

## Organic metals: synthesis and solid state properties of new extended tetrathiafulvalene and selenatrithiafulvalene derivatives

Martin R. Bryce\* and Adrian J. Moore

Department of Chemistry, University of Durham, Durham DH1 3LE, UK.

**Abstract** - New electron donors which are extended analogues of the tetrathiafulvalene and selenatrithiafulvalene systems have been prepared by Horner-Wittig reactions of anthraquinone with 1,3-dithiole and 1-selena-3-thiole anions. The single crystal X-ray structure of 9,10-anthracenediylidene-2,2'-bis(4,5-dimethyl-1,3-dithiole) is presented along with variable temperature conductivity and magnetic data for a highly conducting 1:4 salt of this donor with TCNQ.

### INTRODUCTION

Electron donor molecules containing the 1,3-dithiole ring system have been extensively studied in recent years in the quest for new organic metals and organic superconductors (ref. 1). In this context, tetrathiafulvalene (TTF) is the prototype redox system and the size, shape, symmetry and electronic properties of this basic heterocyclic skeleton have been systematically varied in a number of ways. For example (i) sulphur has been replaced by selenium and tellurium (ref. 2), (ii) alkyl, aryl and heterocyclic substituents have been attached to the periphery of the molecule (ref. 1c), (iii) extended conjugation has been incorporated between the dithiole rings (ref. 3), (iv) radialene structures with higher symmetry have been prepared (ref. 3b, 4), (v) hydrophobic chains have been attached to the ring system (ref. 5).

We now describe new results on the 9,10-anthracenediylidene-2,2'-bis(1,3-dithiole) system (1) (ref. 6) and the preparation of seleno-analogues.

### RESULTS AND DISCUSSION

We have previously described the preparation of compounds (1) and (2) in a one step process from anthraquinone and reagents (6) and (7), respectively, in 70-75% yields (ref. 6b, c). We have now determined the single crystal X-ray structure of compound (1) which reveals a highly distorted structure with the central quinonoid ring bent into a boat conformation (Fig. 1). In this way steric congestion between the peri-hydrogens and the sulphur atoms is relieved. Analogous boat shaped quinonoid moieties are observed in the X-ray structure of 11,11,12,12-tetracyano-9,10-anthraquinodimethane and other sterically crowded TCNQ analogues (ref. 7).

Preliminary attempts at electrocrystallisation of radical ion salts of system (1) have yielded only insulating dication salts which we have prepared previously by an independent, three-step route starting from 9,10-di(chloromethyl)anthracene in 42% overall yield (ref. 6a). Donor (1) forms a 1:2 complex with 2,5-dibromo-TCNQ in acetonitrile which is a poor conductor ( $\sigma_{rt} = 10^{-5} \text{ S cm}^{-1}$ ). However, a 1:4 complex formed by combination of donor (1) and TCNQ is a very interesting material.

Variable temperature conductivity data for complex (1):(TCNQ)<sub>4</sub> are presented in Fig. 2. Data were obtained using standard four probe techniques; samples were in the form of long, thin needles. The room temperature conductivity value is ca.  $50 \text{ S cm}^{-1}$  [cf. the previously reported powder conductivity value for this material is  $10^{-2} \text{ S cm}^{-1}$  (ref. 6c)] and metallic behaviour is observed over the temperature range 300-100 K when a clear transition is observed and the conductivity drops sharply. The static susceptibility data obtained using a Faraday balance are shown in Fig. 3. The data at 300 K are consistent with a two spin system ( $\chi_{300\text{K}} = 2.3 \times 10^{-3} \text{ emu mol}^{-1}$ ;  $\mu_{\text{eff}} = 2.33 \mu_{\text{B}}$ ) that obeys Curie law behaviour down to ca. 80 K. We note that there are very few examples of organic metals formed by complexes of this stoichiometry. Single crystal X-ray analysis of the complex has not been obtained as yet.

