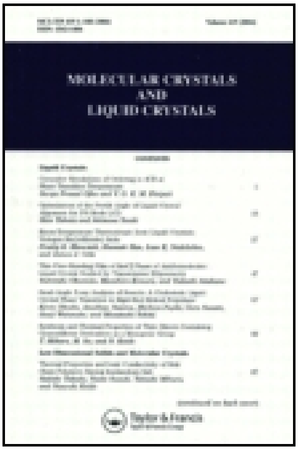

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Highly-Conjugated Bis(1,3-Dithiole) Donors

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HIGHLY-CONJUGATED BIS(1,3-DITHIOLE) DONORS

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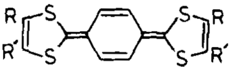
Abstract Routes to new donors (13) and (16) are described.

A considerable amount of work has been directed towards the synthesis of donors related to TTF. In particular fused derivatives, e.g. DBTTF, or derivatives where S has been replaced by Se (TSeF) or Te (TTeF). Far less work has been reported on donors with extended conjugation between the dithiole rings. In this paper we will summarise the published work in this area and describe routes to new donors (13) and (16).

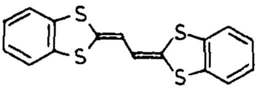
The preparation of (1) is claimed, without details, in an early patent.[1] The diphenyl derivative (2) forms an iodine complex of low conductivity [σ_{rt} 8.5 x 10^{-5} $(\Omega\ \mathrm{cm})^{-1}$] and possibly complexes with TCNQ and DDQ in solution.[2] Tetramethyl derivative (3) forms salts with TCNQ, ClO_4^- and BF_4^-, the last two having a high conductivity [σ_{rt} 10 $(\Omega\ \mathrm{cm})^{-1}$][3] Dibenzo compound (4) forms an insulating complex with DDQ and possibly a complex with TCNQ.[4]

We[5] and Japanese workers[6] have independently synthesised (5) which is a better donor than DBTTF (by c.v.) and a complex of (5) with TCNQ is metallic [σ_{rt} 5 $(\Omega\ \mathrm{cm})^{-1}$].[5] However, we find this complex is unstable as judged by a drop in powder conductivity with time. Donor (5) is one of the first TTF donors that is (presumably) non-planar yet forms a metallic complex. Yoshida et al have described the TTF derivatives (6)[7] and (7),[8] and c.v. shows that, as expected, Coulombic repulsion in the dication of (6) is decreased compared with the TTF dication.

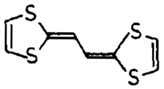
1,1,4,4-Tetrathiabutadiene derivatives with saturated dithiole rings had been studied previously and found to be very weak donors.[9] Salts of TCNQ and DDQ with the extensively-conjugated bis(1,3-dithiole) (8) have recently been reported.[10] We have studied TM-NBDT (9); the neutral compound (9) could not be isolated, but a quinol salt of the radical cation of (9) can be obtained.[11] The diphenyl derivative (10) forms an insulating iodine complex.[11]



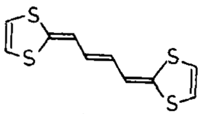
(1) R = R′ = H
(2) R = Ph; R′ = H (or isomer)
(3) R = R′ = Me
(4) R − R′ $+\text{CH=CH}+_2$



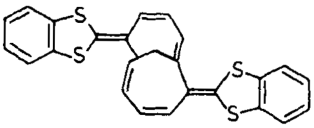
(5)



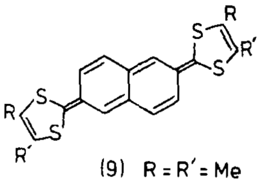
(6)



(7)



(8)

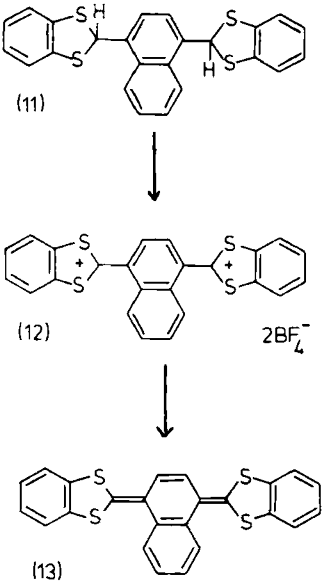


(9) R = R′ = Me
(10) R = H; R′ = Ph (or isomer)

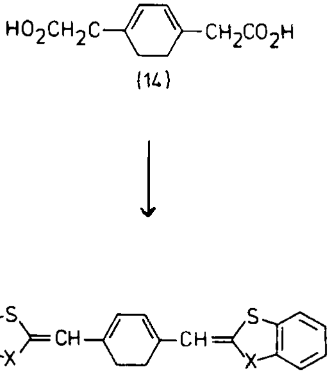
We now describe routes to new donors (13) and (16). Reaction of 2 equiv. of o-benzenedithiol with 1,4-naphthalenedicarbaldehyde gave compound (11) [80% yield; m.p. 190-194°C]; which on reaction with trityl tetrafluoroborate gave dication (12) [60% yield; m.p. 260-264°C]. Cyclic voltammetry of (13) shows a reversible two electron oxidation at 0.03 V (vs S.C.E.).

We have described the synthesis of (14) from 1,4-cyclohexanedione.[13] The diacid chloride of (14) yields bis(benzothiazoline) derivative (15) by sequential reaction with N-methyl-o-aminothiophenol, trityl tetrafluoroborate and triethylamine [Compound (15) m.p. 212-213°C; δ_H (DMSO-d_6) 2.31 (s, 4H), 5.50 (s, 2H), 5.80 (s, 2H), 7.12-7.80 (m, 8H)].

The bis(dithiole) derivative (16) can be prepared similarly from benzenedithiol and (14). At present the structure of (16) is assigned on the basis of high resolution mass spectral and n.m.r. spectral data; analytically pure material has not been obtained.



(11)
(12)
(13)



(14)

(15) X = NMe
(16) X = S

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