Synthesis and Redox Behaviour of Highly Conjugated Bis(benzo-1,3-dithiole) and Bis(benzothiazole) Systems containing Aromatic Linking Groups: Model Systems for Organic Metals[1]

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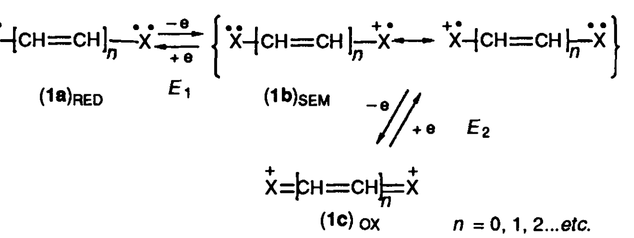
The synthesis and electrochemical redox properties of a series of symmetrical, highly conjugated bis(benzo-1,3-dithiole) and bis(benzothiazole) derivatives (**8**)–(**24**) are described. The heterocyclic end-groups are linked by a conjugated framework that incorporates the following groups: (a) phenyl, (b) naphthyl, (c) thienyl, (d) biphenyl, (e) anthracenyl, and (f) benzanthracenyl. Compounds (**13**) and (**16**)–(**19**) display two, single-electron redox waves in the cyclic voltammogram, while compounds (**8**)–(**12**), (**14**), (**15**), (**20**), (**21**), (**23**), and (**24**) display a single, two-electron redox wave. The redox potentials of these molecules can be correlated with the increased stability of the redox state of the system in which the central, bridging ring is aromatic.

Organic molecules which undergo two-electron redox reactions have been widely studied for many years. Based on the earlier work of Weitz,[2] Hünig[3] developed a general structure for which the existence of stable, intermediate, radical ions is to be expected: *viz:* structure (**1**), in which the end-groups, X, in the reduced form, contain free electron pairs or π-systems. The thermodynamic stability, K_{SEM}, of the radical within the redox systems (**1**) can be determined from the redox potentials, E_1 and E_2, using the equation (1).

$$\log K_{SEM} = (E_1 - E_2)/0.059 \qquad (1)$$

Two variations of structure (**1**) are of special importance:[4]

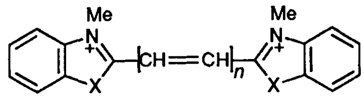


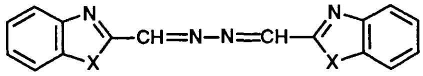
(I) 'Wurster-type' structures, in which the groups X are attached to cyclic π-systems of aromatic character in the reduced form (RED).

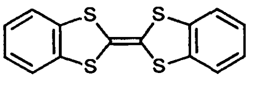
(II) (a) 'Weitz-type' structures in which the groups X are part of a heterocyclic system being aromatic in the oxidized form (OX); *cf.* viologens.

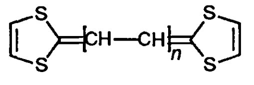
(b) 'Reversed Weitz-type' structures show aromatic properties in the reduced form (RED).

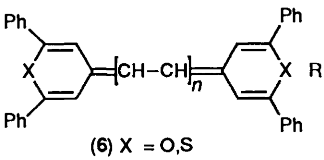
Type-(II) systems have been systematically studied by Hünig.[5] Extensive reviews cover the literature up to *ca.* 1979 on these redox systems.[6] To place the present work in context, a few related systems are worthy of note. Derivatives of structure (**1**) in which the end-groups, X, are five-membered heterocycles form a major class of 'Weitz-type' salts, and some time ago, bis(benzothiazole), bis(benzoxazole), and bis(benzimidazole) derivatives (**2**) and (**3**) in which the heterocycles are linked by a varying number of vinyl or aza-vinyl groups were reported.[7–9] Dibenzotetrathiafulvalene (**4**) has been known for over sixty years,[10] and related bis-(1,3-dithiole) vinylogues (**5**; n = 1, 2) have been studied recently as analogues of tetrathiafulvalene (**5**; n = 0), notably by Yoshida's group, in the search for new organic metals.[11,12] A series of bis(pyran) and bis(thiopyran) vinylogues (**6**) has also been reported.[13] Conjugated polyenes, in general, are of considerable current interest as model compounds for studying the redox and spectroscopic behaviour of conjugated polymers that exhibit novel conductivity and non-linear optical properties.[14] From this viewpoint, Spangler *et al.* have recently synthesized a series of diarylpolyenes (**7**).[15]

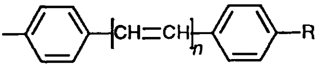

(**2**) X = O, S, NMe
n = 0, 1, 2, 3


(**3**) X = O, S, NMe


(**4**)


(**5**) n = 0, 1, 2


(**6**) X = O,S
n = 0 – 6


(**7**) R = H, alkyl, NO_2, OMe
n = 3 – 6

The present work concerns highly conjugated bis(heterocyclic) systems where the conjugated linking group contains (or comprises) a cyclic molecule that can itself achieve aromaticity at either the oxidized or reduced stage of the system, depending upon the structure of the linking group. A few bis(benzo-1,3-dithiole) and bis-(1,3-dithiole) derivatives of this type have been described previously by us[12,16] and by other workers.[17–19] The study of molecules (**8**)–(**24**) is relevant to the field of organic