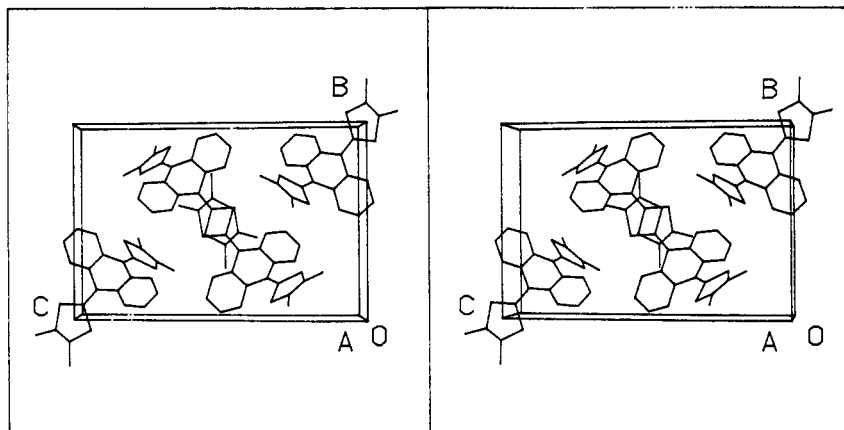


Figure 1. Single crystal X-ray structure of donor (1) : stereo-view down the *a* axis. Crystal data :  $P2_1/a$ ;  $a = 9.007$ ,  $b = 12.719$ ,  $c = 19.332$  Å;  $\alpha = \gamma = 90$ ,  $\beta = 99^\circ$ ;  $R = 0.1067$ ,  $R_w = 0.0854$ .

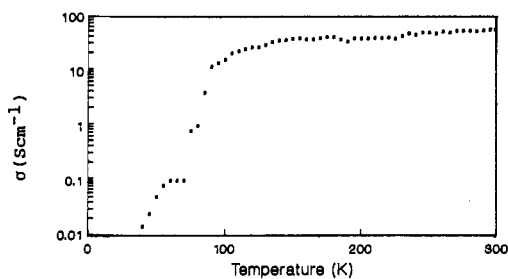


Figure 2. Variable temperature conductivity data for complex (1):(TCNQ)<sub>4</sub> Four-probe, single crystal data.

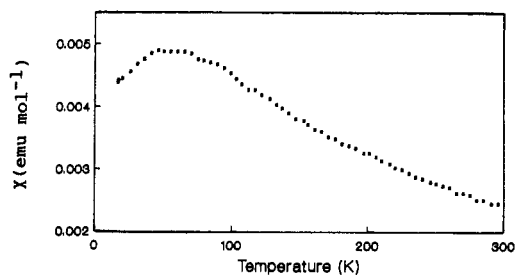
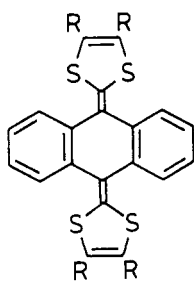
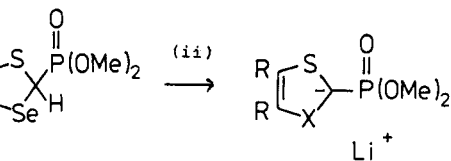
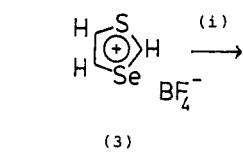


Figure 3. Variable temperature magnetic susceptibility data for complex (1):(TCNQ)<sub>4</sub> (Data obtained by Dr. G.J. Ashwell).



(1) R = Me

(2) R = H

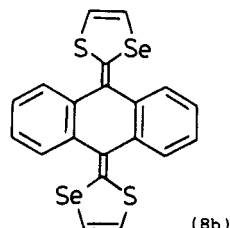
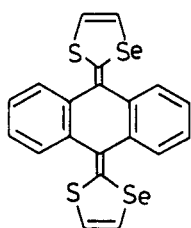


