

# New $\pi$ -electron donor systems based on acenaphtho[1,2-*b*][1,4]-dithiine

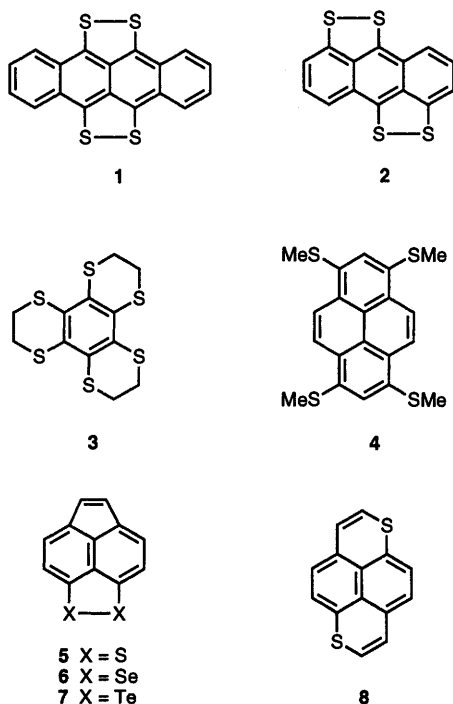
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Syntheses of the acenaphtho[1,2-*b*][1,4]dithiine derivatives **12**, **25** and **29** are reported. Cyclic voltammetric studies reveal that these compounds undergo reversible single-electron oxidations at  $< 1.0$  V, vs. Ag/AgCl. Lithiation of compound **12** with BuLi (2 equiv.) followed by addition of either methyl iodide or ethyl chloroformate yielded the unstable ring-opened acetylene derivatives **22a** and **22b**, respectively. A new synthesis of 1,2-diselenine derivative **33** is reported. Compound **25** formed 1:1 charge-transfer complexes with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and with 2,5-dibromo-TCNQ, both of which were electrical insulators. The X-ray crystal structures of compound **25**, a charge-transfer complex **25**:Br<sub>2</sub>TCNQ (1:1 stoichiometry) and compound **33** are reported. In the structure of **25**:Br<sub>2</sub>TCNQ, molecules of **25** and Br<sub>2</sub>TCNQ form mixed stacks. The folding of the donor along the S...S vector in the complex is 17° (cf. 48° in pure **25**) and the conformation of **25** is discussed in the light of previous studies on 1,4-dithiine derivatives. An interesting feature of the crystal structure of **33** is the formation of pseudo-dimers with two short intermolecular Se...Se contacts.

Although the radical cation salts of simple arenes such as naphthalene, fluoroanthrene, pyrene and perylene are quasi-one-dimensional organic semiconductors ( $\sigma_{\text{H}} = 10^{-1}$ – $10^{-3}$  S cm<sup>-1</sup>) they are, in general, unstable and cannot be handled or stored easily.<sup>1</sup> The introduction of sulfur (or selenium) atoms into the periphery of such systems to form the substituted arenes exemplified by compounds **1**–**4**<sup>2</sup> has imparted greater



stability to the radical cation salts, coupled with increased conductivity, and some systems, notably salts of tetrathio-tetracene **1**, retain metallic conductivity to very low temperatures.<sup>2b</sup> The lone pairs on the heteroatoms are close in energy to the  $\pi$ -orbitals which dominate the intrastack interactions (band formation) and they engage in interstack interactions by overlap of S or Se 'd' orbitals, thereby reducing anisotropy effects and increasing the dimensionality of the system. This is an important topic in the design of new molecular conductors.<sup>3</sup>

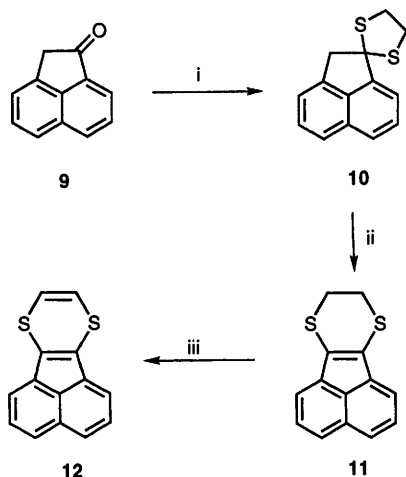
Work has also been carried out on the synthesis of dichalcogenide-bridged acenaphthylenes **5**–**7**, salts of which showed respectable room temperature conductivities but still proved to be too unstable for general applications.<sup>4</sup> Similarly, replacement of two sp<sup>2</sup> carbon atoms within the core framework of simple arenes with the more polarisable sulfur nucleus has led to 1,6-dithiapyrene donors **8** and close analogues.<sup>5</sup> The dication of **8** is isoelectronic with the parent arene, and the charge-transfer salts formed from this donor are air stable and show good electrical conductivities. Recently, Tani *et al.* reported the synthesis of acenaphtho[1,2-*b*][1,4]dithiine **12**, derived from acenaphthenone **9**.<sup>6</sup> This new donor **12** showed a reversible first oxidation wave in solution ( $E_1^{\ddagger} = +0.68$  V versus SCE) and formed a hexafluorophosphate salt by electrocrystallisation. The needles of this salt (**12**)<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup>, showed relatively high room temperature conductivity ( $\sigma_{\text{H}} = 5$  S cm<sup>-1</sup>). The fact that compound **12** possessed interesting donor properties, and could be synthesised from readily available starting materials, made modification of this basic framework an attractive target for our continuing studies on new charge-transfer systems.

Initially, two complementary methodologies to synthesise derivatised systems based on the framework **12** were envisaged. These were (i) functionalisation of the 8 and/or 9 positions (*viz.* the peripheral alkene carbons) of **12**, *via* a lithiation-based protocol, and (ii) the introduction of functionality early in the reaction sequence outlined in Scheme 1, by the use of substituted dithiols in step (i).

## Results and discussion

### Synthesis

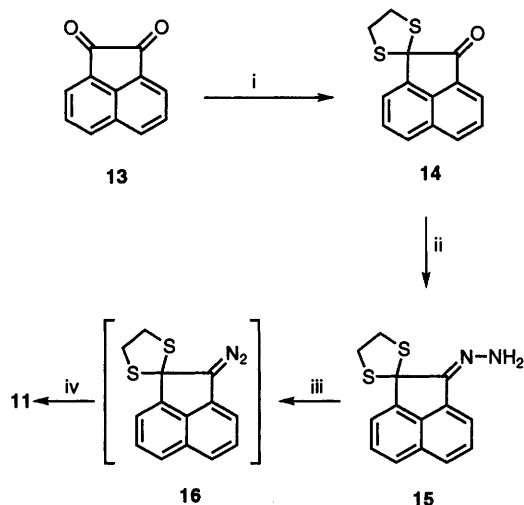
In our hands, the synthesis of **12** by the methodology reported by Tani *et al.*<sup>6</sup> proved capricious: all attempts to perform the aluminium trichloride mediated dithioketalisation of **9** to form **10** using the literature route<sup>6</sup> were unsatisfactory. Instead, this conversion was readily accomplished by the reaction of acenaphthen-1-one **9** with ethane-1,2-dithiol in the presence of a catalytic amount of toluene-*p*-sulfonic acid in refluxing benzene with the azeotropic removal of the residual water by use of a Dean–Stark apparatus. Dithioketal **10** was isolated from this reaction but not purified, and was immediately treated with tellurium tetrachloride in dichloromethane<sup>7</sup> to



**Scheme 1** Reagents and conditions: i,  $(\text{CH}_2\text{SH})_2$ , PhH, *p*-TsOH, heat; ii,  $\text{TeCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ , 45% (based on **9**); iii, DDQ, 1,4-dioxane, 28%

furnish the dihydroacenaphtho[1,2-*b*][1,4]dithiine derivative **11** (45% yield from **9**) which was spectroscopically identical to that reported by Tani *et al.*<sup>6</sup> Dehydrogenation of **11** was achieved using freshly recrystallised 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in anhydrous 1,4-dioxane at 100 °C to afford **12** in 28% yield. Attempts to achieve this transformation using either sulfur or selenium as dehydrogenation reagents at high temperatures proved unsuccessful.

