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THE PREPARATION OF NEW BIS(1,3-DITHIOLE) DERIVATIVES: EXTENDED π-DONORS FOR ORGANIC METALS

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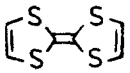
Abstract. The bis(1,3-dithiolium) dications (8) and (12) have been prepared from 1,4-di(bromomethyl)naphthalene and 9,10-di(chloromethyl)-anthracene, respectively; system (8) forms a semiconducting radical ion salt with TCNQ, σ_{rt} 10^{-3} S cm^{-1}.

There is great interest in the synthesis of new π-donors and their derived radical cations and dications. Molecules of this type are components of a wide range of highly conducting complexes that stem from the prototype organic metal TTF (1)-TCNQ.[1] In particular, several radical cation salts of (2),[2] (3),[2] and more recently, (4)[3] are organic superconductors at very low temperatures. Many donors that are subtely different from (1)-(4) in molecular size, shape or symmetry have recently been synthesised.[4] Our work[5] and that of other groups[6] has emphasised that an important concept in the design of organic metals based on TTF (1) is to stabilise the cationic states, in which the dithiolium rings are aromatic, by extending the conjugation between the heterocycles. Several conducting cation radical salts have resulted from these studies.[5,6] With this motivation, herein we report the synthesis of two new bis(dithiolium) dications (8) and (12), along with solid state characterisation of radical cation salts of compound (8).

The route to compound (8) is shown in the Scheme. Reaction of 1,4-di(bromomethyl)naphthalene (5) with sulphur and sodium methoxide followed by acidification gave an unstable bis(dithiocarboxylic acid) which was conveniently isolated as the di(piperidinium) salt (6).[7] Room temperature alkylation of salt (6) with 3-chloro-2-butanone gave bis(dithioester) (7)[8] from which the target dication (8)[9] was readily obtained by acid-promoted cyclisation accompanied by dehydration. The overall yield for the three step conversion of (5) to (8) is 29%. The methyl group protons of structure (8)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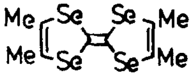
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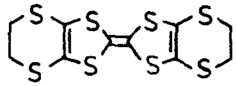
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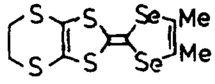
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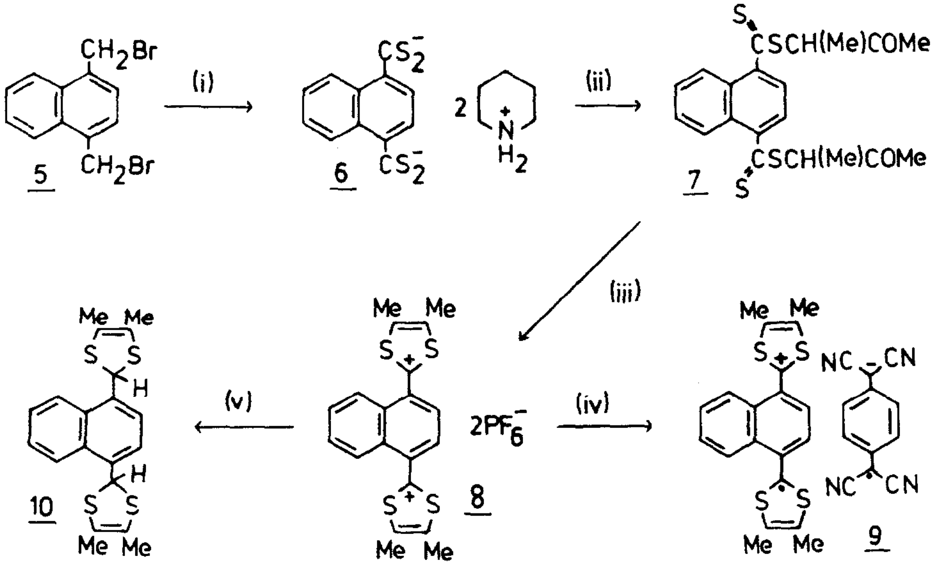
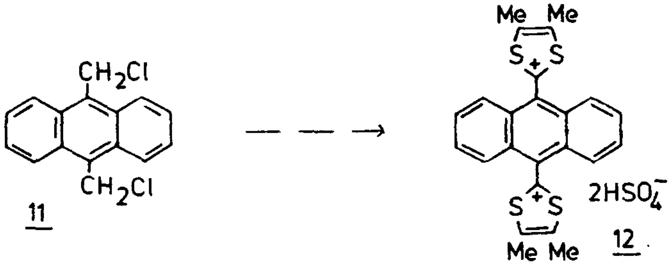


