

Preparation and Properties of a Tetracyanoquinodimethane fused with 1,2,5-Thiadiazole Units

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Bis[1,2,5]thiadiazolo-tetracyanoquinodimethane (**1**) was prepared and found to form a highly conductive complex with tetrathianaphthacene.

There have been several recent reports on 11,11,12,12-tetracyanoanthraquinodimethane (TCNAQ).¹ TCNAQ is a dibenzo analogue of tetracyanoquinodimethane (TCNQ) and was expected to form conductive complexes with electron donors. However, the charge transfer complexes of TCNAQ and its derivatives with donors were found to be insulators because of the non-planar structure of TCNAQ and its derivatives resulting from the steric interaction between the dicyanomethylene groups and peri-hydrogen atoms.² In order to overcome this disadvantage, we have substituted 1,2,5-thiadiazole rings having no peri-hydrogen atoms for the benzene rings. Bis[1,2,5]thiadiazolo-TCNQ (BTDA-TCNQ) (**1**) seems to have several advantages in forming highly conductive complexes with donors. First, (**1**) is planar and symmetrical. Secondly, the thiadiazole rings can stabilize the anion radical of (**1**) by conjugation as well as by the resonance contribution (**2**) generating a new aromatic sextet. Thirdly, heteroatoms in the thiadiazole rings may increase the interaction between the outside and the inside of the stack in the complex. Finally, (**1**) is more easily prepared than substituted

TCNQ derivatives.³ We report the preparation and properties of (**1**) and [1,2,5]thiadiazolo-tetracyanonaphthoquinodimethane (TDA-TCNNQ) (**3**) which provides a useful comparison with (**1**).

BTDA-TCNQ (**1**) (decomp. 375–380 °C) was synthesized by a TiCl₄-catalysed condensation reaction of 4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]bis[1,2,5]thiadiazole-4,8-dione⁴ with malononitrile in 72% yield. TDA-TCNNQ (**3**) (decomp. 276–277 °C) was similarly prepared by the reaction of naphtho[2,3-*c*] [1,2,5]thiadiazole-4,9-dione⁵ with malononitrile in 55% yield. Although (**1**) and (**3**) are stable both in solid state and in solution, they are labile towards silica gel or alumina. The half-wave reduction potentials of (**1**) and (**3**) were measured by cyclic voltammetry, and the semiquinone formation constants K_{sem} were calculated using these values. The data summarized in Table 1 indicate that the anion radical of (**1**) is thermodynamically as stable as the TCNQ anion radical, while the reduction potentials of (**3**) are lower than those of (**1**) and its anion radical is unstable. This can be attributed to the non-planar structure of (**3**) due to steric interactions between

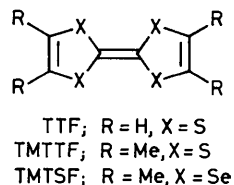
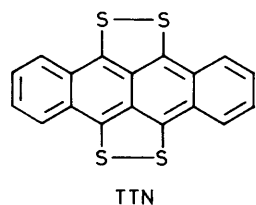
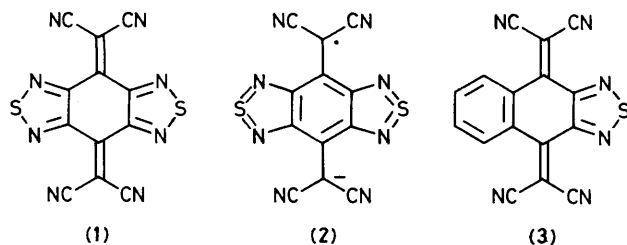


Table 1. Reduction potentials^a and semiquinone formation constants of acceptors.

Acceptor	E_1/V	E_2/V	$\log K_{sem}$
BTDA-TCNQ (1)	-0.02	-0.49	8.10
TDA-TCNQ (3)	-0.21	-0.38	2.93
TCNQ	+0.18	-0.36	9.31
TCNAQ ^b	-0.37		-0.03

^a 0.1 mol dm⁻³ Et₄NClO₄ in MeCN, platinum electrode, scan rate: 100 mV s⁻¹; E vs. standard calomel electrode. ^b Ref. 2.

the dicyanomethylene groups and the peri-hydrogen atoms of the benzene ring. The anion radical of (1) was isolated as the Li⁺, Na⁺, and K⁺ salts by reaction of (1) with LiI, NaI, and KI, respectively, in dry acetonitrile [λ_{max} of the Li⁺ salt (MeCN) 631 (log ϵ 4.53), 575 (4.18), 529 (3.78), 376 (4.12), 350 (4.19), 306 (4.42), 242 (3.93), and 235 sh (3.90) nm]. On the other hand, the anion radical salt of (3) could not be

Table 2. Decomposition points and electrical resistivities^a of complexes^b of BTDA-TCNQ (1) with donors.

Donor	Decomp./°C	ρ/Ω cm
TTN	>400	0.14—0.15 ^c
TTF	247—248	2.49×10^7 ^d
TMTTF	245—246	7.33×10^8 ^d
TMTSF	253—259	1.98×10^7 ^d

^a The electrical resistivities were measured as compacted samples at room temperature. ^b 1:1 molar ratios, based on elemental analyses. ^c Four-probe technique. The electrical resistivity of the TTF-TCNQ complex measured by this method was 0.19. ^d Two-probe technique.

obtained although new peaks [λ_{max} (MeCN) 642, 484, and 466 nm] slowly appeared on reaction of (3) with NaI.

As expected, BTDA-TCNQ (1) gave molecular complexes with electron donors. The electrical resistivities of the complexes shown in Table 2 indicate that the complex of (1) with TTN is highly conductive, while the complexes of (1) with TTF and its analogues exhibit low conductivities. This finding seems to indicate that the conductivities of the complexes of (1) with donors depend on the molecular sizes of donors as well as their oxidation potentials.⁶

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