A new synthesis of **11**, based on the work of Allen *et al.*<sup>8</sup> is outlined in Scheme 2. Acenaphthenequinone **13** was readily



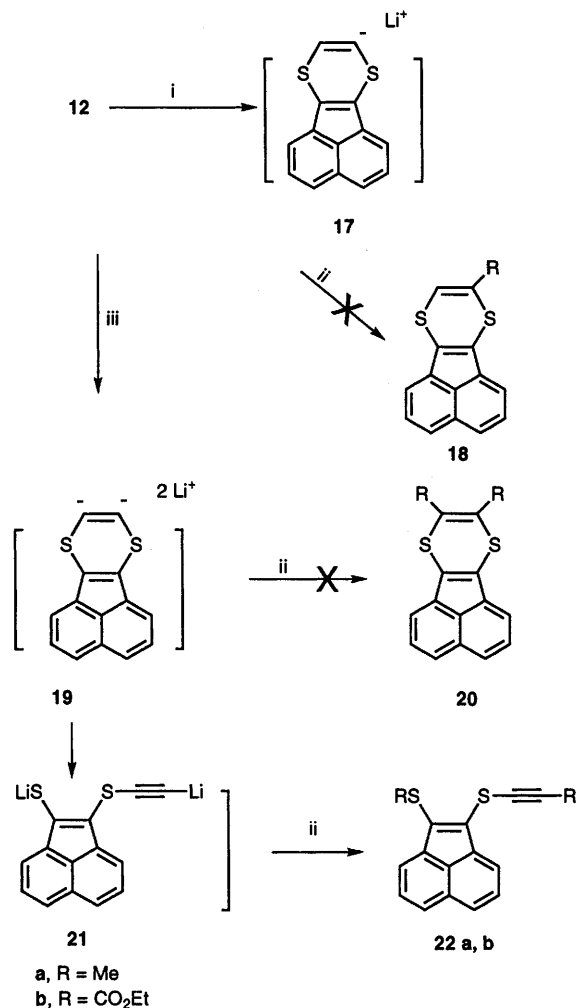
**Scheme 2** Reagents and conditions: i,  $(\text{CH}_2\text{SH})_2$ , PhH, *p*-TsOH, heat, 73%; ii,  $\text{H}_2\text{NNH}_2$ , MeOH, heat, 55%; iii,  $\text{MnO}_2$ , KOH; iv, HCl, 71% (based on **15**)

converted into the dithioketal **14** (73% yield), which reacted with hydrazine hydrate to afford hydrazone derivative **15** in 55% yield. Reaction of **15** with activated manganese dioxide, followed by acidification of the solution, yielded compound **11** in 71% yield, presumably *via* the intermediate diazo derivative **16** which we did not attempt to isolate.

With quantities of compound **12** in hand, we sought to modify the basic skeleton by lithiation at the 8 and/or 9 positions, followed by quenching the anion(s) with electrophiles, as outlined in Scheme 3. Such an approach has been successfully applied to the synthesis of many functionalised tetrathiafulvalene (TTF) derivatives.<sup>9</sup> It was hoped that the known propensity of the parent 1,4-dithiine to ring-open upon lithiation,<sup>10</sup> would be suppressed by the presence of a large fused aromatic moiety within system **12**.

The formation of the mono-lithiated derivative **17** was, therefore, attempted using lithium diisopropylamide (LDA) or

BuLi as base, both at  $-78\text{ }^\circ\text{C}$  and at ambient temperature. Quenching these reactions with either methyl iodide or ethyl chloroformate did not lead to the formation of the mono-functionalised systems **18**, but instead, led to the recovery of starting material **12** in high yield. The use of two equivalents of BuLi in diethyl ether at room temperature induced a distinct colour change of the solution from purple to a deep red colour; however, quenching these reactions did not lead to the mono-substituted derivatives **18**, nor to the disubstituted analogues **20**. The only products isolated were the substituted acetylenic compounds **22a** and **22b**, which were presumably formed by ring-opening of the transient species **19** to afford the dilithio intermediate **21**, which was subsequently trapped by the electrophile (Scheme 3). We cannot exclude the possibility that



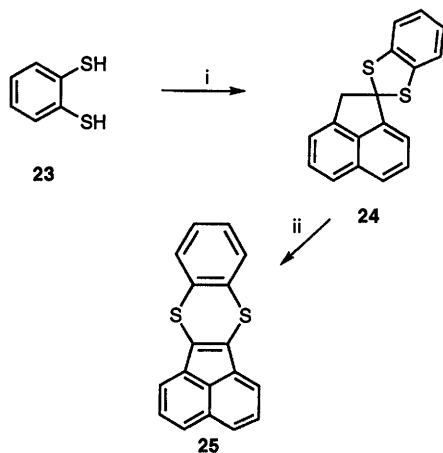
**Scheme 3** Reagents and conditions: i, BuLi (1 equiv.)  $-78\text{ }^\circ\text{C}$ ,  $\text{Et}_2\text{O}$ ; ii, RX; iii, BuLi (2 equiv.),  $\text{Et}_2\text{O}$ ,  $20\text{ }^\circ\text{C}$

the monolithiated species **17** ring opens, and the ensuing acetylene is then deprotonated, but the precedents suggest that dianion **19** will be formed under these conditions.<sup>10</sup> Compounds **22** were clearly identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and by the presence of an acetylenic absorption peak in the IR spectra. Both derivatives **22a** and **22b** decomposed rapidly at room temperature, and all attempts to purify them for elemental analysis and/or high resolution mass spectrometry proved futile, with only the diester **22b** giving a parent ion in the mass spectrum.

The failure of the lithiation protocol to produce a viable route to substituted derivatives of **12** is indicative of the propensity of the 1,4-dithiine dianion system to undergo ring opening. The dianion of **12** does not ring-open below  $0\text{ }^\circ\text{C}$ , demonstrating that it is significantly more stable than the dianion formed from the parent 1,4-dithiine, which opens

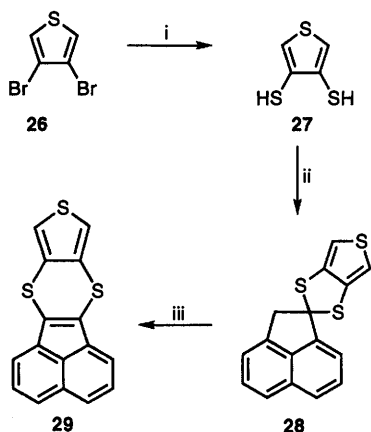
spontaneously at above  $-30\text{ }^{\circ}\text{C}$ .<sup>10</sup> An alternative approach to the analogue of **20b** via a Diels–Alder cycloaddition between dimethyl acetylenedicarboxylate and acenaphthenedithione was not viable, as previous workers had reported that such a reaction affords a dithiine and none of the desired cycloadduct.<sup>11</sup>

The incorporation of secondary functionality via the use of different dithiols following the route in Scheme 1 was addressed. Two new targets were envisaged, those containing a benzo- or thienyl-fused ring, viz compounds **25** and **29**. These particular substituents were chosen for the following reasons: (i) an aromatic ring fused to the dithiine system may increase the amount of  $\pi$ – $\pi$  interactions in the solid state,<sup>12</sup> and (ii) the presence of a thienyl unit allows the possibility of additional intermolecular  $\text{S}\cdots\text{S}$  interactions, and polymerisation of the system by chemical<sup>13</sup> or electrochemical methods<sup>14</sup> which, in turn, could lead to 1,4-dithiine substituted conducting polymers. The synthesis of the benzodithiine donor **25** is outlined in Scheme 4. This straightforward route proceeded from the commercially



