Unsymmetrical and Highly-conjugated Tetrathiafulvalene and Selenatrithiafulvalene Derivatives: Synthesis and Reactions of Novel Heterocyclic Wittig–Horner Reagents

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Novel 1,3-dithiole and 1-selena-3-thiole Wittig–Horner reagents have been developed and used in the efficient synthesis of a range of new, unsymmetrical tetrathiafulvalene and selenatrithiafulvalene derivatives (**6**)—(**10**) and (**16**); cyclic voltammetry establishes that these molecules are efficient π-donors.

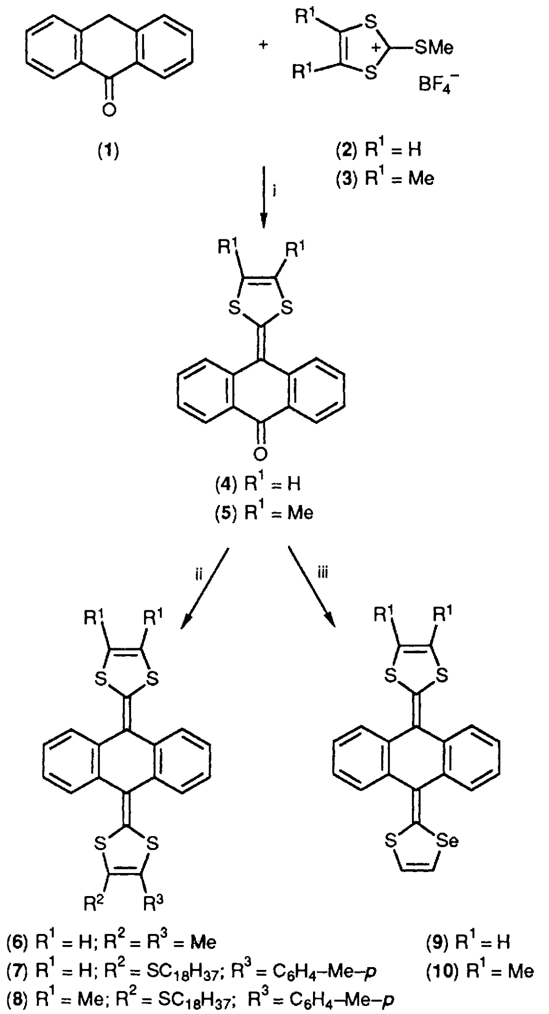
Tetrathiafulvalene (TTF) derivatives and related heterocyclic π-donors remain the focus of attention in the search for new organic materials that display high electrical conductivity.[1] There is considerable interest in new systems for which on-site Coulombic repulsion in ionised states is diminished relative to the parent donor TTF. In this context, molecules that contain extended conjugation between the 1,3-dithiole rings are prime synthetic targets.[2] The insertion of a rigid, cyclic, linking group, rather than a flexible ethylenic link, is desirable for ordered intermolecular packing in the solid state. Consequently, *p*-quinodimethane analogues of TTF have been prepared and shown to form conducting complexes with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).[3]

We now describe the synthesis and electrochemical behaviour of several new unsymmetrical analogues (**6**)—(**10**) of the anthracenediylidene system. Notably, we have prepared the first derivatives of selenatrithiafulvalene (STTF), *viz* compounds (**9**) and (**10**), which have been obtained by reactions of the novel mixed sulphur–selenium Wittig–Horner reagent (**13c**). The routes to the extended TTF and STTF derivatives are summarised in Scheme 1.

Several unsymmetrical TTF derivatives have been prepared previously by cross-coupling methods which invariably suffer the drawbacks of low yields and tedious chromatographic separation from a range of coupled products.[4] Our two-step methodology to donors (**6**)—(**10**) *via* intermediates (**4**) and (**5**)

Table 1. Cyclic voltammetric data for TTF and STTF derivatives. *Experimental conditions*: NBu_4^+ ClO_4^- (0.1 M) in dry acetonitrile under argon, 20 °C, *vs.* Ag/AgCl, Pt electrode, scan rate 100 mV s^{-1} using a BAS 100 Electrochemical Analyser.

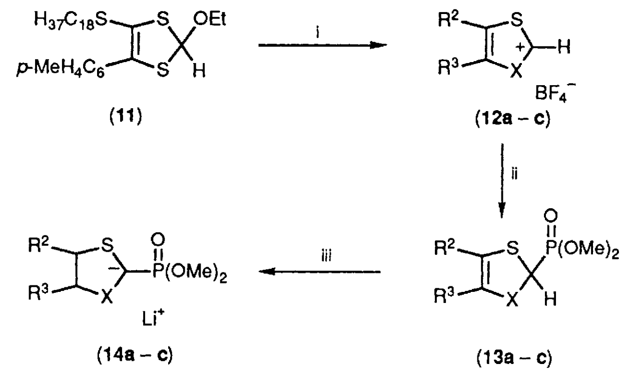
Donor	$E_1^{1/2}$/V	E_{ox}/V	$E_2^{1/2}$/V	M.p./°C
TTF	0.34		0.78	
(6)		0.36		>260
(7)		0.56		59
(8)		0.54		45
(9)		0.45		>260
(10)		0.47		>260
(16)	0.47		0.82	65—70



Scheme 1. *Reagents and conditions*: i, pyridine, acetic acid, reflux; ii, reagent (**13a**) or (**13b**), n-butyl lithium (1.1 equiv.), tetrahydrofuran (THF), −78 °C; iii, reagent (**13c**), n-butyl lithium (1.1 equiv.), THF, −78 °C.