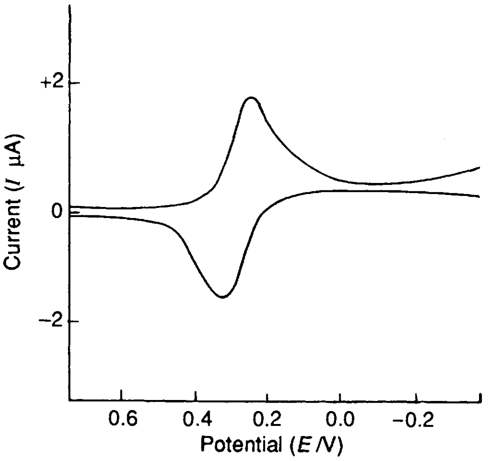


Figure 1. Cyclic voltammogram for compound (**12**).

metals, as compounds (**8**)–(**24**) can be viewed as extended analogues of tetrathiafulvalene (**5**; $n = 0$). Furthermore, the redox behaviour associated with the central, cyclic linking group in systems (**8**)–(**24**) may shed light on the properties of conjugated polymers which are comprised solely of this linking group (*e.g.*, polyphenylene, polyphenylenevinylene, polythiophene, *etc.*).

Results and Discussion

We now describe the synthesis and redox properties of a range of new symmetrical bis(benzo-1,3-dithiole) and bis(benzothiazole) derivatives in which the heterocyclic end groups [X in structure (1)] are linked through the C(2) positions by a conjugated framework that incorporates the following aromatic groups: (a) phenyl, (b) naphthyl, (c) thienyl, (d) biphenyl, (e) anthracenyl and (f) benzanthracenyl. These molecules (**8**)–(**24**) conveniently fall into four classes, based on the structure of the linking group which is incorporated into the system, as follows.

Class 1—directly attached to the heterocycles, *i.e.* compounds (**8**)–(**15**).

Class 2—attached through methine carbons, *i.e.* compounds (**16**)–(**19**).

Class 3—attached through imine nitrogens, *i.e.* compounds (**20**)–(**22**).

Class 4—attached through vinyl groups, *i.e.* compounds (**23**) and (**24**).

In general, the molecules (**8**)–(**24**) are conveniently prepared and purified in the redox state in which the bridging group is aromatic; this is the redox state in which the formulae are drawn. Exceptions to this principle are molecules (**14**) and (**15**) which are prepared in the reduced form with a quinonoid bridging group.

Synthesis of Compounds (**8**)–(**24**).—*Class* 1 *Compounds* (**8**)–(**15**). Dication (**11**) has been described previously[17] so preparative details will not be repeated here. During the preparation of this manuscript, Japanese workers reported the synthesis of compound (**13**),[18] using essentially the same route as ours.[1] Compounds (**8**)–(**10**) were prepared in the oxidized form by methylation with trimethyloxonium tetrafluoroborate of known bis(benzo-1,3-thiazole) derivatives (**25**)–(**27**). Compounds (**12**) and (**13**) were prepared as follows. Benzene-1,2-dithiol (2 mol equiv.) was treated with the dialdehyde of the bridging group under acidic conditions to afford the dihydro derivatives (**28**) and (**29**). Reaction of compounds (**28**) and (**29**) with trityl tetrafluoroborate (2 mol equiv.) led to the removal of hydride ions and the formation of dication salts (**12**) and (**13**), respectively, which could be conveniently handled in air for a period of hours without decomposition. Darkening and decomposition of the salts (**8**)–(**15**) occurred over a period of a few weeks in air but the compounds were stable for months in an inert atmosphere at 0 °C.

System (**14**), with a bridging anthracene group, was synthesized by a different route that yields the product in the reduced (neutral) form: namely, by reaction of anthraquinone with the Horner–Wittig carbanion (**34**), which was generated *in situ*, as described by Akiba *et al.*[20] from 2-dimethoxyphosphinoyl-1,3-benzodithiole and butyllithium. [We have also recently shown that the related 2-dimethoxyphosphinoyl-1,3-dithiole carbanions (**35**) and (**36**) react similarly to reagent (**34**) to yield compounds (**37**) and (**38**) in good yields.[16b,c]] Benz[*a*]anthracene-5-12-dione (**39**) also reacted with carbanion (**34**) (generated *in situ* from 2-dimethoxyphosphinoyl-1,3-benzodithiole and butyllithium) to furnish compound (**15**) in the reduced form as an air-stable, orange solid. However, attempts to use this one-step methodology to synthesize system (**12**), in the reduced form, from 1,4-naphthoquinone and carbanion (**34**) were unsuccessful: the complex product mixture we obtained could not be purified.

Class 2 *Compounds* (**16**)–(**19**). Reaction of *N*-methyl-*o*-aminothiophenol or benzene-1,2-dithiol (2 mol equiv.) with the appropriate dialdehyde, in the presence of acid, followed by addition of trityl tetrafluoroborate, formed dications (**30**)–(**33**), which were deprotonated with triethylamine to yield the target molecules (**16**)–(**19**), respectively, in the reduced form. Yields for this two-step procedure are typically 50–60%.