**Scheme 4** Reagents and conditions: i, **9**, PhH, *p*-TsOH, heat, ca. 98%; ii,  $\text{TeCl}_4$ , dichloromethane, 13%

available benzene-1,2-dithiol **23** and ketone **9**. The dithioketal **24** was isolated in sufficient purity to be treated directly with tellurium tetrachloride in dichloromethane, affording compound **25**, albeit in only 13% isolated yield. An analogous procedure enabled the four-step synthesis of the thienyl analogue **29** (Scheme 5). The thiophene-3,4-dithiol **27** required for this route

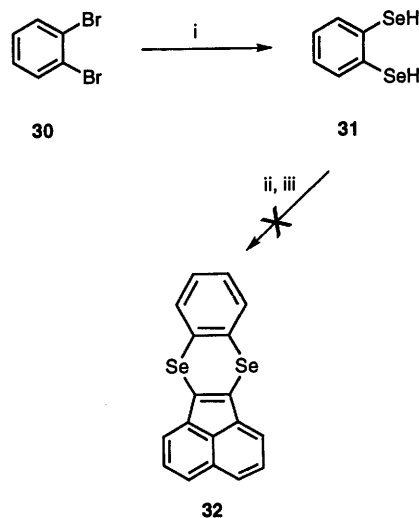


**Scheme 5** Reagents and conditions: i,  $2 \times \text{Bu}^t\text{Li}$ ,  $\text{S}_8$ ,  $-78\text{ }^{\circ}\text{C}$ ,  $\text{Et}_2\text{O}$ ; ii, **9**, PhH, *p*-TsOH, heat; iii,  $\text{TeCl}_4$ , dichloromethane, 19% (based on **26**)

was obtained by lithium–bromine exchange on 3,4-dibromothiophene **26**, followed by sulfur insertion.<sup>15</sup> We chose not to purify either dithiol **27** or dithioketal **28**, because the reaction mixtures were extremely malodorous. The target molecule **29** was obtained as a purple solid in 19% overall yield from **26**.

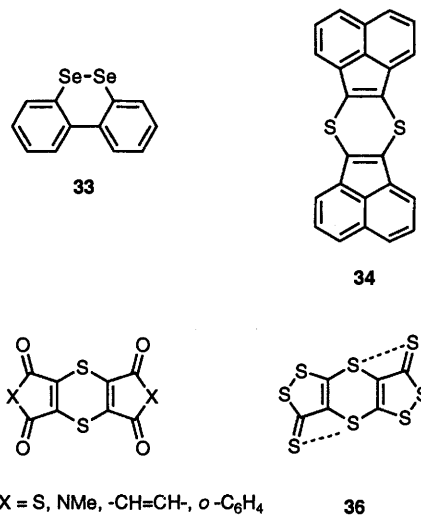
In an attempt to introduce selenium atoms into the framework of these donor systems, the synthesis of **32** was

proposed via benzene-1,2-diselenol **31**, which we attempted to generate *in situ* from 1,2-dibromobenzene **30** using the protocol previously employed to produce **27**<sup>15</sup> (Scheme 6). Only one



**Scheme 6** Reagents and conditions: i,  $2 \times \text{Bu}^t\text{Li}$ ,  $\text{Se}_8$ ,  $-78\text{ }^{\circ}\text{C}$ ,  $\text{Et}_2\text{O}$ , then HCl; ii, **9**, PhH, *p*-TsOH, heat; iii,  $\text{TeCl}_4$ , dichloromethane

product, a red crystalline solid, was isolated from the reaction sequence, and spectroscopic and analytical data clearly showed that it was not the expected benzodiselenine derivative **32**. Instead, the product was dibenzo[*c,e*][1,2]diselenine, **33**, which had been synthesised previously by different routes.<sup>16</sup> In the present case, **33** is presumably formed during the attempted preparation of **31** from 1,2-dibromobenzene; indeed, aromatic diselenides have very recently been prepared by an analogous lithiation and selenium insertion sequence from the corresponding aryl bromides, followed by oxidative work-up.<sup>17</sup>



**35** X = S, NMe,  $-\text{CH}=\text{CH}-$ ,  $o\text{-C}_6\text{H}_4$

#### Cyclic voltammetric studies and charge-transfer complex formation

The electrochemical redox properties of the new donors **25** and **29** have been studied by cyclic voltammetry in acetonitrile solution. The cyclic voltammograms of both compounds showed a reversible one-electron oxidation wave to form the cation radical species,  $\mathbf{25}^{+\bullet}$  and  $\mathbf{29}^{+\bullet}$ , respectively. Compound **29** is the more easily oxidised ( $E_1^{\ddagger} = +0.93\text{ V}$  for **25** and  $+0.77\text{ V}$  for **29**, versus Ag/AgCl) which is consistent with the known trend that thienyl compounds usually have lower ionisation potentials than analogous aromatic hydrocarbons.<sup>18</sup> For both compounds **25** and **29** a complex, irreversible second oxidation wave was observed at  $E_2^{\ddagger} = \text{ca. } 1.5\text{ V}$ ). Thus, both **25** and **29** are slightly harder to oxidise than the parent system **12** ( $E_1^{\ddagger} = +0.68\text{ V}$ ).<sup>6</sup> The attempted electropolymerisation of compound

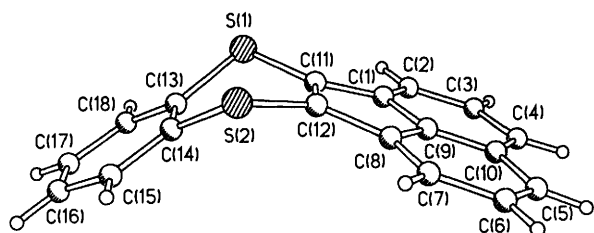


Fig. 1 Molecular structure of compound **25**

**29** did not afford any discernible deposition of material on a platinum electrode (dichloromethane, 20 °C, 10–12  $\mu$ A). However, this compound proved to be stable at high constant current (unlike many other organic donor molecules) presumably due to the high second oxidation potential of this system. This makes **29** a promising candidate for the electrochemical growth of cation radical salts with inorganic anions, which we are currently exploring.

Both donors **25** and **29** formed 1:1 complexes with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) which were electrical insulators (two-probe, compressed pellet method).<sup>19</sup> The presence of a nitrile absorption peak at 2215  $\text{cm}^{-1}$  (**25**:TCNQ) and 2217  $\text{cm}^{-1}$  (**29**:TCNQ) suggested that there was a small degree of charge-transfer from the donor to TCNQ within the complexes.<sup>20</sup> The use of the more powerful electron acceptor 2,5-dibromo-TCNQ also afforded a 1:1 complex with donor **25**, although all attempts to form an analogous salt with **29** failed. The complex **25**:Br<sub>2</sub>TCNQ was also an insulator although a greater degree of charge-transfer was suggested by the shift of the nitrile absorption peak to 2209  $\text{cm}^{-1}$ .

#### X-Ray crystal structures of **25**, **25**:Br<sub>2</sub>TCNQ and **33**

Compounds **25**, **25**:Br<sub>2</sub>TCNQ and **33** were characterised by single-crystal X-ray analyses.

The molecular structure of **25** (Fig. 1) is folded along the S(1)⋯S(2) vector by 48°, with both parts of the molecule being planar to within  $\pm 0.04$  Å. This conformation is similar to that of 1,4,2-dithiazine derivatives in which the heterocycle folds by 48–50°,<sup>21</sup> but it is in sharp contrast to the conformation of bisacenaphtho[1,2-*b*:1,2-*e*][1,4]dithiine **34**,<sup>22</sup> which, remarkably for an uncharged 1,4-dithiine derivative,<sup>10b</sup> is planar. The crystal packing of **25** [Fig. 2(a) and (b)] is dominated by stacks of molecules (related *via* the glide plane *c*), with their acenaphthene moieties parallel to within 1.3° and with interplanar separations of *ca.* 3.54 Å.

