Organic Metals: Synthesis and Properties of Bis-(1,3-benzodithiole-2-ylidene)ethane [Bi-(benzo-1,3-dithiafulven-6-yl)]

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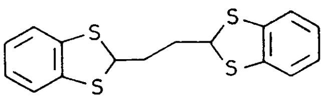
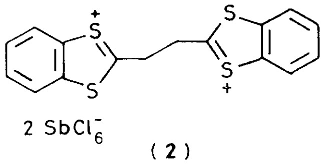
The synthesis and properties of the new electron donor (**3**) are described; it forms a 1 : 1 complex with tetracyano-*p*-quinodimethane (TCNQ) that is metallic at room temperature.

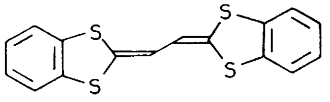
Since the discovery of high electrical conductivity in the charge-transfer complex of tetrathiafulvalene and tetracyano-*p*-quinodimethane (TTF–TCNQ) there has been continued great interest in the design and synthesis of new organic metals.[1] The preparation of new donors analogous to TTF[2] has received added impetus with the recent discovery of superconductivity in salts of tetramethyltetraselenafulvalene (TMTSeF).[3] We now report the preparation and some properties of the dimer (**3**),† a vinylogue of dibenzo-TTF. Compound (**3**) was designed as a donor with a similar electronic state to dibenzo-TTF but incorporating the desirable features of more widely spaced sites of maximum spin, and a certain amount of disorder due to rotation about the central C–C bond. It has recently been stressed that in metallic complexes the periodic distortions of the lattice responsible for metal to insulator transitions could be destroyed by the introduction of disorder which in effect increases the dimensionality of the solid.[4] Along these lines donor (**4**) was prepared and found to form a metallic 1 : 1 complex with TCNQ.[2a]



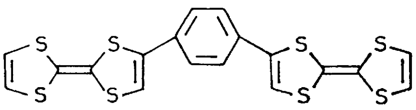
(**1**)



(**2**)



(**3**)



(**4**)

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† All new compounds gave satisfactory analytical data.

Compound (**1**) was prepared in 97% yield by reaction of 1,2-benzenedithiol with 2,5-dimethoxytetrahydrofuran in the presence of toluene-4-sulphonic acid. Conversion of (**1**) into the dication (**2**) (95% yield) was accomplished with 2 equivalents of trityl hexachloroantimonate. Subsequent deprotonation of (**2**) with triethylamine afforded (**3**) (80% yield) as slightly air-sensitive, red crystals, m.p. 225 °C; $\delta_H(CS_2)$ 7.24—6.90 (br. s, 8H, ArH) and 5.86 (s, 2H, *exo*-olefin); λ_{max}(MeCN) 374 and 392 nm (log ϵ 4.81 and 4.94).

The solution electrochemistry of (**3**) in benzonitrile shows two reversible one-electron oxidation waves at 0.26 and 0.41 V *vs.* standard calomel electrode (S.C.E.). Controlled-potential coulometry for the first wave confirmed a one-electron oxidation, and coulombic oxidation including both waves resulted in a net change of 1.9 electrons. Thus the reduction potential of (**3**) lies within the narrow range which favours incomplete charge-transfer from donor to TCNQ, a characteristic of organic metals stressed by Torrance.[5]

Compound (**3**) formed a black 1 : 1 complex with TCNQ in 1,2,4-trichlorobenzene which is metallic at room temperature [σ (compressed pellet) 5 Ω^{-1} cm^{-1}; e.s.r. (powder) strong singlet, *g* 2.0025]. As yet, good crystals of the complex have not been obtained.

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References

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