

Novel Quinone-type Acceptors fused with Sulphur Heterocycles and their Highly Conductive Complexes with Electron Donors

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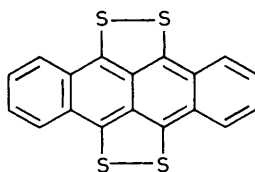
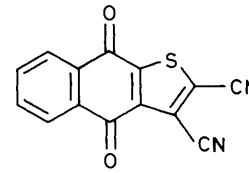
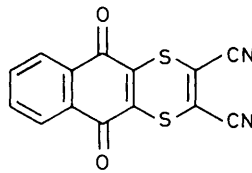
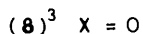
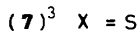
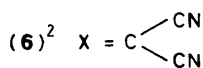
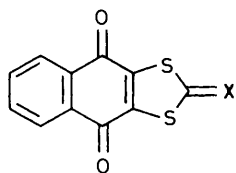
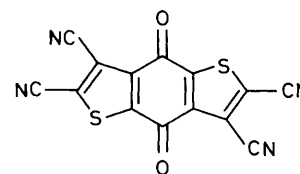
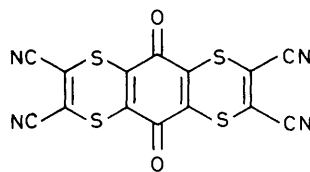
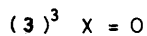
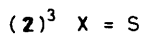
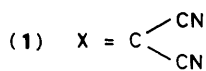
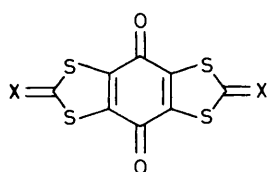
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p-Benzoquinone derivatives fused with sulphur-containing heterocycles are strong electron acceptors and some of their charge transfer complexes with electron donors show high electrical conductivities.

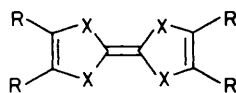
Electron acceptors containing sulphur atoms¹ are rare and of interest since the inter-stack interaction in the complex states which suppresses the Peierls-transition may be increased by the incorporation of sulphur atoms. On the other hand, 1,3-dithiol rings have not been used as electron acceptor moieties, probably because TTF (tetrathiafulvalene) and its derivatives containing 1,3-dithiol rings are well known as electron donors. We have found that 1,3-dithiol rings substituted with electron withdrawing groups have good electron affinities. We report here the properties of *p*-benzoquinones fused with sulphur-containing heterocycles such as 1,3-dithiols.

Quinone (**1**) (m.p. > 397 °C) was synthesized by oxidation of the corresponding hydroquinone.² Quinones (**2**)—(**10**) were synthesized according to the literature.^{2–4} The reduction potentials measured by cyclic voltammetry are shown in Table 1. The first reduction potentials of *p*-benzoquinone, naphtho-

quinone, anthraquinone, chloranil, and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) measured under the same conditions are -0.53, -0.71, -0.95, +0.01, and +0.51 V vs. s.c.e., respectively. This result shows that the sulphur-heterocycles work as strong electron-withdrawing rings. It should be noted here that quinones (**1**)—(**5**) fused with bis-heterocycles are stronger electron acceptors than chloranil. The semiquinone formation constants shown in Table 1 indicate that the anion radicals of (**1**)—(**10**) are thermodynamically stable. In fact, reactions of (**1**), (**2**), (**4**), and (**5**) with iodides such as *N*-methylpyridinium (NMPy⁺) iodide gave the corresponding anion radical salts [λ_{max} of the NMPy⁺ salts (MeCN), NMPy⁺-(**1**)⁻ 476 nm (log ϵ 4.16), 465 (4.14), 444 sh (4.09), 384 (4.78), 369 sh (4.56), 308 (3.89), 277 (4.10), 267 (4.02), 261 (3.99), 232 (4.35), 220 sh (4.25); NMPy⁺-(**2**)⁻ 489 (4.05), 443 (4.10), 387 (4.75), 319 sh (3.64), 305 sh (3.70), 278 (4.06), 266 (4.09), 259 (4.12), 255 sh (4.10), 237 (4.28), 215 (4.25);




TTT




TTF; R = H, X = S

TMTTF; R = Me, X = S

TMTSF; R = Me, X = Se

BEDT-TTF; R,R = , X = S

BMDT-TTF; R,R = , X = S

TTM-TTF; R = SMe, X = S


DBTTF; R,R = , X = S

Table 1. Reduction potentials^a and semiquinone formation constants of quinones.

Quinone	E_1/V	E_2/V	$\log K_{sem}^b$
(1)	+0.30	-0.44	12.96
(2)	+0.14	-0.60	12.76
(3)	+0.05	-0.70	12.93
(4)	+0.27	-0.39	11.38
(5)	+0.04	-0.66	12.07
(6)	-0.28	-0.93	11.21
(7)	-0.37	-1.05	11.72
(8)	-0.42	-1.10	11.72
(9)	-0.23	-0.81	10.00
(10)	-0.41	-1.12	12.24

^a 0.1 M Et₄NClO₄ in MeCN, Pt electrode, scan rate: 100 mV s⁻¹; E vs. standard calomel electrode (s.c.e.). ^b $\log K_{sem}$ values were calculated as $(E_1 - E_2)/0.058$.

Table 2. Electrical resistivities^a of the complexes^b of quinones with donors.

Donor/Quinone	(1)	(2)	(4)	(5)
TTT	4.4×10^2	9.9	2.5×10^5	1.8×10^2
TTF	1.3×10^4	7.0×10^4	7.2×10^3	1.7×10^3
TMTTF	3.5×10^3	5.7×10	1.2×10^4	3.2×10^5
TMTSF	1.1	2.4	3.0×10^2	— ^c
BEDT-TTF	1.3×10^3	2.1×10^4	4.7×10^3	— ^c
BMDT-TTF	1.0×10^3	2.2×10^3	7.1×10^3	— ^c
TTM-TTF	2.0×10	4.5×10^5	9.7	— ^c
DBTTF	4.1×10^4	3.1×10^6	10	— ^c

^a Measured at room temperature on compressed pellets by two-probe technique. The electrical resistivity of the TTF-tetracyanoquinodimethane (TCNQ) complex measured by this method was 0.37. ^b 1 : 1 molar ratios based on elemental analyses. ^c No attempt.

NMPy⁺-(**4**)⁻ 764 (3.81), 466 (3.57), 267 sh (4.37), 256 (4.42), 238 (4.41), 220 (4.32); NMPy⁺-(**5**)₂⁻ 736 (3.56), 430 (3.81), 405 (3.83), 357 sh (3.79), 296 (4.70), 281 (4.74), 269 sh (4.69), 216 (4.46)]. Quinones (**1**), (**2**), (**4**), and (**5**) gave charge transfer complexes with electron donors. The electrical resistivities of the complexes are shown in Table 2. Some of the complexes show high electrical conductivities, indicating that quinones (**1**), (**2**), and (**4**) are promising electron acceptors to form organic metals.

Received, 9th June 1986; Com. 785

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