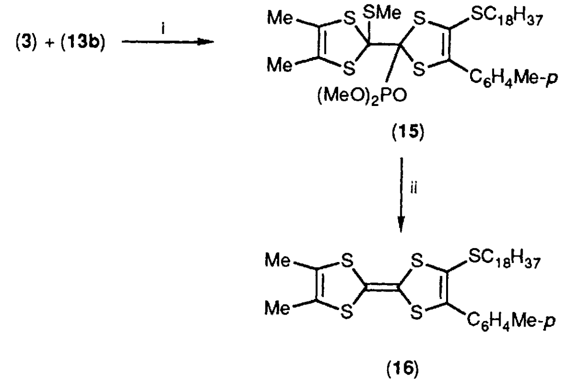
(Scheme 1) completely avoids these problems; this emphasises the fact that anthracenediylidene derivatives are very attractive targets for studies on unsymmetrical TTF analogues.

Reaction of anthrone (**1**) with 1,3-dithiolium cations (**2**) and (**3**), under conditions used previously by Gompper and Kutter for the analogous benzodithiolium system,[5] afforded half-quinones (**4**) and (**5**) (85% yield). Compound (**4**) reacted with carbanion (**14a**) [generated from reagent (**13a**) and butyl lithium] to yield the unsymmetrical 9,10-anthracenediylidene-2,2′-bis(1,3-dithiole) derivative (**6**) (70% yield). The preparation of the highly-substituted Wittig–Horner reagent (**13b**) is shown in Scheme 2. 1,3-Dithiole derivative (**11**)[7] on reaction with tetrafluoroboric acid was converted into cation (**12b**) (>95% yield) which on treatment with trimethylphosphite in the presence of sodium iodide (Akiba's conditions)[6] afforded phosphonate ester (**13b**) [95% yield, a viscous oil, δ_H ($CDCl_3$) 4.85, J_{HP} 6 Hz]. Carbanion (**14b**) was subsequently generated with butyl lithium and trapped cleanly by half-quinones (**4**) and (**5**) to yield extended TTF donor molecules (**7**) and (**8**), respectively (55% yield).



(**a**) X = S; $R^2 = R^3$ = Me
(**b**) X = S; $R^2 = SC_{18}H_{37}$; $R^3 = C_6H_4Me$-*p*
(**c**) X = Se; $R^2 = R^3$ = H

Scheme 2. *Reagents and conditions*: i, tetrafluoroboric acid, ether, 0° C; ii, trimethylphosphite, sodium iodide, acetonitrile, 20 °C; iii, n-butyl lithium (1.1 equiv.) THF, −78 °C.



Scheme 3. *Reagents and conditions*: i, n-butyl lithium (1.1 equiv.), THF, −78 °C; ii, silica.

The incorporation of one selenium atom into the TTF system has not been described previously although several other mixed sulphur–selenium donors are known.[4c,8] For this purpose, the mixed sulphur–selenium phosphonate carbanion (**14c**) has been generated in two steps from 1-selena-3-thiolium cation (**12c**)[9] using analogous procedures (Scheme 2). Reagent (**13c**) was isolated as a hygroscopic oil [δ_H ($CDCl_3$) 6.67 and 6.43, (each 1H, AB, *J* 25 Hz), 5.26 (1H, d, J_{HP} 4.5 Hz), 3.81 (6H, d, J_{HP} 10 Hz), 90% yield from cation (**12c**)]. The derived carbanion (**14c**) was trapped cleanly by ketones (**3**) and (**4**) to yield the first selenatrithiafulvalene derivatives, (**9**) and (**10**), respectively (65—75% yield). Cyclic voltammetric data and melting points for the new donors

(**6**)—(**10**) and (**16**) (see below) are collated in Table 1; data for TTF are included for comparison. For extended donor systems (**6**)—(**10**), the second oxidation (*i.e.*, radical cation to dication) occurs at a significantly lower potential than for TTF, and the first and second oxidation waves coalesce into a single wave which corresponds to the overall transfer of two electrons. This is clear evidence that 'stretching' the TTF molecule stabilises the dication state due to reduction of on-site Coulombic repulsion, and these new data are in agreement with those reported previously for related multistage redox systems.[2,3,10] Donor ability of the anthracenediylidene-bis(1,3-dithiole) system is significantly reduced by incorporation of one selenium atom into the ring system [ΔE_{ox} = 0.11 V for donors (**6**) and (**10**)]. This is consistent with known data on diselenadithiafulvalene and tetraselenafulvalene[11] and is attributable to selenium forming weaker π-bonds with carbon than does sulphur. Thus, the selenium-containing cations are less stable than their sulphur counterparts as the former are less able to redistribute charge; this raises the overall energy required for ionisation as selenium is substituted for sulphur. Derivatives (**7**) and (**8**), bearing thioalkyl- and aryl-substituents, are also poorer donors than system (**6**). The two-electron oxidation process for donors (**6**)—(**10**) is quasi-reversible.

The high reactivity of carbanion (**14b**) has also been utilised in a new synthetic route to the TTF system bearing one hydrophobic side-chain (Scheme 3). This class of TTF compounds is currently of interest as components of electroactive Langmuir–Blodgett films.[12] Cation (**3**) was added to a solution containing carbanion (**14b**) at −78 °C.[13] The resulting adduct (**15**) was not purified, but converted directly into TTF derivative (**16**) by addition of silica, then column chromatography [20% yield, based on reagent (**13b**)]. Compound (**16**) undergoes two, separate, one-electron oxidations at higher potentials than TTF (Table 1).

In conclusion, we have established that Wittig–Horner reagents (**13a**—**c**) are versatile precursors for synthesising highly-substituted TTF derivatives, and analogues that incorporate one selenium atom.

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