Class 3 *Compounds* (**20**)–(**22**). Benzothiazolium salt (**40**) (2 mol equiv.), substituted with either a chloro- or methylthio-group at C-2, was condensed with the appropriate aromatic diamine to yield compounds (**20**)–(**22**), respectively, in the reduced form.

Class 4 *Compounds* (**23**) *and* (**24**). Two representatives of this class of compound, *viz.* (**23**) and (**24**), are described; these are the most extensively conjugated molecules we have studied. The synthetic route used is similar to that of Class 2 compounds, except that for Class 4 compounds the diacid chloride of the bridging group (*viz. p*-phenylenediacroyl dichloride) was used and thus dications (**23**) and (**24**) were obtained directly as the dichloride salts, which were purified as the bis(tetrafluoroborate) salts.

Electrochemical, Redox Properties of Compounds (**8**)–(**24**).—As mentioned earlier in this paper, contemporary interest in extended π-electron systems is focused on the high intrinsic electrical conductivity associated with the radical-ion states of these systems. For example, organic metals of the TTF–TCNQ* genre are composed of segregated stacks of radical cations and radical anions, repectively. Likewise, high conductivity in conjugated polymers is a feature of the partially ionized (doped) state of the material, not the neutral state. The technique of cyclic voltammetry has, for some years, been firmly established as a reliable experimental method for the determination of redox potentials in this class of materials. The cyclic voltammetric data for compounds (**8**)–(**24**) are collated in the Table. A striking feature of these data is that the majority of these molecules undergo reversible, two-electron redox behaviour, which for most of the compounds tested is observed as a *single*, *two-electron couple*; Figure 1 shows the cyclic voltammogram for compound (**12**) which is a representative example. [The exceptions to this are molecules (**13**) and (**16**)–(**19**) which are considered in detail below.] Coulometric analysis of the redox wave was carried out for each compound to

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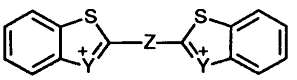
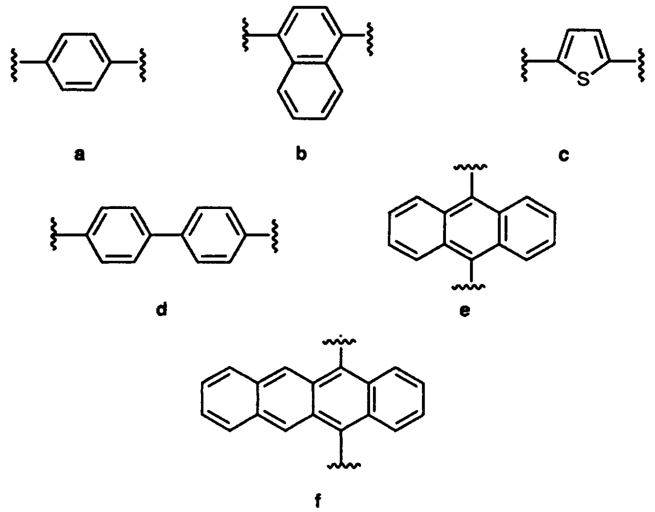
* Tetrathiafulvalene–tetracyanoquinodimethane.

Table. Structures and cyclic voltammetric data for the title compounds. (Redox potentials recorded *versus* Ag/AgCl; Pt electrode in acetonitrile; *ca.* 1×10^{-5} mol dm^{-3} redox species; supporting electrolyte tetrabutylammonium perchlorate or tetraethylammonium tetrafluoroborate).

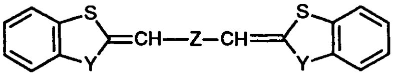


	Y	Z	E_1(V)	E_m(V)	E_2(V)	ΔE_p(V)[a]
(8)	NMe	**a**		−0.493		0.040
(9)	NMe	**b**		−0.500		0.037
(10)	NMe	**c**		−0.337		0.042
(11)	S	**a**		+0.272		0.040
(12)	S	**b**		+0.273		0.040
(13)	S	**c**	+0.32		+0.57	0.062 (E_1), 0.070 (E_2)
(14)	S	**e**		+0.390		0.033
(15)	S	**f**		+0.394		0.035

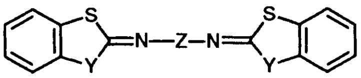
[a] $\Delta E_p = E_p$ anodic $- E_p$ cathodic.



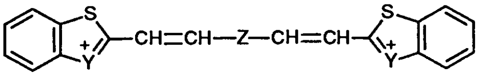
Structures **a**–**f** for the linking group Z.



