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Preparation and Properties of Tetrathio-derivatives of Quinodimethanes Fused to a 1,2,5-Thiadiazole Unit and Related Heterocycles

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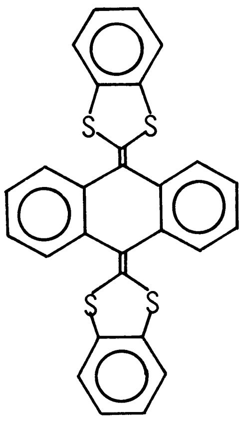
Wittig-Horner reaction of 2-dimethoxyphosphinyl-1,3-benzodithiole with 1,4-benzoquinones fused to a 1,2,5-thiadiazole unit and related heterocycles gave a new type of donors which show reversible two-electron oxidation waves and formed conductive complexes with iodine and DDQ.

Recently bis(1,3-dithiole) donors containing quinodimethane structures have received considerable attention since the cation radical states are stabilized by formation of a new aromatic sextet as well as extended conjugation.[1)] In this connection, anthraquinodimethane **1** is an interesting donor. Although the preparation is reported,[2)] the properties have not been described. **1** seems to be a nonplanar molecule due to the steric interaction caused by the peri-hydrogens as found in tetracyanoanthraquinodimethane (TCNAQ).[3)] The steric interaction in TCNAQ has been removed by the replacement of the benzene rings with 1,2,5-thiadiazole rings.[4)] It seems also possible to remove the steric interaction in donor **1** by the replacement to give mono-substituted derivative **2a** and bis-substituted derivative **3a**. Another advantage of the replacement is that S---N interactions can be expected in **2a** and **3a**, which lead to high-dimensional structures in their complexes and ion radical salts.[5)] From these viewpoints, we have prepared donors **2a**, **3a**, and related heterocycles **2b**, **3b**, and investigated their properties.

Bis(1,3-dithiole) donors seem to be prepared by the Wittig reaction of the corresponding diones, which is the most straight-forward and simple method, however such methods have not been used except for the preparation of **1**. We have succeeded in preparing the donors **2** and **3** by using the Wittig-Horner reaction. Thus, the reaction of 2-dimethoxyphosphinyl-1,3-benzodithiole[2),6)] (**4**) with naphtho[2,3-c][1,2,5]thiadiazole-4,9-dione[7)] in the presence of n-BuLi gave **2a** (mp 367-370 °C) in 90% yield with a small amount of ketone **5a** (mp 289-291 °C). The similar reaction of naphtho[2,3-c][1,2,5]selenadiazole-4,9-dione[8)] gave **2b** (mp 345-347 °C) in 69% yield with a small amount of ketone **5b** (mp 281-283 °C). The ketones **5a,b** were mainly obtained when one equivalent of the Wittig reagent was used. Ketone **6** (mp 186-189 °C) was also obtained along with **1** in the reaction of **4** with anthraquinone. Bis-substituted derivative **3a** (mp >400 °C) and **3b** (mp 376-



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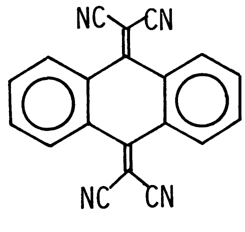
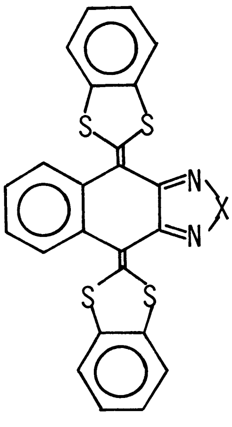
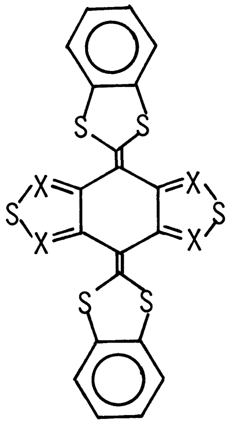


TCNAQ



2a; X=S
2b; X=Se



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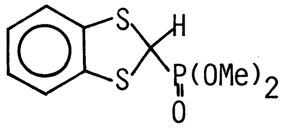
3b; X=CH



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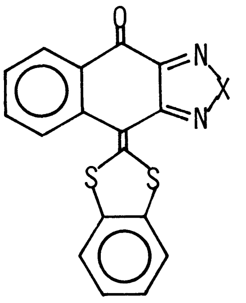
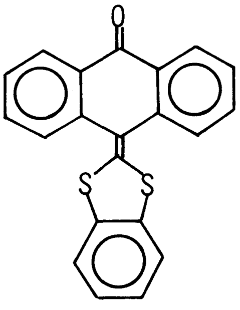


5a; X=S
5b; X=Se



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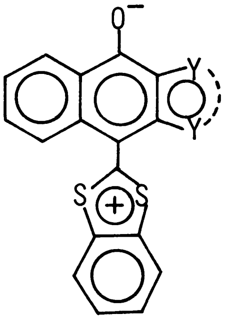