(5) X = Se; R = H

(6) X = S; R = Me

(7) X = S; R = H

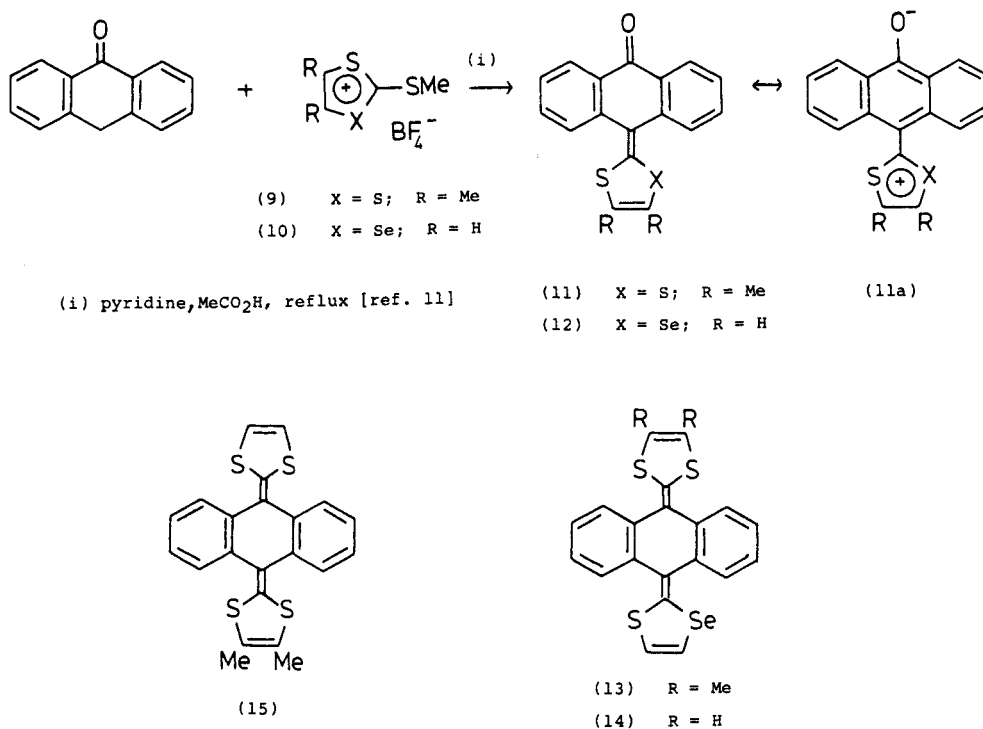
(i)  $P(OMe)_3$ , NaI, MeCN,  $20^\circ C$ ; (ii) BuLi, THF,  $-78^\circ C$ .



Several unsymmetrical TTF and TSeF derivatives have been prepared previously by cross-coupling methods which generally suffer the drawbacks of low yields and tedious chromatographic separation from a range of coupled products (ref. 8). Notable among these compounds is the DMET donor [dimethyl(ethylenedithio)diselenadithiafulvalene] which forms superconducting ion radical salts (ref. 9). We have now prepared several unsymmetrical derivatives of system (1) by high yielding, clean, stepwise procedures. Notably we have developed the novel mixed sulphur-selenium Horner-Wittig reagent (4) which we have obtained from the 1-selena-3-thiolium cation (3) (ref. 10) (Scheme 1).

The efficient trapping of ylid (5) was established by adding anthraquinone to anion (5) which was generated from reagent (4) (2.1 equiv) and *n*-BuLi: the diselenadithiafulvalene system (8) was isolated in 65% yield, presumably as a mixture of *cis/trans* isomers (8a) and (8b). A better approach to unsymmetrical derivatives of (1) that avoids the formation of isomeric mixtures is via intermediate compounds (11) and (12) which were obtained (85% yield) from reaction of anthrone with cations (9) and (10) respectively. Compound (11) is an orange-red crystalline solid, and based on u.v. data the aromatic dipolar form (11a) may contribute to the overall electronic structure [ $\lambda_{\text{max}}$  (MeCN) 194, 247, 272, 370 and 481 nm]. On the other hand, the  $^1\text{H}$  nmr chemical shift data for the methyl protons of structures (1) and (11) are virtually identical, supporting canonical form (11) [viz  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) for (1) 1.91 ppm, for (11) 1.98 ppm]. A methyl substituent on a cationic dithiolium ring [e.g. structure (11a)] should be observed at  $\delta_{\text{H}}$  ca. 2.9 ppm (ref. 6a).

Compound (11) was reacted with ylids (5) and (7) to yield unsymmetrical analogues (13) and (15) respectively (65-75% yields). Alternatively, half-quinone (12) could be prepared first, using reagent (10), and thence converted efficiently into compounds (13) and (14) by reaction with anions (6) and (7). Compounds (13) and (14) are especially notable as they are among the first analogues of the selenatrithiafulvalene system to be characterised. Compounds (8), (13)-(15) are all orange, air-stable solids.