In the structure of the complex **25**:Br<sub>2</sub>TCNQ (1:1 stoichiometry) molecules of **25** and Br<sub>2</sub>TCNQ form mixed stacks (Fig. 3) parallel to the *x* axis and symmetrically generated by the translation along that axis. This stacking motif explains the low conductivity of this complex.<sup>3a</sup> The folding of the donor molecule is reduced significantly to 17° (*cf.* 48° in pure compound **25**, Fig. 1) and the  $\pi$ - $\pi$  conjugation in the dithiine ring is increased, as indicated by a contraction of the S–C(phenylene) and S–C(acenaphtho) bonds to 1.765(5) and 1.730(4) Å, respectively, compared to 1.780(2) and 1.747(2) Å in the crystal of **25** (*cf.* 1.745 Å in the planar molecule **35**).<sup>22</sup> However, other bond distances in the complex **25**:Br<sub>2</sub>TCNQ do not differ significantly from those in the pure components, **25** and Br<sub>2</sub>TCNQ<sup>23</sup> (Tables 1 and 2). It is difficult to estimate the degree of charge-transfer in **25**:Br<sub>2</sub>TCNQ from an analysis of the bond lengths, as the only fully reported structures containing Br<sub>2</sub>TCNQ anions of definite charges, (DEM)(Br<sub>2</sub>-TCNQ)<sub>*n*</sub> (where DEM = 4,4-diethylmorpholinium cation, and *n* = 1 or 2) were studied on very imperfect crystals and are of limited accuracy.<sup>24</sup>

Distortion of the cyano groups in *syn*-positions to the bromine atoms, observed both in **25**:Br<sub>2</sub>TCNQ and in Br<sub>2</sub>TCNQ (see Table 2), can be attributed to secondary

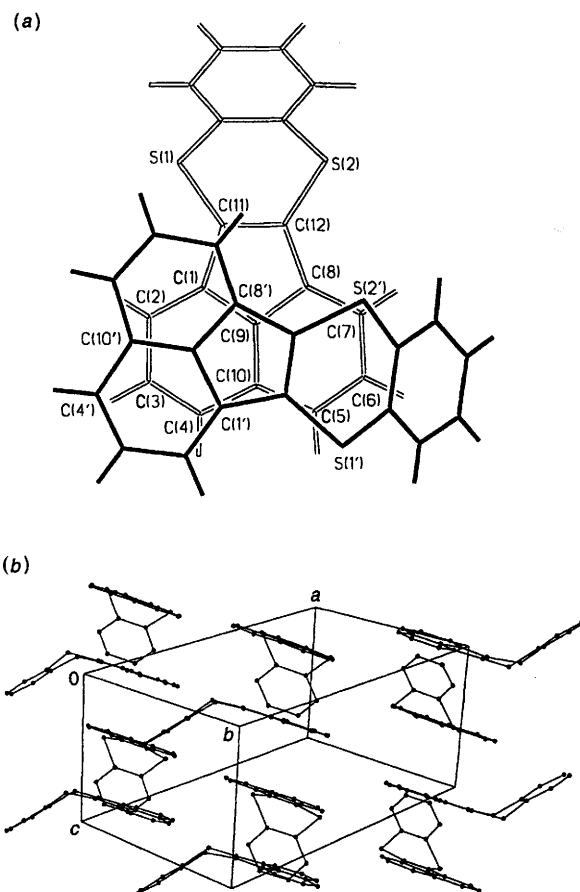


Fig. 2 (a) Overlap of the molecules of **25** in a stack, viewed down *z* axis; (b) crystal packing of compound **25** (H atoms are omitted)

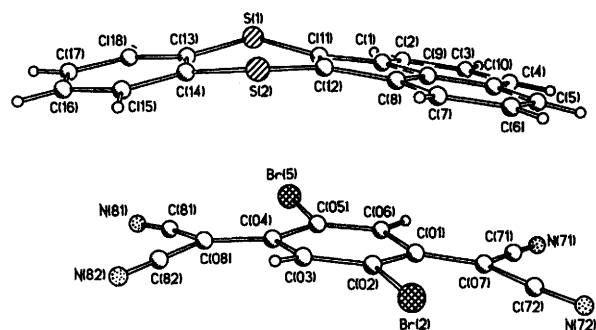


Fig. 3 Molecules of **25** and dibromo-TCNQ in the crystal of **25**:Br<sub>2</sub>TCNQ

Br⋯C bonding, rather than to Br⋯N repulsion. While the neutral Br<sub>2</sub>TCNQ molecule is perfectly planar,<sup>23</sup> in **25**:Br<sub>2</sub>TCNQ it is folded in a boat fashion along the C(02)⋯C(06) and C(03)⋯C(05) vectors by 4.5 and 7°, respectively. The direction of folding is the same as in both adjacent dithiine moieties, *i.e.* 'polar' throughout the stack. The main planar moieties of the **25** and Br<sub>2</sub>TCNQ molecules are parallel to within 1°, with nearly uniform interplanar separations of 3.31 and 3.36 Å, and the shortest contacts are C⋯C 3.32–3.35, and S⋯C 3.20–3.31 Å, which imply substantial  $\pi$ - $\pi$  overlap along the stack. The S and Br atoms, which will bear  $\delta+$  and  $\delta-$  charges, respectively, form intrastack contacts of 3.66–3.82 Å (*cf.* the normal van der Waals distance<sup>25</sup> of 3.75 Å), but surprisingly no short interstack contacts exist. On the other hand, the moieties related *via* a crystallographic translation along the [110] axis, are linked into an infinite chain (Fig. 4) by pairs of roughly linear contacts Br(2)⋯N(81) 3.17 and Br(5)⋯N(72) 2.95 Å (*cf.* 3.12 Å in Br<sub>2</sub>TCNQ).<sup>23</sup>

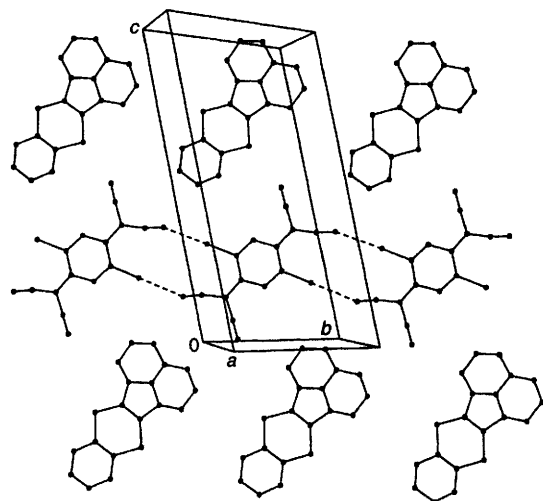
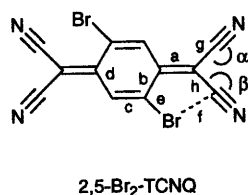
The conformation of the 1,4-dithiine ring deserves some comment, in view of substantial theoretical interest in this