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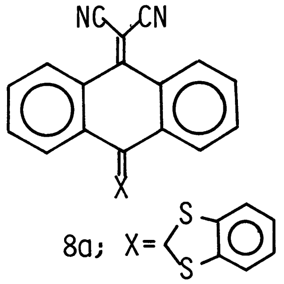
Table 1. Absorption maxima in the electronic spectra

Compoud	λmax/nm (logε) in CH_2Cl_2
1	237(4.85), 348(4.29), 398sh(4.42), 415(4.19)
2a	235(4.58), 360(4.21), 422(4.64)
2b	233(4.57), 305(4.19), 414(4.60)
3a	240sh, 257sh, 302, 380sh, 400, 420
3b	248(4.60), 335sh(4.36), 374(4.59)
5a	254(4.42), 280sh(4.24), 306sh(3.97), 404(4.39), 480(4.01)
5b	252(4.29), 266sh(4.26), 322(4.01), 334sh(3.99), 407(4.42), 492(3.59)
6	248(4.67), 272sh(4.18), 347(3.95), 452(4.19)
8a	251(4.49), 320(4.28), 520(3.91)



8a; X=
8b; X=O

Table 2. Decomposition points, molar ratios,a) and electrical resistivities, ρ,b) of complexes of donors **1**, **2**, and **3** with iodine and DDQ

	I complex			DDQ complex		
Donor	Decomp/°C	Ratio	ρ/Ω cm	Decomp/°C	Ratio	ρ/Ω cm
1	302-305	1:5.9	$>10^8$	360-363	0.5:1:H_2O	8.8×10^7
2a	300-310	1:2.6	8.1×10	>300	0.7:1	1.4×10^2
2b	343-346	1:2.6	1.8×10^2	>230	0.7:1	4.8×10^2
3b	>400	1:2.6	3.5×10		---c)	

a) Determined on the basis of elemental analyses. b) Measured by a two-probe technique on compaction samples. c) No attempt.

378 °C) were also prepared by the similar reaction of the corresponding quinones8,9) in 50% and 38% yields, respectively. These results show that the Wittig-Horner reaction of 2-dimethoxyphosphinyl-1,3-benzodithiole with 1,4-benzoquinones fused to aromatic rings provides a useful method to prepare highly-conjugated bis(1,3-dithiole) donors.

The absorption maxima in the electronic spectra of the bis(1,3-dithiole) donors **1**, **2a**,**b**, **3a**,**b**, and ketones **5a**,**b**, **6** are shown in Table 1. The absorptions of the ketones are red-shifted as compared with those of the corresponding bis(1,3-dithiole) donors. This can be attributed to the contribution of the dipolar structure **7**. For a comparison, dicyanomethylene compound **8a** (mp > 250 °C), which is considered to be more polarized, was synthesized by the reaction of **4** with **8b**, and was found to have an absorption maximum at 520 nm.

The cyclic voltammetry of **1**, **2a**, and **2b** in acetonitrile10) showed reversible two-electron oxidation waves at 0.39, 0.65, 0.70 V vs. SCE, respectively, indicating that Coulombic repulsion is decreased in the dications of these conjugated molecules. Two-electron oxidation waves are also observed in analogous bis(1,3-dithiole) donors with a naphthalene1f) or 1,6-methano[10]annulene moiety.1d) The higher values in **2a** and **2b** reflect the electron withdrawing property of a 1,2,5-thiadiazole ring and a 1,2,5-selenadiazole ring.11) On the other hand, the oxidation potential of **3b** in dichloromethane was 0.78 V vs. SCE (irreversible).12)

Anthraquinodimethane (**1**) formed complexes with iodine and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) whose electrical resistivities are high as shown in Table 2. On the other hand, heterocycles **2a** and **2b** gave better conductive complexes with iodine and DDQ than **1**, in which the molar ratios are also different from those of the complexes of **1**. In addition, electrochemical oxidation of a solution containing **2a** or **2b** (10^{-3} mol dm^{-3}) and tetraethylammonium perchlorate (0.06 mol dm^{-3}) in dichloromethane using platinum electrodes at 10 μA/cm^2 gave perchlorate salts of the cation radicals. The molar ratios were 1:1.2 (**2**:ClO_4^-) in both salts based on elemental analyses, indicating that these are novel salts in which the dication states are involved.[13] The electrical resistivities of these salts of **2a** and **2b** were 7.1×10^2 and 7.4×10^2 Ω cm, respectively.

In the case of bis-substituted derivative **3a**, the low solubility in solvents prevented the study on complexes with acceptors. However, the iodine complex of bisthieno derivative **3b** exhibited higher conductivity as shown in Table 2, indicating that the bis-substituted derivatives of **1** are promising electron donors to provide highly conductive compounds.

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10) Measured at a platinum electrode with 0.1 mol dm^{-3} of tetraethylammonium perchlorate as a supporting electrolyte; scan rate 100 mV s^{-1}.

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12) The oxidation potential of **3b** could not be measured in acetonitrile due to the low solubility. The irreversible potential was calculated as E_{pa} (anodic peak potential) - 0.03. That of **1** in dichloromethane was 0.68 V vs. SCE (irreversible). That of **3a** could not be measured even in dichloromethane due to the low solubility.

13) The salts were obtained as fine black needles and the analytical data were reproducible.

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