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PREPARATION AND PROPERTIES OF TETRACYANOQUINODIMETHANS FUSED WITH PYRAZINE UNITS

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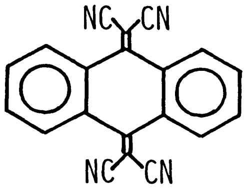
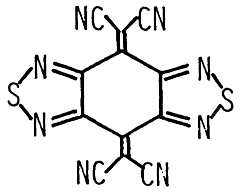
The title compounds were prepared by a $TiCl_4$-catalyzed condensation reaction of corresponding quinones with malononitrile. The data of the cyclic voltammogram show that the anion radicals of dipyrazino-TCNQ derivatives are thermodynamically stable. The anion radical salts were isolated.

Since tetracyanoanthraquinodimethan (TCNAQ) and its derivatives are nonplanar molecules due to the steric interaction between the dicyanomethylene groups and peri-hydrogen atoms,1) their charge-transfer complexes with donors are insulators.2) In contrast, bis-1,2,5-thiadiazolo-TCNQ (BTDA-TCNQ) having no peri-hydrogen atoms forms highly conductive complexes with some donors.3) For the same reason, dipyrazino-TCNQ and its derivatives are expected to form conductive complexes with donors. We report here the preparation and properties of dipyrazino-TCNQ derivatives 1a,b and pyrazino-tetracyanonaphthoquinodimethans (pyrazino-TCNNQ) 2a-c.

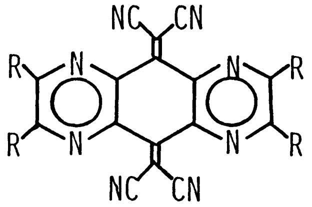
New acceptors 1a,b and 2a-c4) were synthesized by a $TiCl_4$-catalyzed condensation reaction of corresponding quinones 35) and 46) with malononitrile (Table 1). The cyclic voltammograms of these new acceptors showed reversible two waves and the reduction potentials are summarized in Table 2 along with those of TCNQ, TCNAQ and BTDA-TCNQ which were measured under the same conditions. The first reduction potentials of acceptors get higher as the benzene rings are substituted



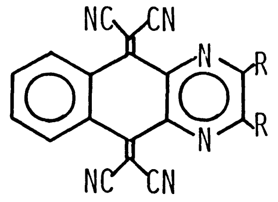
TCNAQ



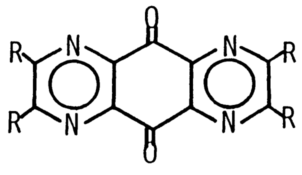
BTDA-TCNQ



dipyrazino-TCNQ
1a; R=Me
1b; R=Ph



pyrazino-TCNNQ
2a; R=H
2b; R=Me
2c; R=Ph



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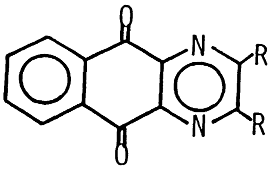

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Table 1. Yields and decomposition points of dipyrazino-TCNQs 1 and pyrazino-TCNNQs 2, and reaction conditions for the formation of 1 and 2

Compd	Decomp./°C	Yield/%[a)]	Reaction temp./°C	Reaction time/h
1a	>200	50	-30, -10	3, 3
1b	336-340	72	-30	5
2a	>260	13	-10	3.5
2b	>230	35	-10	7
2c	292-294	80	-10	9

a) Isolated yields in the reaction of quinones 3 and 4 with malononitrile.

Table 2. Reduction potentials[a)] and semiquinone formation constants K_{sem}[b)] of acceptors

Compd	1a	1b	2a	2b	2c	TCNQ	TCNAQ	BTDA-TCNQ
E_1	-0.10	+0.10	-0.23	-0.27	-0.22	+0.18	-0.37	-0.22
E_2	-0.54	-0.38	-0.32	-0.39	-0.31	-0.36	-	-0.49
$\log K_{sem}$	7.59	6.72	1.55	2.07	1.55	9.31	-0.03	8.10

a) 0.1 mol dm^{-3} Et_4NClO_4 in MeCN, Pt electrode, scan rate 100 mV s^{-1}, V vs. SCE. b) $\log K_{sem}$ values were calculated as $(E_1-E_2)/0.058$.