**Table 1** Selected bond lengths (Å) and angles (°) in 7,10-dithiabenzofluoranthene moieties

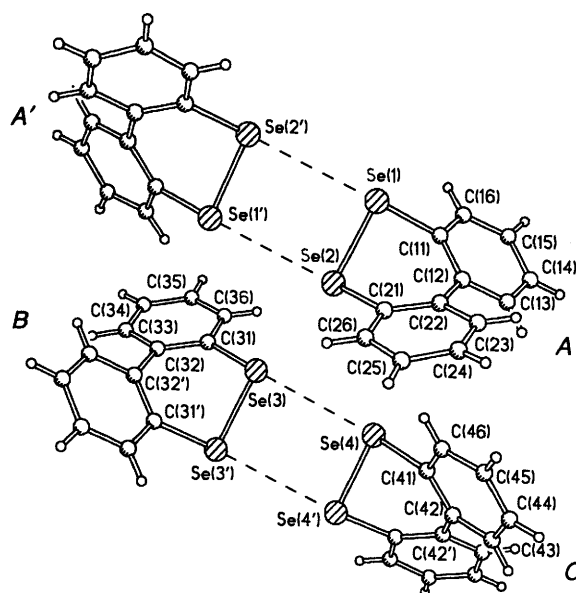
	<b>25</b>	<b>25:Br<sub>2</sub>TCNQ</b>
S(1)–C(11)	1.747(2)	1.734(4)
S(1)–C(13)	1.781(2)	1.761(5)
C(1)–C(2)	1.371(3)	1.375(6)
C(1)–C(9)	1.416(3)	1.409(6)
C(1)–C(11)	1.470(3)	1.473(6)
C(2)–C(3)	1.418(3)	1.430(7)
C(3)–C(4)	1.369(3)	1.366(8)
C(4)–C(10)	1.424(3)	1.426(8)
C(9)–C(10)	1.387(3)	1.398(6)
C(13)–C(14)	1.394(3)	1.394(7)
C(11)–S(1)–C(13)	100.0(1)	103.1(2)
S(2)–C(12)	1.747(2)	1.726(4)
S(2)–C(14)	1.778(2)	1.768(5)
C(7)–C(8)	1.365(3)	1.381(6)
C(8)–C(9)	1.410(3)	1.426(6)
C(8)–C(12)	1.476(3)	1.474(6)
C(6)–C(7)	1.416(3)	1.425(7)
C(5)–C(6)	1.370(3)	1.381(8)
C(5)–C(10)	1.421(3)	1.418(7)
C(11)–C(12)	1.361(3)	1.366(6)
C(12)–S(2)–C(14)	99.6(1)	103.1(2)

**Table 2** Selected bond lengths (Å) and angles (°) in dibromo-TCNQ moieties (mean of chemically equivalent bonds)

	<b>25:Br<sub>2</sub>TCNQ</b>	<b>Br<sub>2</sub>TCNQ</b>
a	1.389(6)	1.378(6)
b	1.454(6)	1.446(6)
c	1.350(6)	1.344(6)
d	1.450(6)	1.460(6)
e	1.879(4)	1.874(6)
f	3.016(4)	3.011(6)
g	1.429(6)	1.439(6)
h	1.439(6)	1.432(6)
C–N	1.149(6)	1.141(7)
α	177.7(5)	177.9(5)
β	170.6(5)	171.0(4)

**Fig. 4** Crystal packing in **25:Br<sub>2</sub>TCNQ**; layer parallel to the (1 - 1 0) plane (H atoms are omitted)

system and its biological significance. The preferable ring conformation, both in solid state and in solution, is known to be a boat with folding along the S(1)⋯S(4) vector.<sup>26</sup> On the other hand, extensive MO studies<sup>27</sup> give divided evidence as to whether a boat or a planar conformation is the more stable; in any case, the barrier between them is supposed to be very

**Fig. 5** Pseudo-dimers in the crystal of **33**. Atoms generated by twofold axis are primed. Bond distances (Å): Se(1)–Se(2) 2.323(2), Se(3)–Se(3') 2.321(2), Se(4)–Se(4') 2.326(2), Se(1)–C(11) 1.907(6), Se(2)–C(21) 1.912(7), Se(3)–C(31) 1.906(7), Se(4)–C(41) 1.893(7); angles (°): Se(2)–Se(1)–C(11) 93.3(2), Se(1)–Se(2)–C(21) 93.7(3), Se(3')–Se(3)–C(31) 93.1(3), Se(4')–Se(4)–C(41) 93.3(2).

low. Both empirical trends<sup>28</sup> and MO calculations<sup>27b</sup> indicate that electron-withdrawing substituents favour the planar conformation.

Our search of the October 1995 release of the Cambridge Structural Database<sup>29</sup> yielded 21 X-ray structures containing the 1,4-dithiine ring, 19 of them as a part of a fused system. The only two monocyclic compounds, *viz.* the parent 1,4-dithiine<sup>30</sup> and its tetracyano derivative,<sup>31</sup> adopt boat conformations, folding by 43 and 56°, respectively. Twelve other structures have folding angles between these values. Two compounds show different degrees of folding in symmetrically independent rings, 48 *vs.* 35° in the radical cation of bis(vinylenedithio)-TTF,<sup>32</sup> and 39 *vs.* 28° in the bis(1,4-dithiine-2,3-dithiolato)-nickelate(III) anion,<sup>33</sup> participating in strong charge-transfer interactions.

On the other hand, in six structures (**34–36**) the conformation is planar to within 2° or by crystallographic symmetry. In four of these, the dithiine ring is fused between two quinone or similar moieties; here the planarity can be easily explained by mesomeric stabilization (MO calculations give the charges of +0.5 on the sulfur and –0.25 on the oxygen atoms).<sup>27b</sup> Intramolecular charge transfer can also be invoked for the planarity of **36** (together probably with the non-covalent S⋯S interactions),<sup>27c</sup> but that of **34** is more difficult to explain.

Thus the conformation of **25** and its partial planarisation in the complex with Br<sub>2</sub>TCNQ are in accordance with the general trend and are indicative of substantial charge transfer in **25:Br<sub>2</sub>TCNQ**. However, the existence of two 'clusters' of ring conformations with practically nothing in between is rather surprising, if the potential barrier is really low. Especially intriguing is the contrast between the conformations of closely related molecules **25** and **34**. One is tempted to suggest that the system is really quite close to the threshold of stability, and more detailed investigation of these and similar compounds may reveal different polymorphs.

The crystal structure of **33** has been reported earlier,<sup>16a</sup> but with rather low precision [*R*(F) = 0.107] and slightly different unit cell parameters (see Experimental section), therefore we performed a full structure determination. The tetragonal structure contains three crystallographically non-equivalent molecules (Fig. 5), one (*A*) in a general position and two others (*B* and *C*) located on twofold axes. All three molecules have essentially the same geometry, their benzene rings forming

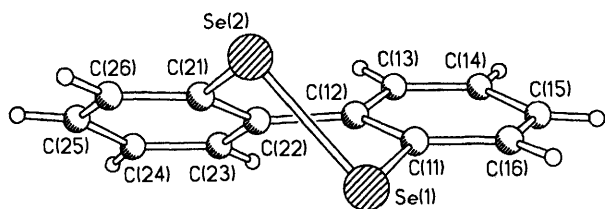


Fig. 6 Molecular conformation of 33

dihedral angles of 38, 41 and 36°, and the heterocycles adopting a puckered conformation with C–Se–Se–C torsion angles of 59, –59 and –57°, respectively (see Fig. 6).

It is well known<sup>34</sup> that the most favourable torsion angle ( $\tau$ ) around a S–S bond is *ca.* 90°, and deviation from such a conformation causes lengthening of this bond. To find out whether or not the same is true about the Se–Se bond, we reviewed the structures of diselenide compounds, using the Cambridge Structural Database.<sup>29</sup> It yielded 70 symmetrically independent moieties (besides the present compound), falling into three groups: (i) heterocycles fused to aromatic systems, which force a planar, or nearly planar, conformation,  $\tau \leq 10^\circ$  (28 cases); (ii) acyclic RSeSeR units on a crystallographic inversion centre, with an ideal *trans*-conformation,  $\tau = 180^\circ$  (6 cases) and (iii) cyclic and acyclic molecules with twisted conformations (36 cases, in 31 of which  $\tau$  falls within the range 71–113°, and in 20 within the range 71–88°). Thus the most favourable conformation is a twisted one, similar to disulfides, unless the system is sterically constrained. The earlier suggestion<sup>35</sup> that acute  $\tau$  angles are preferable, is also confirmed. However, Se–Se distances, unlike S–S distances, are practically independent of  $\tau$ . Their ranges for groups (i) and (iii) are 2.29–2.36 and 2.29–2.36 Å, respectively, with an average of 2.33 Å for either group. Se–Se bonds are longer in group (ii), which includes the most sterically overcrowded molecules and dications, but even then only up to 2.33–2.39 Å, with the single exception being the diylide [(Ph<sub>3</sub>P)<sub>2</sub>C<sup>+</sup>Se]<sub>2</sub>. In this compound the Se–Se distance [2.492(2) Å] is outside the range in all three groups, though the authors<sup>36</sup> regard it as ‘not unusual’. Thus the conformation around the Se–Se bond in 33 is not the most favourable, but this does not lead to any stretching of the bond [mean length 2.323(2) Å].