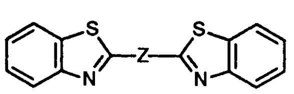
	Y	Z	E_1	E_2	ΔE	K_{SEM}	ΔE_p
(16)	NMe	**a**	−0.039	+0.16	0.153	3×10^3	0.057 (E_1), 0.060 (E_2)
(17)	NMe	**b**	−0.040	+0.14	0.154	3×10^3	0.060 (E_1), 0.062 (E_2)
(18)	NMe	**c**	+0.018	+0.110	0.092	36	0.070 (E_1), 0.070 (E_2)
(19)	S	**a**	+0.778	+0.778	0.138	2×10^2	0.064 (E_1), 0.065 (E_2)



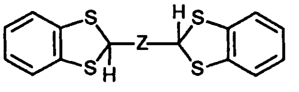
	Y	Z	E_m(V)	ΔE_p
(20)	NMe	**a**	+0.825	0.037
(21)	NMe	**b**	+0.678	0.037
(22)	NMe	**d**	insoluble	



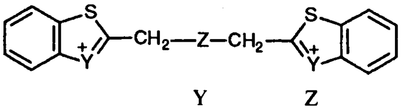
	Y	Z	E_m(V)	ΔE_p
(23)	NMe	**a**	−0.240	0.043
(24)	S	**a**	+0.400	0.041



	Z
(25)	**a**
(26)	**b**
(27)	**c**



	Z
(28)	**b**
(29)	**c**



	Y	Z
(30)	NMe	**a**
(31)	NMe	**b**
(32)	NMe	**c**
(33)	S	**a**

confirm the number of electrons involved in the process, and current *versus* charge profiles were unambiguous in all instances. This single, two-electron wave in the voltammogram is in marked contrast with the behaviour of dibenzotetrathiafulvalene (**4**),[21] dibenzothiazoles,[22] and other TTF derivatives in which the heterocyclic rings are directly joined to each other, which display *two, reversible, single-electron* redox waves.[4b] Our observations (Table) are consistent with previous observations for vinylogues (**2**),[8] (**3**),[7–9] (**5**),[11] and (**6**)[13] where the difference in potential between the first and second redox waves decreases as the number of vinyl groups, *n*, increases, thus confirming a general rule.[23] For example, coalescence into a single, two-electron wave has been reported for compound (**2**) (n = 3),[8] compound (**5**) (n = 2),[11] and compound (**6**) (X = O and S, n = 4).[13] A single, two-electron redox wave was also reported for compound (**14**).[20] Qualitatively, this behaviour is due to reduced Coulombic repulsion of positive charges which accompanies increased separation, by the linking group, of the heterocyclic rings: the SEM stage will, therefore, more easily gain or lose an electron. In other words, ΔE is reduced with increased separation until, with the insertion of four sp^2 carbon atoms, the two redox waves merge into one wave which corresponds to the transfer of two electrons. Therefore, only E_m is observed in these examples.

The position of the potentials for systems (**8**)–(**24**) is influenced by two general factors:

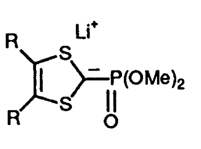
(i) *The structure of the heterocyclic end-group.* The data in the Table clearly show that benzodithiolium cations are easier to reduce (potentials more positive) than benzothiazolium cations with the same linking group. We note that it is well established from previous studies that benzodithiole derivatives are significantly poorer donors than are the dithiole[4b] analogues, *e.g.* DBTTF (4) E_1 +0.72, E_2 + 1.06 V; TTF (5; n = 0), E_1 +0.33, E_2 +0.70 V. It is also known for tetrathiafulvalene (**5**; n = 0) and its derivatives, including dibenzo-TTF (**4**), that an appreciable amount of positive charge [in the SEM and OX states (**1b**) and (**1c**)] is carried by the heterocyclic ring:[24] for the 1,3-dithiole system a major driving force for this charge distribution is the aromaticity of the 1,3-dithiolium cation.[25]

(ii) *The structure of the linking group.* Within each of the four classes of compound studied, the position of E_m is relatively insensitive to the change in structure of the cyclic linking group (**a**)–(**f**). However, as expected, there are significant differences in E_m depending upon the mode of attachment of the group (**a**)–(**f**) to the heterocyclic end groups. Thus, Class 1 and 4 systems are easier to oxidize (potentials more negative) than Class 2 and 3 systems. This is undoubtedly related to the greater stability of the redox stage of the molecule in which the central bridging ring is stabilized by aromatic resonance (*viz.* the OX stage for Class 1 and 4 systems, and the RED stage for Class 2 and 3 systems). For example, compound (**8**), with a central ring aromatic in the OX form of the system, exhibits a redox wave at a strongly negative potential, *viz.* E_m −0.493 V, while compound (**16**), which contains an additional two methine groups, and so has the central ring as a quinodimethane structure in the OX form, is oxidized at a potential which is *ca.* 0.45 V more positive than that for compound (**8**). In other words, compound (**8**) needs significantly more energy for reduction than does compound (**16**). Directly comparable behaviour to this ($\Delta E_m \simeq 0.5$ V) is observed at more positive potentials for the bis(benzodithiole) analogues (**11**) and (**19**).

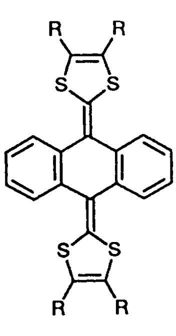
Substitution of N for CH adjacent to the heterocyclic ring [*viz.* compounds (**20**)–(**22**)] has the effect of considerably stabilizing the reduced form of the molecule. Indeed, the redox potential of compound (**20**) is *ca.* 0.8 V more positive than that of compound (**16**), *i.e.* the aza-compounds (**20**) and (**21**) are, comparatively, very poor electron donors. The extreme insolubility of the biphenyl derivative (**22**) in all solvents suitable for cyclic voltammetry has precluded our obtaining reliable data for this compound.

