), 3·567 (8H, t, J = 6 Hz); IR (KBr) 2130 cm^{-1} (CN). Calculated for $C_{14}H_{12}N_4S_4$: C, 46·13; H, 3·32; N, 15·37. Found: C, 46·13; H, 3·06; N, 15·08%.

2,3-(Ethylenedithio)- and 2,3-(trimethylenedithio)-N,N′-dicyano-1,4-naphthoquinonediimine (**14**) and (**15**) were similarly prepared from the corresponding naphthoquinones **11** and **12**. The reactions were complete within 12 h at room temperature. The work-up was carried out by addition of a large amount of pentane into the reaction mixtures followed by recrystallization of the resulting deposit from acetonitrile. **14**: yield 86%, deep blue crystals, mp>300°C; ^{1}H-NMR ($CDCl_3$) δ = 3·352 (4H, s), 7·82 (2H, m), 9·01 (2H, m); IR(KBr) 2159 cm^{-1} (CN); MS *m/z* 296 (M^+). Calculated for $C_{14}H_8N_4S_2$: C, 56·74; H 2·72; N, 18·90%. Found: C, 56·64; H, 2·68; N, 18·73%. **15**: yield 77%, dark blue columns, mp 197–198°C; ^{1}H-NMR ($CDCl_3$) δ = 2·193 (2H, quint, J = 6·1 Hz), 3·678 (4H, t, J = 6·1 Hz), 7·79 (2H, m), 8·84 (2H, m); IR (KBr) 2152 cm^{-1} (CN). Calculated for $C_{15}H_{10}N_4S_2$: C, 58·04; H, 3·25; N, 18·05%. Found: C, 58·04; H, 3·24; N, 18·05%. The half-substituted compounds **17** and **18** were obtained from column chromatography of these mother liquors on silica gel with 1:1 benzene-hexane. **17:** yield 1·9%, deep violet crystals from acetonitrile, mp 203°C; ^{1}H-NMR ($CDCl_3$) δ = 3·31 (4H, s), 7·50–7·87 (2H, m), 8·00–8·27 (1H, m), 8·87–9·10 (1H, m); IR (KBr) 1636 (CO), 2155 (CN) cm^{-1}; MS *m/z* 272 (M^+). Calculated for $C_{13}H_8N_2OS_2$: C, 57·33; H, 2·96; N, 10·29%. Found: C, 57·03; H, 2·80; N, 9·49%. **18:** a trace amount of yield, blue needles from acetonitrile, mp 239–240°C; ^{1}H-NMR ($CDCl_3$) δ = 2·17 (2H, quint, J = 5·9 Hz), 3·62 (2H, t, J = 5·9 Hz), 3·67 (2H, t, J = 5·9 Hz), 7·55–7·85 (2H, m), 7·95–8·25 (1H, m), 8·75–9·00 (1H, m); IR (KBr) 1645 (CO), 2157 (CN) cm^{-1}; MS *m/z* 286 (M^+). Calculated for $C_{14}H_{10}N_2OS_2$: C, 58·72; H, 3·52; N, 9·78%. Found: C, 58·66; H, 3·43; N, 9·50%.

2,3-(Ethylenedithio)-9,9 10,10-tetracyano-1,4-naphthoquinone (13) and 2,3-(ethylenedithio)-4-dicyanomethylene-1,4-dihydro-1-naphthalenone (16)

Titanium tetrachloride (0·3 cm^3) was slowly added over a period of 5 min into a suspension of quinone **11** (123 mg, 0·5 mmol) and malononitrile (92 mg, 1·4 mmol) in dry dichloromethane (20 cm^3) at ice-cooling under nitrogen. The dry pyridine (0·9 cm^3) was added over a period of 6 min. The mixture was stirred at room temperature for one day and concentrated in vacuo. The residue was treated with 10% hydrochloric acid, and the insoluble solid was chromatographed on silica gel with 1:2 benzene-hexane to give firstly compound **13** (38 mg, 22%) and secondly **16** (45 mg, 30%). **13:** deep purple powder from acetonitrile, mp>300°C; ^1H-NMR ($CDCl_3$) δ = 3·474 (4H, s), 7·67 (2H, m), 8·18 (2H, m); IR (KBr) 2225 cm^{-1} (CN); MS *m/z* 344 (M^+). Calculated for $C_{18}H_8N_4S_2$: C, 62·77; H, 2·34; N, 16·27%. Found: C 62·60; H, 2·30; N, 15·83%. **16:** purplish red powder from acetonitrile, mp 247°C (dec.); ^1H-NMR ($CDCl_3$) δ = 3·396 (4H, s), 7·56–7·78 (2H, m), 8·00–8·23 (2H, m); IR (KBr) 1649 (CO), 2223 (CN) cm^{-1}; MS *m/z* 296 (M^+). Calculated for $C_{15}H_8N_2OS_2$; C, 60·79; H, 2·72; N, 9·45%. Found: C, 60·76; H, 2·62; N, 9·39%.

Complexation

The **9** $(TTT)_2$ complex was formed by an equimolar mixing of both components in hot chlorobenzene solution. The copper complexes were prepared by mixing hot acetonitrile and solutions of the acceptor and copper iodide except complexation of **9** in hot benzonitrile. The sodium and potassium complexes were also prepared by mixing the hot chlorobenzene solution of the acceptor with the hot acetonitrile solution of NaI or KI . All these deeply colored complexes precipitated out immediately or on cooling in a refrigerator, and were collected by filtration.

ACKNOWLEDGEMENTS

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 62550635 from the Ministry of Education, Science and Culture, Japan and Mazda Science Foundation's Research Grant.

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