The peculiar feature of the crystal packing in 33 is that molecule *A* and its equivalent *via* a twofold axis form a pseudodimer with two short intermolecular Se(1)⋯Se(2) contacts of 3.64 Å, and a similar dimer is formed by molecules *B* and *C*, with two Se(3)⋯Se(4) contacts of 3.59 Å. These distances, which are considerably less than double the van der Waals radius of Se (2.0 Å),<sup>37</sup> together with the rather narrow ranges of Se–Se⋯Se (88–90°) and C–Se⋯Se (149–163°) angles, probably indicate some specific non-bonded interactions. Other Se⋯Se contacts are much longer (4.14–4.31 Å).

## Conclusions

Derivatives of the title ring system have been synthesised, and compound 25 has been studied in detail as an electron donor for the formation of charge-transfer complexes. The X-ray crystal structures of 25 and of a 1:1 charge-transfer complex with the electron acceptor 2,5-dibromo-TCNQ have been obtained: the mixed stacking motif of the complex explains its low conductivity. The relatively low oxidation potentials of compounds 25 and 29 ( $E_1^{\ddagger} = +0.93$  and  $+0.77$  V, respectively, *vs.* Ag/AgCl) makes them promising  $\pi$ -donors for further studies on charge-transfer complexes with strong  $\pi$ -electron acceptors, and for electrocrystallisation with inorganic anions, which may yield highly-conducting radical ion salts. These experiments, and the synthesis of new analogues of 25 which should possess lower oxidation potentials, are ongoing in our laboratory.

## Experimental

<sup>1</sup>H NMR Spectra were obtained on a Bruker AC 250 spectrometer operating at 250.134 MHz. *J* Values are given in Hz. Mass spectra were recorded on a VG7070E spectrometer operating at 70 eV. IR Spectra were recorded on a Perkin-Elmer 1615 FTIR spectrometer operated from a Grams Analyst 1600. UV Spectra were obtained on a Kontron Uvicon 930 spectrophotometer. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. Cyclic voltammetric data were obtained on a BAS 50S electrochemical analyser (*ca.*  $1 \times 10^{-5}$  M solution of donor in MeCN, Bu<sub>4</sub>NClO<sub>4</sub> ( $1 \times 10^{-1}$  M) supporting electrolyte, platinum working and counter electrodes, Ag/AgCl reference electrode, scan speed of 200 mV s<sup>-1</sup>). All reagents were of commercial quality and dried where necessary using standard procedures.

### Acenaphthen-1-one 9

This compound was prepared by a modification of the literature route.<sup>31</sup> Acenaphthen-1-ol (25 g, 148 mmol) was suspended in a mixture of ethanol–dichloromethane (1:1 v/v) (200 cm<sup>3</sup>) and stirred at 0 °C. Chromic acid (0.66 M, 150 cm<sup>3</sup>) was added dropwise over 10 min, after which the mixture was stirred for a further 5 min. The aqueous layer was removed and washed with dichloromethane (2 × 100 cm<sup>3</sup>). The organic layers were combined and washed with 10% aqueous sodium hydrogen carbonate (2 × 50 cm<sup>3</sup>) and water (100 cm<sup>3</sup>) and then dried (MgSO<sub>4</sub>). Removal of the solvent *in vacuo* gave 10 (20.12 g, 81%) as a white solid, mp 115–117 °C (lit.,<sup>38</sup> 119–120 °C).

### Spiro[acenaphthene-1,2'-(1',3'-dithiolane)] 10

To a solution of ketone 9 (4.05 g, 23.78 mmol) in benzene (200 cm<sup>3</sup>) was added ethane-1,2-dithiol (2.4 cm<sup>3</sup>, 28.67 mmol) and a catalytic quantity of toluene-*p*-sulfonic acid. A Dean–Stark trap was fitted and the mixture refluxed for 12 h, during which time the solution turned orange. The mixture was diluted with dichloromethane (200 cm<sup>3</sup>), washed with water (100 cm<sup>3</sup>) and dried (MgSO<sub>4</sub>). Removal of the solvent *in vacuo* afforded compound 10 mp 54–55 °C (lit.,<sup>6</sup> 57–58 °C) of sufficient purity for use in the next reaction.

### 8,9-Dihydroacenaphtho[1,2-*b*][1,4]dithiine 11

Dithioketal 10 (5.8 g, 23.8 mmol) was dissolved in dichloromethane (200 cm<sup>3</sup>) under an argon atmosphere with stirring, and tellurium tetrachloride (7.7 g, 28.5 mmol) was added portionwise over 5 min. After 30 min at room temperature, a black precipitate was observed which was removed by filtration. The solution was washed sequentially with saturated aqueous sodium hydrogen carbonate (2 × 50 cm<sup>3</sup>) and water (2 × 50 cm<sup>3</sup>). The organic layer was dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo* to afford a brown residue. Column chromatography [silica, cyclohexane–dichloromethane (1:1 v/v)] and recrystallisation from hexane gave 11 as a red crystalline solid (2.5 g, 45% based on 9); mp 130–132 °C (lit.,<sup>6</sup> 135–137 °C); the <sup>1</sup>H NMR spectrum was identical with the literature.<sup>6</sup>

### Acenaphtho[1,2-*b*][1,4]dithiine 12

This compound was prepared by the literature method<sup>6</sup> from 11 and DDQ in dioxane. For a successful reaction it was essential that the DDQ was recrystallised from hot benzene and dried under vacuum prior to use. The product 12 was obtained as a purple solid (28%) mp 91–93 °C (lit.,<sup>6</sup> 92–94 °C).

### Spiro[acenaphthene-1,2'-(1',3'-dithiolane)]-2-one 14

To a suspension of acenaphthenequinone 13 (5.0 g, 27.5 mmol) in benzene (200 cm<sup>3</sup>) was added ethane-1,2-dithiol (2.3 cm<sup>3</sup>, 27.4 mmol) and a catalytic quantity of toluene-*p*-sulfonic acid. The mixture was refluxed under Dean–Stark conditions for 2 h during which time the solid dissolved. The mixture was cooled

and the solvent removed *in vacuo* to afford a brown waxy solid, repeated recrystallisation of which from methanol afforded **14** as colourless needles (5.15 g, 73%) mp 141–145 °C (Found: C, 65.14; H, 3.81. C<sub>14</sub>H<sub>10</sub>OS<sub>2</sub> requires C, 65.09; H, 3.90%); *m/z* (EI) 258 (M<sup>+</sup>, 40%), 230 (100); δ<sub>H</sub>(CDCl<sub>3</sub>) 8.10 (1 H, d, *J* 7.3), 8.00 (1 H, d, *J* 7.5), 7.80–7.65 (4 H, m), 4.04–3.89 (2 H, m), 3.82–3.67 (2 H, m); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2929, 1712 (C=O), 1001, 970, 829, 775, 541.

#### Spiro[acenaphthene-1,2'-(1',3'-dithiolane)]-2-one hydrazone **15**

To a solution of compound **14** (3.0 g, 11.6 mmol) in methanol (75 cm<sup>3</sup>) was added hydrazine hydrate (15 cm<sup>3</sup> of 85% aqueous solution) and the resultant mixture was refluxed overnight, cooled and filtered to afford compound **15** (1.75 g, 55%) as colourless prisms, mp 188–191 °C (Found: C, 61.43; H, 4.38; N, 10.01. C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub> requires C, 61.73; H, 4.44; N, 10.28%); *m/z* (EI) 272 (M<sup>+</sup>, 40%), 196 (100); δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>CO] 8.27 (1 H, d, *J* 7.2), 8.00 (1 H, d, *J* 8.4), 7.95 (1 H, d, *J* 7.2), 7.92 (1 H, d, *J* 8), 7.70 (2 H, m), 6.02 (2 H, s), 4.15 (2 H, m) and 3.90 (2 H, m); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 1489, 1416, 809, 773, 717, 673, 581, 546.