To explain the anomalous redox behaviour of compounds (**16**)–(**19**), for which the two, single-electron waves do not coalesce it is instructive to compare the bis(benzothiazole) derivatives (**16**), (**41**)[7,8] and (**42**),[1,26] which are all conjugated through six bridging sp^2 carbons. Compound (**41**) has an open-chain, polyene bridge, while compound (**42**) has the bridge incorporated into a central cyclohexa-1,3-diene ring, and compound (**16**) contains a central benzene ring. Compounds (**41**) and (**42**) both display a single, reversible two-electron wave at E_m −0.145 and −0.115 V, respectively, while compound (**16**) displays two, reversible, single-electron waves at E_1 −0.039 and E_2 +0.16 V, with a K_{SEM} constant *ca.* 10^3 times greater than that for compounds (**41**) and (**42**). The different behaviour of derivative (**16**) is, therefore, clearly due to the aromaticity of the central ring, not the steric requirements of a six-atom group. An explanation for this is that the olefinic bridges of compounds (**41**) and (**42**) hardly need to change in energy during a two-electron redox process, whereas compound (**16**) can undergo only a one-electron oxidation without significantly changing the energy of the bridging group, *i.e.* by forming the stabilized radical cation $(\mathbf{16})_{SEM}$. The second electron transfer $(\mathbf{16})_{SEM} \longrightarrow (\mathbf{16})_{OX}$ is then pushed to a more positive potential to offset the loss of aromaticity in the bridging ring, and two distinct oxidation waves are observed. If this explanation is true, the radical stability should grow with increasing aromaticity of the central linking group. A comparison of compounds (**16**)–(**18**) shows that this is, indeed, the case. The values of ΔE and K_{SEM} are significantly smaller for the thienyl-bridged derivative (**18**) (least aromatic linking group) than for the benzeno- and naphthaleno-derivatives (**16**) and (**17**). Compound (**19**), the only bis(benzodithiole) derivative in Class 2, undergoes similar behaviour to compound (**16**), at the expected, considerably higher, potential. With N substitution for CH in the bridge [*viz.* compounds (**20**) and (**21**)] the OX stage is stabilized, relative to the SEM stage, presumably by interaction of the nitrogen lone pairs and the heterocyclic cations, so the two waves coalesce.

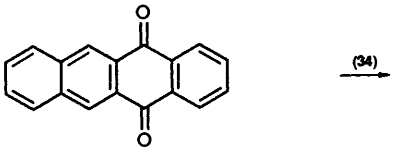
The cyclic voltammetric behaviour of compound (**13**) also warrants discussion. Our results are in agreement with those of



(34) RR = [CH=CH]$_2$
(35) R = H
(36) R = Me

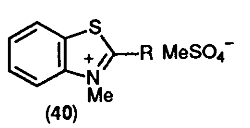


(37) R = H
(38) R = Me



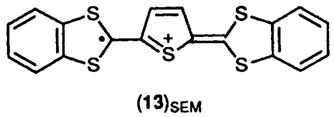
(39)

(15) RED

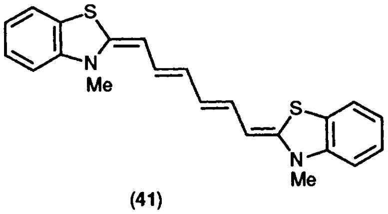


(40)

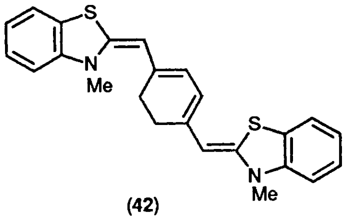
R = Cl, SMe



(13)SEM



(41)



(42)

Takahashi *et al.*[18] who have reported the same redox behaviour for compound (**13**) isolated in the neutral form. Dication (**13**) is the only example within the Class 1 systems for which two, separate one-electron waves are observed. Both redox waves are fully reversible. The relatively large difference between the values of E_1 and E_2 (ΔE 250 mV, K_{SEM} 4 × 10^3) shows that the radical cation of this system has considerable thermodynamic stability. This is ascribed to involvement of the heteroatom of the central bridging ring in stabilizing the radical cation stage, *e.g.* structure (**13**)$_{\text{SEM}}$. The cyclic voltammogram for compound (**13**) is shown as Figure 2.

The neutral species (**13**) has been prepared[1] by the same method used by Takahashi *et al.*[18] Comproportionation reactions of (**13**)$_{\text{RED}}$ and (**13**)$_{\text{OX}}$ species in solution, using the method described previously for related systems,[8] has enabled the radical cation (**13**)$_{\text{SEM}}$ to be detected spectroscopically (Figure 3). The characteristic long-wave length UV–visible absorption of the delocalized radical is observed (λ_{max} 700–900 nm).

In summary, we have synthesized and investigated the electrochemical redox behaviour of several new conjugated polyene systems; these molecules (**8**)–(**24**) are of interest both as model compounds for the design of polymeric conductors, and as extended analogues of electron donors used in conducting charge-transfer complexes.

Experimental

Class 1 Compounds.—Compounds (**25**)–(**27**) were prepared as described in the literature.[27] Methylation was accomplished by refluxing the bis(benzothiazole) derivative with a tenfold excess of trimethyloxonium tetrafluoroborate in methylene dichloride for 1 h. The solution was then cooled to room temperature and the product was collected by filtration. By this method the following compounds were obtained.