Cyclic voltammetric data for the new donors are as follows:  $E_{\text{ox}}$  (V) (1) 0.42; (2) 0.40; (8) 0.51; (13) 0.47; (14) 0.45; (15) 0.36 (ref. 12). One, two-electron redox couple is observed, although this process is not cleanly reversible (ref. 6c). All the compounds (1), (2), (8), (13)-(15) are poorer donors than TTF (for which  $E_1 = +0.34$  V,  $E_2 = +0.78$  V vs Ag/AgCl) when  $E_1$  values are considered, although in all cases the second electron is donated more readily than for TTF. This behaviour has precedent in other systems with a similar conjugation length between the dithiole moieties and is indicative of reduced Coulombic repulsion in the dication states, relative to TTF (ref. 6d, 13). Donor ability is gradually reduced by sequential incorporation of one and two selenium atoms into the ring system.

## REFERENCES

1. (a) M. Narita and C.U. Pittman, Synthesis 489 (1976); (b) M.R. Bryce and L.C. Murphy, Nature 309, 119 (1984); (c) A. Krief, Tetrahedron 42, 1209 (1986); (d) F. Wudl, Acc. Chem. Res. 17, 227 (1984); (e) D.O. Cowan and F.M. Wiygul, Chem Eng. News 64(29), 28 (1986).
2. (a) D. Cowan and A. Kini in Chemistry of Organic Selenium and Tellurium Compounds, Vol. 2, Ed. S. Patai, J. Wiley, Chapter 12 (1987); (b) F. Wudl in Organoselenium Chemistry, Ed. D. Liotta, J. Wiley, Chapter 9 (1987).
3. (a) M.R. Bryce, J.C.S. Perkin Trans 1 1675 (1985); (b) Z. Yoshida and T. Sugimoto, Angew. Chem. Int. Edn. Engl. 27, 1573 (1988).
4. T. Sugimoto, Y. Misaki, T. Kajita, Z. Yoshida, J. Amer. Chem. Soc. 109, 4106 (1987).
5. (a) G. Saito, Pure Appl. Chem. 59, 999 (1987); (b) A.S. Dhindsa, M.R. Bryce, J.P. Lloyd and M.C. Petty, Thin Solid Films 165, L97 (1988).
6. (a) M.R. Bryce and A.J. Moore, Tetrahedron Lett. 29, 1075 (1988); (b) Synthetic Metals 25, 203 (1988); (c) Synthetic Metals 27, B557 (1988); (d) The bis(benzodithiole) analogue has also been prepared recently: Y. Yamashita and T. Miyashi, Chem. Lett. 661 (1988).
7. (a) A.M. Kini, D.O. Cowan, F. Gerson and R. Mockel, J. Amer. Chem. Soc. 107, 556 (1985) and references therein; (b) K. Maruyama, H. Imahori, K. Nakagawa and N. Tanaka, Bull. Chem. Soc. Jpn. 62, 1626 (1989).
8. (a) E.M. Engler and V.V. Patel, J.C.S. Chem. Commun. 671 (1975); (b) J-M. Fabre, L. Giral, E. Dupart, C. Coulon, J.P. Manceau and P. Delhaes, ibid. 1477 (1983); (c) K. Kikuchi, T. Namiki, I. Ikemoto and K. Kobayashi, ibid. 1472 (1986); (d) Y. Shiomi, Y. Aso, T. Otsubo and F. Ogura, ibid. 822 (1988).
9. K. Kikuchi, M. Kikuchi, T. Namiki, K. Saito, I. Ikemoto, K. Murata, T. Ishiguro and K. Kobayashi, Chem. Lett. 931 (1987).
10. M.V. Lakshmikantham and M.P. Cava, J. Org. Chem. 45, 2632 (1980)
11. For the analogous reaction of anthrone with a benzodithiolium cation see: R. Gompper and E. Kutter, Chem. Ber. 98, 1365 (1965).
12. Experimental conditions: 0.1 M  $\text{NBu}_4^+\text{ClO}_4^-$  in dry acetonitrile under argon, 20°C, versus Ag/AgCl, Pt electrode, scan rate 100 mV sec<sup>-1</sup> using a BAS100 Electrochemical Analyser.
13. T. Sugimoto, H. Awaji, I. Sugimoto, Y. Misaki and Z. Yoshida, Synthetic Metals 19, 569 (1987).