#### Compound **11**: alternative synthesis

A mixture of compound **15** (0.5 g, 1.8 mmol) and activated manganese dioxide (1.6 g, 18 mmol) in diethyl ether (200 cm<sup>3</sup>) was treated with saturated ethanolic potassium hydroxide (0.13 cm<sup>3</sup>) and stirred for 1 h at 20 °C. Filtration afforded a pale red–purple filtrate which was shaken with 2 M aqueous hydrochloric acid (2 cm<sup>3</sup>), whereupon the solution turned bright red. This solution was washed with water (2 × 50 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo* to yield a red oil which was purified by chromatography (silica, hexane–dichloromethane, 1 : 1 v/v) to afford compound **11** (0.31 g, 71%) whose mp and <sup>1</sup>H NMR spectrum were identical to a sample of **11** synthesised from **10**, as described above.

#### 1-Methylsulfonyl-2-(prop-1-ynylsulfonyl)acenaphthylene **22a**

Compound **12** (0.05 g, 0.21 mmol) was dissolved in dry THF (50 cm<sup>3</sup>) under argon and stirred at room temperature. BuLi (1.6 M in hexanes, 0.3 cm<sup>3</sup>, 0.48 mmol) was slowly syringed into the solution, the colour of which changed from purple to red during 15 min. Methyl iodide (0.1 cm<sup>3</sup>, 0.84 mmol) was added and the solution stirred for 30 min, whereupon hydrochloric acid (0.5 M, 50 cm<sup>3</sup>) was added and the mixture washed with water (3 × 25 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo*. The resulting residue was chromatographed (silica, dichloromethane) to afford **22a** as an unstable yellow oil (21 mg, 38%); δ<sub>H</sub>(CDCl<sub>3</sub>) 8.30–8.10 (1 H, m), 7.80–7.70 (2 H, m), 7.60–7.50 (3 H, m), 2.62 (3 H, s), 2.02 (3 H, s); δ<sub>C</sub>(CDCl<sub>3</sub>) 137.4, 135.6, 133.4, 129.7, 129.0, 128.7, 128.5, 128.1, 127.9, 125.8, 123.9, 123.8, 84.3, 80.1, 26.1, 15.0; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2250, 1430, 1245, 1039, 908, 734, 651.

#### S-[2-(Ethoxycarbonylethynylsulfonyl)acenaphthylene-1-yl] ethyl thiocarbonate **22b**

This compound was prepared as described for **22a** using ethyl chloroformate (0.1 cm<sup>3</sup>, 0.84 mmol) instead of methyl iodide, and hexane–dichloromethane (4 : 1 v/v) as the eluent, to afford **22b** as an unstable yellow oil (48 mg, 65%); *m/z* (EI) 384 (M<sup>+</sup>, 20%), 239 (100); δ<sub>H</sub>(CDCl<sub>3</sub>) 8.40–8.25 (1 H, m), 8.0–7.5 (5 H, m), 4.4–4.2 (4 H, m), 1.4–1.3 (6 H, m); δ<sub>C</sub>(CDCl<sub>3</sub>) 166.7, 152.7, 137.4, 136.3, 135.5, 129.7, 129.1, 128.7, 128.3, 128.0, 127.9, 125.6, 124.9, 123.8, 88.1, 79.7, 64.9, 62.0, 14.25, 14.06; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2253, 2154, 1702, 1426, 1242, 1034, 911, 728, 651.

#### Spiro[acenaphthene-1,2'-(1',3'-benzodithiole)] **24**

To a solution of acenaphthenone **9** (2.5 g, 14.8 mmol) in benzene (125 cm<sup>3</sup>), was added benzene-1,2-dithiol **23** (2.0 g, 14.0 mmol) and a catalytic amount of toluene-*p*-sulfonic acid. A Dean–Stark trap was placed on the flask and the mixture

refluxed under argon for 2 days. The benzene was removed under reduced pressure, but due to the extreme malodour of the product mixture, the residue containing **24** (ca. 4.0 g, ca. 98% crude yield) was not purified but was used directly in the next reaction.

#### Acenaphtho[1,2-*b*][1,4]benzodithiine **25**

Crude compound **24** (ca. 4.0 g, 13.7 mmol) was dissolved in dichloromethane (200 cm<sup>3</sup>) and stirred under argon. Tellurium tetrachloride (3.8 g, 14.1 mmol) was added portionwise, and the solution turned dark brown. After 2 h at 20 °C, aqueous sodium hydrogen carbonate (50 cm<sup>3</sup>) was added and the mixture filtered through Celite. The organic layer was separated and washed with water (3 × 50 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo* to afford a brown oil which was chromatographed [silica, hexane–dichloromethane (5 : 1 v/v)] to yield **25** as red crystals [from hexane–dichloromethane (5 : 1 v/v)] (0.53 g, 13%) mp 117–120 °C (Found: C, 74.27; H, 3.07. C<sub>18</sub>H<sub>10</sub>S<sub>2</sub> requires C, 74.45; H, 3.47%); *m/z* (EI) 290 (M<sup>+</sup>); λ<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 316 (9284), 332 (9763), 347 (10 870) and 481 (525); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.25–7.15 (2 H, m), 7.45–7.35 (2 H, m), 7.55–7.45 (2 H, m), 7.65–7.60 (2 H, m), 7.80–7.70 (2 H, m).

**Complex of 25 and TCNQ.** Hot solutions of **25** (15 mg, 0.05 mmol) and TCNQ (10 mg, 0.05 mmol) each dissolved in anhydrous acetonitrile (15 cm<sup>3</sup>) were mixed and the solid which formed upon cooling was removed by filtration, and isolated as a black solid (22 mg, 88%) [Found: C, 73.11; H, 2.63; N, 11.42. C<sub>30</sub>H<sub>14</sub>N<sub>4</sub>S<sub>2</sub> (a 1 : 1 complex) requires C, 72.85; H, 2.85; N, 11.33%]; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2215 (CN).

**Complex of 25 and 2,5-dibromo-TCNQ.** The complex was prepared analogously to **25**:TCNQ, from **25** (15 mg, 0.05 mmol) and 2,5-dibromo-TCNQ<sup>23</sup> (23 mg, 0.05 mmol) each dissolved in anhydrous acetonitrile (10 cm<sup>3</sup>) and isolated as black needles (30 mg, 79%) [Found: C, 54.67; H, 1.87; N, 7.99. C<sub>30</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (a 1 : 1 complex) requires C, 55.23; H, 1.85; N, 8.59%]; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2209 (CN).