N,N′-*Dimethyl*-2,2′-(p-*phenylene*)*bis*-(1,3-*benzothiazolium*) *bis*(*tetrafluoroborate*) (**8**) (90% yield), m.p. 268 °C [from dimethylformamide (DMF)] (Found: C, 48.5; H, 3.6; N, 5.0. $C_{22}H_{18}B_2F_8N_2S_2$ requires C, 48.2; H, 3.3; N, 5.1%).

N,N′-*Dimethyl*-2,2′-(*naphthalene*-1,4-*diyl*)*bis*-(1,3-*benzothiazolium*) *bis*(*tetrafluoroborate*) (**9**) (80%) m.p. 333 °C (from acetonitrile–chloroform) (Found: C, 51.7; H, 3.7; N, 4.5. $C_{26}H_{22}B_2F_8N_2S_2$ requires C, 52.0; H, 3.7; N, 4.7%).

N,N′-*Dimethyl*-2,2′-(*thiophene*-2,5-*diyl*)*bis*-(1,3-*benzothiazolium*) *bis*(*tetrafluoroborate*) (**10**) (74%) m.p. >350 °C (from DMF) (Found: C, 44.2; H, 2.5; N, 5.0. $C_{20}H_{16}B_2F_8N_2S_3$ requires C, 43.9; H, 2.9; N, 5.1%).

Compound (**29**) was prepared from benzene-1,2-dithiol and thiophene-2,5-dicarboxaldehyde[28] in 91% yield, m.p. 148–149 °C (from aq. acetic acid), by the same method that Takahashi *et al.* published while this manuscript was in preparation[18] (Found: C, 55.4; H, 3.0; S, 41.5. $C_{18}H_{12}S_5$ requires C, 55.6; H, 3.1; S, 41.2%); *m*/*z* 388 (M^+); δ_H($CDCl_3$) 7.23–6.88 (8 H, AA′BB′), 6.85 (2 H, s, thiophene CH), and 6.16 (2 H, s).

2,2′-(*Thiophene*-2,5-*diyl*)*bis*-(1,3-*benzodithiolium*) *Bis*(*tetra*-

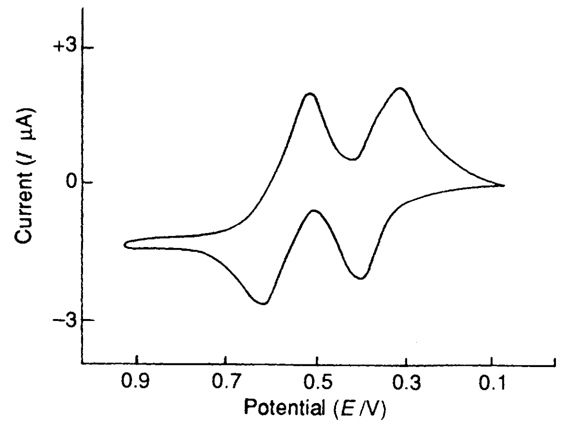


Figure 2. Cyclic voltammogram for compound (**13**).

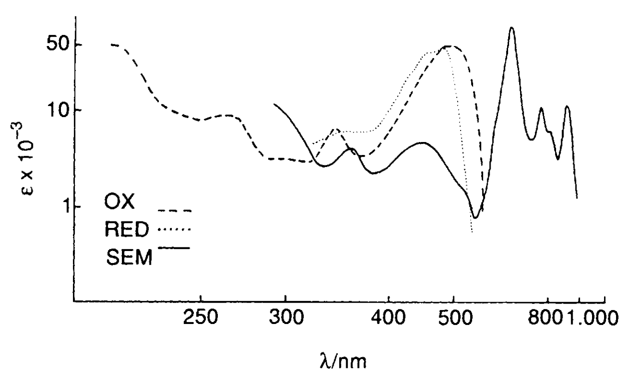


Figure 3. UV–visible spectrum for compound (**13**) in acetonitrile.

fluoroborate) (**13**).—Compound (**29**) (388 mg, 10 mmol) was dissolved in methylene dichloride (15 cm^3) and trityl tetrafluoroborate (660 mg, 20 mmol) was added. The mixture was stirred at reflux for 6 h. After the solution had cooled and been treated with diethyl ether the solid was collected and identified as *compound* (**13**), a red powder (190 mg, 34%), m.p. 240–245 °C (Found: C, 38.3; H, 1.8; S, 28.7. $C_{18}H_{10}B_2F_8S_5$ requires C, 38.6; H, 1.8; S, 28.6%); $\delta_H(CF_3CO_2H)$ 8.22–7.50 (8 H, AA′BB′) and 8.00 (2 H, s); λ_{max} $(\mathbf{13})_{OX}$ (MeCN) 491 (log ε 4.68), 340 (3.81), 303 (3.51), 262 (4.63), and 219 nm (4.87).

There was similarly prepared: 2,2′-(*Naphthalene*-1,4-*diyl*)*bis*-(1,3-*benzodithiole*) (**28**) (48%), m.p. 192–193 °C (from nitromethane) (Found: C, 66.7; H, 4.0; S, 29.4. $C_{24}H_{16}S_4$ requires C, 66.7; H, 3.7; S, 29.6%); *m/z* 432 (M^+).

