Preparation and Properties of 2,4-Bisdicyanomethylene-1,3-dithietan, a Sulphur Analogue of Tetracyanoquinodimethane

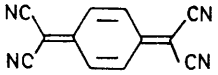
By Neil F. Haley

(*Eastman Kodak Company, Research Laboratories, Rochester, New York* 14650)

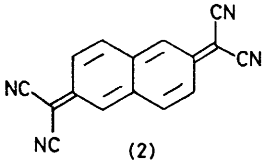
Summary The title compound has been synthesized and its electrical and complexing properties are compared to those of its carbon analogue, 7,7,8,8-tetracyanoquinodimethane.

Recent interest in highly conducting charge-transfer salts derived from the electron acceptor TCNQ (**1**) has prompted the design of new organic acceptors whose structures would enhance their electrical properties when complexed with donor molecules (*e.g.*, tetrathiafulvalene). The quinodimethanes (**2**) and (**3**) are two recent examples[1] wherein the conjugation between the dicyanomethylene groups is extended.

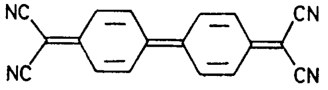
It has been known for some time that replacing a carbon-carbon double bond in a cyclic system by a sulphur atom gives an isoelectronic system of comparable stability.[2] Classic examples are tropylium and 1,3-dithiolium salts, both highly stabilized 6π aromatic cations. We were intrigued as to the effect substitution of sulphur for the two ring double-bonds of TCNQ would have on its stability and electron-acceptor properties.



(1)



(2)



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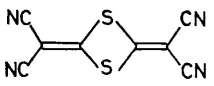

(4)

Such substitution would give compound (**4**), which is isoelectronic with TCNQ. Compound (**4**) was easily synthesized from 1,1-dichloro-2,2-dicyanoethylene[3] and dipotassium 2,2-dicyanoethylene-1,1-dithiolate[4] in methylene chloride solution and was obtained as a high-melting (228 °C, decomp.) orange [λ_{max} (CH_2Cl_2) 332 nm, $\epsilon = 3{\cdot}5 \times 10^4$]

crystalline solid.† The i.r. spectrum of (**4**) exhibited only three major absorption bands indicative of the D_{2h} symmetry expected [2235 (C≡N), 1540 (C=C), and 950 (C–S) cm^{-1}]. The Raman spectrum also supports the structure.[5] The ^{13}C n.m.r. spectrum showed only three single lines corresponding to the three different types of carbon atoms in (**4**) (157·8, 109·6, and 85·6 p.p.m. with respect to Me_4Si in CD_2Cl_2).

Cyclic voltammetry of (**4**) at a platinum electrode in MeCN shows an irreversible reduction occurring at −0·62 V (0·1 V s^{-1} scan) quite unlike TCNQ (+0·17 V and reversible). However, (**4**) does show electron-acceptor properties by forming a 1 : 1 charge-transfer salt with the donor molecule tetrathiafulvalene (TTF). This salt, unlike TTF–TCNQ, proved to be electrically insulating.[6]

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† Satisfactory elemental analyses were obtained for (**4**); the ^{13}C n.m.r. and mass spectrum supported the assigned structure.

[1] A. F. Garito and A. J. Heegar, *Accounts Chem. Res.*, 1974, **7**, 232; J. Dickman, W. R. Herther, and R. E. Benson, *J. Org. Chem.*, 1963, **28**, 2719; D. J. Sandman and A. F. Garito, *ibid.*, 1974, **39**, 1165; H. D. Hartzler, *J. Amer. Chem. Soc.*, 1964, **86**, 2174.
[2] H. Prinzbach and E. Futterer, *Adv. Heterocyclic Chem.*, 1966, **7**, 39.
[3] A. D. Josey, C. L. Dickinson, K. C. Dewhirst, and B. C. McKusick, *J. Org. Chem.*, 1967, **32**, 1941.
[4] W. R. Hatchand, *J. Org. Chem.*, 1964, **29**, 663.
[5] G. Bottger, personal communication.
[6] J. Perlstein, personal communication.