for the pyrazine rings (TCNAQ < **2** < **1**) which reflects the electron attracting property of the pyrazine ring. And the reduction potentials of **1b** are nearly the same values with those of BTDA-TCNQ. The semiquinone formation constants K_{sem} which are also shown in Table 2 indicate that the anion radicals of **1a**,**b** are thermodynamically stable, whereas those of **2a**-**c** are unstable. This result shows that **2a**-**c** still have the steric interaction between the dicyanomethylene groups and peri-hydrogen atoms which is observed in the case of TCNAQ. The anion radical salt of **1a** was isolated as the Na^+ salt including water [Na^+**1a**$^{\bar{\cdot}}$·$\mathrm{2H_2O}$, mp >400 °C, IR (KBr) 2172 cm^{-1} (CN), UV (MeCN) nm (log ε) 672(4.52), 614(3.92), 604(3.81,sh), 402(4.36), 380(4.32,sh), 366(4.33), 322(4.29), 238(4.38)]$^{7)}$ by the reaction of **1a** with NaI in acetonitrile. It should be noted that the electrical resistivity of the salt (ρ 1.3 x 10^2 Ω cm)$^{8)}$ is lower than that of the sodium salt of TCNQ$^{\bar{\cdot}}$.$^{9)}$ The anion radical of **1b** was also isolated as the tetraethylammonium salt including acetonitrile [$\mathrm{Et_4N}^+$(**1b**)$_2^{\bar{\cdot}}$·MeCN, decomp. 261-262 °C, IR (KBr) 2165 cm^{-1} (CN), UV (MeCN) nm (log ε) 702(4.63), 632(4.12), 580(4.02,sh), 430(4.59,sh), 392(4.95), 375(4.88,sh), 263(4.81), 249(4.29)]$^{7)}$ by the reaction of **1b** with $\mathrm{Et_4NI}$ in acetonitrile.

Dipyrazino-TCNQ **1a** gave charge-transfer complexes with BEDT-TTF (1:1, decomp. >250 °C, IR (KBr) 2197 cm^{-1} (CN))$^{10)}$ and TMTTF (1:1, decomp. 250-260 °C, IR (KBr) 2198 cm^{-1} (CN))$^{10)}$ whereas complexes of **1b** with donors could not be obtained probably due to the steric interaction of phenyl groups. The resistivities of BEDT-TTF-**1a** and TMTTF-**1a** complexes measured as compaction pellets at room temperature are 2.0 x 10^{10} Ω cm and 4.3 x 10^7 Ω cm, respectively. These high values may be attributed to the low reduction potential of **1a** resulting in the small degree of the charge transfer from donor to **1a**, which is suggested from the CN stretching frequencies of the complexes.

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3) Y. Yamashita, T. Suzuki, T. Mukai, and G. Saito, J. Chem. Soc., Chem. Commun., **1985**, 1044; Y. Yamashita, T. Suzuki, G. Saito, and T. Mukai, Chem. Lett., **1985**, 1759.

4) These structures were confirmed by elemental analyses and the following spectral data. **1a**; IR (KBr) 2204 cm^{-1} (CN), UV (MeCN) nm (log ε) 398(4.60), 382(4.53,sh), 318(4.44), 307(4.25,sh), 262(3.81,sh), 238(4.27). **1b**; IR (KBr) 2220 cm^{-1} (CN), UV (MeCN) nm (log ε) 435(4.37,sh), 398(4.56), 295(4.30), 239 (4.59), 216(4.52). **2a**; IR (KBr) 2216 cm^{-1} (CN), UV (MeCN) nm (log ε) 350 (4.36), 295(4.05). **2b**; IR (KBr) 2213 cm^{-1} (CN), UV (MeCN) nm (log ε) 352 (4.40), 296(4.29), 218(4.34). **2c**; IR (KBr) 2212 cm^{-1} (CN), ^{1}H-NMR ($CDCl_3$) δ_{ppm} 7.2-7.5 (2H,m), 7.6-8.0 (6H,m), 8.5-8.7 (2H,m), UV (MeCN) nm (log ε) 370(4.49), 318(4.35), 277(4.20,sh), 227(4.54), 216(4.54).

5) Quinones **3a** (R=Me) and **3b** (R=Ph) are new compounds which were prepared by a condensation reaction of tetraaminobenzoquinone with biacetyl and benzil, respectively. **3a**; decomp. 326-327 °C, IR (KBr) 1695 cm^{-1} (CO), ^{1}H-NMR ($CDCl_3$) δ_{ppm} 2.87 (s), UV (MeCN) nm (log ε) 303(4.36), 281(4.31), 228(4.38), 226(4.38,sh). **3b**; decomp. 403-410 °C, IR (KBr) 1705 cm^{-1} (CO), UV (MeCN) nm (log ε) 363(4.48), 275(4.29), 262(4.29,sh), 255(4.34,sh), 251(4.34), 223 (4.69), 218(4.68,sh).

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7) The molar ratios were determined on the basis of the elemental analyses.
Na^+**1a**$^{\cdot-}\cdot 2H_2O$, Found: C, 57.08; H, 4.03; N, 25.93%. Calcd for $NaC_{20}H_{12}N_8\cdot 2H_2O$: C, 56.70; H, 3.81; N, 26.47%.
Et_4N^+(**1b**)$_2^{\cdot-}\cdot$MeCN, Found: C, 77.40; H, 4.49; N, 18.19%. Calcd for $C_{88}H_{60}N_{17}\cdot CH_3CN$: C, 77.40; H, 4.55; N, 18.05%.

8) The resistivity was measured as a compaction pellet at room temperature by a two-probe technique.

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10) BEDT-TTF; bis(ethylenedithio)tetrathiafulvalene ($E_{1/2}^{ox}$ +0.45 V).
TMTTF; tetramethyltetrathiafulvalene ($E_{1/2}^{ox}$ +0.24 V).

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