2,2′-(*Naphthalene*-1,4-*diyl*)*bis*-(1,3-*benzodithiolium*) *bis*(*tetrafluoroborate*) (**12**) was obtained from compound (**28**), by the method described above for compound (**13**), as a buff powder, (60%), m.p. 260–264 °C (Found: C, 47.7; H, 2.1; S, 21.2. $C_{24}H_{14}B_2F_8S_4$ requires C, 47.7; H, 2.3; S, 21.5%).

Class 2 *Compounds*.—The precursor dications (**30**)–(**33**) were prepared as follows: the preparation of compound (**33**) is representative. A solution of benzene-1,2-dithiol (1.42 g, 10 mmol), *p*-phenylenediacetaldehyde (810 mg, 5 mmol), and toluene-4-sulphonic acid (340 mg) in methanol (10 ml) was stirred at 20 °C for 12 h. The mixture was cooled to 0 °C and the solid product was collected and added directly to an excess of trityl tetrafluoroborate in stirred acetonitrile (15 cm^3).

2,2′-(p-*Phenylenedimethylene*)*bis*-[1,3-*benzodithiolium*) *bis*-(*tetrafluoroborate*) *salt* (**33**) precipitated as a buff powder (1.44 g, 50%), m.p. >300 °C (Found: C, 45.3; H, 3.0; S, 22.1. $C_{22}H_{16}B_2F_8S_4$ requires C, 45.3; H, 2.7; S, 21.9%).

There was similarly prepared: N,N′-*Dimethyl*-2,2′-(p-*phenylenedimethylene*)*bis*-(1,3-*benzothiazolium*) *bis*(*tetrafluoroborate*) (**30**) (52%), m.p. >350 °C (Found: C, 47.6; H, 3.9; N, 5.4. $C_{22}H_{22}B_2F_8N_2S_2$ requires C, 47.8; H, 4.0; N, 5.1%); $\delta_H(CF_3CO_2H)$ 7.74–7.22 (8 H, m), 7.20 (4 H, s), 4.46 (4 H, s, methylene), 3.98 (6 H, s); λ_{max}(aq. MeCN) 278 (4.23) and 238 (4.31) nm.

N,N′-*Dimethyl*-2,2′-(*naphthalene*-1,4-*diyldimethylene*)*bis*-(1,3-*benzothiazolium*) *bis*(*tetrafluoroborate*) (**31**) (66%), m.p. >350 °C (Found: C, 54.4; H, 1.6; N, 4.4; S, 10.1. $C_{28}H_{12}B_2F_8N_2S_2$ requires C, 54.7; H, 2.0; N, 4.6; S, 10.4%); δ_H 7.75–7.20 (14 H, m), 4.46 (4 H, s), and 3.99 (6 H, s).

N,N′-*Dimethyl*-2,2′-(*thiophene*-2,5-*diyldimethylene*)*bis*-(1,3-*benzothiazolium*) *bis*(*tetrafluoroborate*) (**32**) was a powder (70%), m.p. 330–335 °C [lit.,[29] 325–330 °C (decomp.) for the bis(perchlorate) salt] (Found: C, 45.5; H, 2.9; N, 4.4; S, 16.6, $C_{22}H_{20}B_2F_8N_2S_3$ requires C, 45.4; H, 3.4; N, 4.8; S, 16.5%).

Compounds (**16**)–(**19**).—The preparation of compound (**19**) is representative. A mixture of dication salt (**33**) (1.0 g) and triethylamine (3 cm^3, excess) in acetonitrile (15 cm^3) was stirred for 16 h at 20 °C. Partial evaporation of the solvent yielded a brown solid, which was recrystallized from DMF to afford *compound* (**19**) (530 mg, 72%) as red crystals, m.p. 292–294 °C (Found: C, 64.7; H, 3.1; S, 31.8. $C_{22}H_{14}S_4$ requires C, 65.0; H, 3.4; S, 31.5%); *m/z* 406 (M^+); $\delta_H(CDCl_3)$ 7.34–6.84 (12 H, m) and 5.90 (2 H, s); λ_{max} 409 (4.70), and 390 nm (4.75).

There were similarly prepared: *compound* (**16**) (93%), m.p. 260–261 °C (Found: C, 72.0; H, 4.9; N, 7.0. $C_{24}H_{20}N_2S_2$ requires C, 72.0; H, 5.0; N, 7.0%); *m/z* 400 (M^+); $\delta_H(CDCl_3)$ 7.5–6.8 (12 H, m), 5.80 (2 H, s), and 3.54 (6 H, s); λ_{max}(MeCN) 417 (4.79), 398 (4.82), 321 (4.32), and 225 nm (4. 71).

Compound (**17**) (81%), m.p. 270–274 °C (Found: C, 74.8; H, 4.6; N, 6.0. $C_{28}H_{22}N_2S_2$ requires C, 74.6; H, 4.9; N, 6.2%); *m/z* 450 (M^+); $\delta_H(CDCl_3)$ 7.5–6.8 (14 H, m), 5.79 (2 H, s), and 3.44 (6 H, s).