Scheme (i) S_8, NaOMe in refluxing MeOH, followed by HCl, then piperidine.
(ii) MeCH(Cl)COMe in EtOH at 20°C.
(iii) conc. H_2SO_4 at -5°C, followed by 60% HPF_6 at 20°C.
(iv) Li^+ $TCNQ^-$ in refluxing MeCN; (v) $NaBH_4$ in MeOH at 20°C.



are observed as a singlet at δ(H) 2.97; this downfield shift relative to the normal value for Me-C=C protons is consistent with the cationic dithiolium structure.

Dication (8) reacts with the lithium salt of TCNQ, in a metathesis reaction, to give, in high yield, a product identified from elemental analysis, i.r., u.v. and e.s.r. spectroscopic data[10] as salt (9) formed from the radical cation of structure (8) and the TCNQ radical anion: the stoichiometry is ca. 1:2.4. The material is a semi-conductor σ (20°C, compressed pellet) 10^{-3} S cm^{-1}. The i.r. spectrum of the salt shows a very broad charge transfer band centred at 3300 cm^{-1}, characteristic of an organic conductor and a cyanide absorption at 2177 cm^{-1} due to anionic TCNQ.[11] The salt gives a very strong singlet signal at g = 2.0003 in the solid state e.s.r. spectrum, indicative of an organic radical.

The electrochemical reduction of dication (8) has been studied by cyclic voltammetry.[12] A reversible two-electron reduction to the neutral species occurs at Ep + 0.034 V (vs Ag/AgCl); this is considerably lower than the first reduction potential for $TTF^{2+} \rightarrow TTF^{+}$ (Ep + 0.78 V) demonstrating the increased stability of the dication state (8) relative to TTF^{2+}. The coalescence of the two single electron waves characteristic of TTF into one two-electron redox couple, as we observe for (8), has precedent in systems with a similar conjugation length between the dithiole moieties.[6a,c]

Reduction of dication (8) with sodium borohydride yields dihydro derivative (10)[13] which reacted with 2,3-dichloro-5,6-dicyanobenzoquinone to yield a 1:1 DDQ radical anion salt,[14] analogous to (9). The DDQ salt is an insulator, and it exhibits the expected phenoxy radical anion band at ν max 1566 cm^{-1} in the i.r. spectrum, and a broad charge transfer band at 3250 cm^{-1}.

9,10-Di(chloromethyl)anthracene (11) has been converted by a directly analogous three-step route to dication salt (12) (42% overall yield) which is isolated as the di(hydrogen sulphate) salt.[15] The extreme insolubility of salt (12) has so far precluded the characterisation of any of its radical cation complexes; the structure of neutral species derived from (12) is expected to deviate considerably from planarity, by analogy with the recently reported TCNQ analogue, 11,11,12,12-tetracyano-9,10-anthraquinodimethane.[16]

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7. All new compounds gave satisfactory microanalytical data except compound (7) (see ref. 8). Compound (6), 55% yield, m.p. 154-155°C, i.r. 1035 cm^{-1} (CS_2^-).
8. Compound (7), ca. 63% yield, i.r. 1700, 1470, 1350, 1240, 1025, 837 and 760 cm^{-1}; this compound was used directly in the next step without purification.
9. Compound (8), 84% yield, n.m.r. δ(H) 8.31 and 7.99 (AA'BB', 4H), 8.14 (2H) and 2.97 (12H).
10. TCNQ salt, (9), 41% yield, m.p. ca. 168°C (dec.), i.r. 3300, 2177, 1568, 1327, 1138 cm^{-1}, u.v. λ_{max} 380, 780, 835 and 880 nm.
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12. 0.1 M $NBu_4^+ ClO_4^-$ in dry MeCN under Ar, 20°C, Ag/AgCl, Pt electrode, scan rate 100 mV sec^{-1}, using a BAS 100 Electrochemical Analyser.
13. Compound (10), 58% yield, n.m.r. δ_H 8.00 (2H, s) 7.97 and 7.56 (AA'BB', 4H), 6.48 (2H, s) and 1.90 (12H, s).
14. DDQ salt, 20% yield, m.p. 85-90°C (dec), i.r. 3250, 2222, 1566, 1450, 1199 and 684 cm^{-1}.
15. Compound (12), m.p. ca. 160°C (dec).
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