Compound (**18**) (80%), m.p. 260–264 °C (Found: C, 65.4; H, 4.4; N, 7.1. $C_{22}H_{18}N_2S_3$ requires C, 65.0; H, 4.4; N, 6.9%); *m/z* 406 (M^+); $\delta_H(CDCl_3)$ 7.5–6.6 (10 H, m), 5.90 (2 H, s), and 3.40 (6 H, s).

Class 3 *Compounds* (**20**)–(**22**).—The preparation of compound (**21**) is representative. A solution of naphthalene-1,4-diamine (0.80 g, 5.0 mmol) in methanol (20 cm^3) was added dropwise to a solution of methyl 3-methyl-2-(methylthio)benzothiazolium sulphate (**40**; R = SMe)[30] (2.93 g, 10 mmol) in a mixture of methanol (10 cm^3) and pyridine (10 cm^3). After 15 min at reflux the solution was cooled and the precipitated product (**21**) was collected by filtration and recrystallized from DMF to yield *compound* (**21**), m.p. 306 °C (2.28 g, 97%) (Found: C, 69.3; H, 4.6; N, 12.1. $C_{26}H_{20}N_4S_2$ requires C, 69.0; H, 4.4; N, 12.4%); *m/z* 452 (M^+); $\delta_H(CF_3CO_2H)$ 9.51 (2 H, s, NH), 7.79–7.28 (12 H, m), and 3.84 (6 H, s, NMe); $\lambda_{max}(C_2H_4Cl_2)$ 362 (4.29) and 309 nm (4.24).

There was similarly prepared: *Compound* (**20**) (84%), m.p. 287 °C (from DMF) (Found: C, 66.0; H, 4.8; N, 13.6. $C_{22}H_{18}N_4S_2$ requires C, 65.7; H, 4.5; N, 13.9%); *m/z* 402 (M^+).

Compound (**22**) (92%), m.p. 348–350 °C (from DMF) (Found: C, 70.6; H, 4.5; N, 11.9. $C_{28}H_{22}N_4S_2$ requires C, 70.2; H, 4.6; N, 11.7%); *m/z* 478 (M^+).

Class 4 *Compounds* (**23**) *and* (**24**).—The preparation of compound (**23**) is representative: a solution of *p*-phenylenediacryloyl dichloride (1.24 g, 5.0 mmol) in methylene dichloride (20 cm^3) was added dropwise into a stirred solution of *N*-methyl-*o*-aminothiophenol (1.39 g, 10 mmol) in methylene dichloride (20 cm^3) at 0 °C. After being stirred at 20 °C for 1 h, the solution was heated at reflux for 1 h. After cooling, the solution was partially evaporated to precipitate compound (**23**) as the dichloride salt. The precipitate was collected, dissolved in water, and reprecipitated as the *bis(tetrafluoroborate) salt* (**23**) (4.40 g, 77%), m.p. 340 °C (Found: C, 52.1; H, 3.9; N, 4.3; S, 10.2. $C_{26}H_{22}B_2F_8N_2S_2$ requires C, 52.0; H, 3.7; N, 4.7; S, 10.7%); $\delta_H(CF_3CO_2H)$ 7.86–7.34 (16 H, m), and 3.95 (6 H, s); λ_{max}(MeCN) 445sh (4.68) and 432 nm (4.85).

There was similarly prepared: *Compound* (**24**) (64%), m.p. >340 °C (Found: C, 47.7; H, 2.3; S, 20.7. $C_{24}H_{16}B_2F_8S_4$ requires C, 47.5; H, 2.6; S, 21.1%).

Compound (**15**).—2-Dimethoxyphosphinoyl-1,3-benzodithiole[20] (238 mg, 1 mmol) and butyllithium (1 mol equiv.) were mixed at −78 °C in tetrahydrofuran (THF) (10 cm^3). After the mixture had been stirred for 20 min, a suspension of benz[*a*]anthracene-5,12-dione (**39**) (130 mg, 0.5 mmol) in THF (10 cm^3) was added and the mixture was stirred at −78 °C for 1 h, then allowed to warm to room temperature, and stirred for a further 24 h. Aqueous work-up, followed by extraction into methylene dichloride, yielded a crude red solid, which was chromatographed on an alumina column [eluant hexane–diethyl ether (3:1 v/v)] to furnish *compound* (**15**) as an orange solid (128 mg, 48%), m.p. 285–290 °C (decomp.) (Found: C, 72.5; H, 3.6. $C_{32}H_{18}S_4$ requires C, 72.4; H, 3.4%); *m*/*z* 530 (M^+); $\delta_H(CDCl_3)$ 7.90 (2 H, s) and 7.80–7.24 (16 H, m).

There was similarly prepared, from anthraquinone and carbanion (**34**), *compound* (**14**) (68%), m.p. 263–264 °C (lit.,[20] 262–263 °C) (Found: C, 69.9; H, 3.6; S, 26.4. $C_{28}H_{16}S_4$ requires C, 70.0; H, 3.3; S, 26.7%); *m*/*z* 480 (M^+); $\delta_H(CDCl_3)$ 7.81–7.21 (m).

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Paper 0/01662D
Received 12*th April* 1990
Accepted 29*th May* 1990