#### Acenaphtho[1,2-*b*]thieno[3,4-*e*][1,4]dithiine **29**

A solution of 3,4-dibromothiophene **26** (1.09 g, 4.5 mmol) in dry diethyl ether (30 cm<sup>3</sup>) under argon was cooled to –78 °C and treated with BuLi (1.6 M in hexanes, 2.8 cm<sup>3</sup>, 4.5 mmol). After stirring at –78 °C for 30 min, sulfur (144 mg, 4.5 mmol) was added and stirring continued for a further 1 h. The above lithiation and sulfur addition sequence was repeated and the solution allowed to warm to ambient temperature. A solution of hydrogen chloride in diethyl ether (1 M, 10 cm<sup>3</sup>) was added, whereupon the reaction turned black. Filtration and removal of the diethyl ether *in vacuo* afforded a malodorous solution containing thiophene-3,4-dithiol **27** which was immediately dissolved in benzene (125 cm<sup>3</sup>) containing acenaphthenone **9** (0.75 g, 4.5 mmol) and a catalytic amount of toluene-*p*-sulfonic acid. The resultant mixture was refluxed for 3 h with the removal of water (Dean–Stark) and was then reduced *in vacuo* to yield a viscous brown oil containing dithioketal **28**. The oil was dissolved in dichloromethane (50 cm<sup>3</sup>) and tellurium tetrachloride (1.4 g, 5.4 mmol) was added in one portion with stirring, whereupon the solution began to darken slowly. After 16 h at room temperature, a black precipitate was observed and aqueous sodium hydrogen carbonate (10%, 50 cm<sup>3</sup>) was added and the solution filtered through Celite. The organic phase was separated, washed with water (2 × 50 cm<sup>3</sup>) and dried (MgSO<sub>4</sub>). Removal of the solvent *in vacuo* afforded a dark red oil which was purified by column chromatography [silica, hexane–dichloromethane (10 : 1 v/v)] to afford **29** (0.25 g, 19%) as a purple solid; mp 125–127 °C (Found: C, 64.63; H, 2.84. C<sub>14</sub>H<sub>8</sub>S<sub>3</sub> requires C, 64.83; H, 2.72%); *m/z* (CI) 297 (MH<sup>+</sup>, 100%); λ<sub>max</sub>(CH<sub>2</sub>Cl<sub>2</sub>)/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 318 (18 322), 347 (17 081), 486 (1382); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.80–7.70 (2 H, m), 7.60–7.50 (4 H, m), 7.08 (2 H, s).

Table 3 Crystal data

Compound	25	25·Br <sub>2</sub> TCNQ	33
Formula	C <sub>18</sub> H <sub>10</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>10</sub> S <sub>2</sub> ·C <sub>12</sub> H <sub>2</sub> Br <sub>2</sub> N <sub>4</sub>	C <sub>12</sub> H <sub>8</sub> Se <sub>2</sub>
<i>M</i>	290.38	652.38	310.10
<i>T</i> /K	293	150	293
Radiation	Mo-K $\alpha$	Cu-K $\alpha$	Mo-K $\alpha$
$\lambda$ /Å	0.710 73	1.541 84	0.710 73
Symmetry	monoclinic	triclinic	tetragonal
<i>a</i> /Å	16.562(8)	7.065(1)	14.126(2)
<i>b</i> /Å	10.664(4)	10.287(1)	14.126(2)
<i>c</i> /Å	7.645(3)	18.822(2)	21.574(3)
$\alpha$ /°	90	97.34(1)	90
$\beta$ /°	94.55(3)	98.58(1)	90
$\gamma$ /°	90	109.07(1)	90
<i>U</i> /Å <sup>3</sup>	1346(1)	1255.4(2)	4305(1)
Reflection/unit cell	317	25	24
$\theta$ range/°	2–20	24–25	12–13
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2
<i>Z</i>	4	2	16
<i>F</i> (000)	600	644	2368
$\mu$ /cm <sup>-1</sup>	3.8	58.8	68.3
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.43	1.73	1.91
Crystal size/mm	0.4 × 0.3 × 0.3	0.68 × 0.16 × 0.04	0.5 × 0.5 × 0.36
Scan mode	$\omega$	2 $\theta$ / $\omega$	2 $\theta$ / $\omega$
2 $\theta$ <sub>max</sub> /°	46.5	150	52
Data total	4957	6696	6865
Data unique	1915	4568 (4564 used)	3789
Data observed, <i>I</i> > 2 $\sigma$	1771	3875	1770
<i>R</i> <sub>int</sub> ( <i>F</i> <sup>2</sup> )	0.034	0.053	0.067
Refined variables	222	392	254
Absorption corr.	none	analytical	analytical
Transmission min, max		0.349, 0.796	0.034, 0.057
Extinction, <sup>a</sup> <i>x</i>	0.027(2)	0.0030(4)	0.001 03(4)
<i>wR</i> ( <i>F</i> <sup>2</sup> ), all data	0.076	0.142	0.046
Goodness-of-fit	1.09	1.11	0.66
<i>R</i> ( <i>F</i> ), obs. data	0.029	0.046	0.036
Weights, <sup>b</sup> A, B	0.029, 0.59	0.074, 2.73	0.003, 0
$\Delta\rho$ <sub>max</sub> /e Å <sup>-3</sup>	0.18	0.92	0.39
$\Delta\rho$ <sub>min</sub> /e Å <sup>-3</sup>	-0.17	-1.60	-0.33

<sup>a</sup> Empirical extinction correction,  $[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1}$ . <sup>b</sup> Weight  $w^{-1} = \sigma^2(F^2) + (AP)^2 + BP$ , where  $P = (F_o^2 + 2F_c^2)/3$ , for  $F_o^2 < 0$ ,  $P = 2F_c^2/3$ .

**Complex of 29 and TCNQ.** The complex was prepared analogously to 25:TCNQ from 29 (15 mg, 0.05 mmol) and TCNQ (10 mg, 0.05 mmol) and isolated as shining black plates (21 mg, 84%) (Found: C, 66.84; H, 2.48; N, 10.74. C<sub>28</sub>H<sub>12</sub>N<sub>4</sub>S<sub>3</sub> requires C, 67.18; H, 2.42; N, 11.19%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 2217 (CN).

#### Dibenzo[*c,e*][1,2]diselenine 33

A solution of 1,2-dibromobenzene 30 (1.4 g, 6.0 mmol) in dry diethyl ether (30 cm<sup>3</sup>) under argon was cooled to -78 °C and treated with Bu<sup>t</sup>Li (1.6 M in hexanes, 6 mmol, 3.0 cm<sup>3</sup>). After stirring at -78 °C for 30 min, grey selenium powder (240 mg, 6 mmol) was added and stirring continued for a further 1 h. The above lithiation and selenium addition sequence was repeated and the solution allowed to warm to ambient temperature. A solution of hydrogen chloride in diethyl ether (1 M, 10 cm<sup>3</sup>) was added, whereupon the reaction turned dark brown. Filtration and removal of the diethyl ether *in vacuo* afforded a malodorous oil which was immediately dissolved in benzene (125 cm<sup>3</sup>) containing acenaphthenone 9 (1.2 g, 6 mmol) and a catalytic amount of toluene-*p*-sulfonic acid. The resultant mixture was refluxed for 3 h with the removal of water (Dean-Stark) and solvent was then removed *in vacuo*. The resultant viscous brown oil was dissolved in dichloromethane (50 cm<sup>3</sup>) and tellurium tetrachloride (2.0 g, 7.1 mmol) was added in one portion with stirring. After 16 h at room temperature, a black precipitate was observed and aqueous sodium hydrogen carbonate (10%, 50 cm<sup>3</sup>) was added and the solution filtered through Celite. The organic phase was separated, washed with water (2 × 50 cm<sup>3</sup>) and dried (MgSO<sub>4</sub>). Removal of the solvent *in vacuo* afforded a dark red oil which was purified by column chromatography

[silica, hexane-dichloromethane (10:1 v/v)] to afford 33 (0.15 g, 7%) as an orange solid, which upon recrystallisation from hexane-dichloromethane furnished red crystals, mp 104–105 °C, which is significantly different from the literature values (lit., 110–111 °C<sup>16a</sup> and 114–115 °C<sup>16b</sup>) (Found: C, 46.22; H, 2.42. C<sub>12</sub>H<sub>8</sub>Se<sub>2</sub> requires C, 46.48; H, 2.60%;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.77 (2 H, d, *J* 6.7), 7.67 (2 H, d, *J* 6.7), 7.1–7.2 (4 H, m) [cf. lit.,<sup>16a</sup>  $\delta_{\text{H}}$  7.8–7.1 (m)].

#### X-Ray single crystal diffraction studies

Experiments were carried out on a Siemens three-circle diffractometer equipped with a CCD area detector (25), a Rigaku AFC6S four-circle diffractometer, equipped with a Cryostream open-flow N<sub>2</sub> gas cryostat<sup>39</sup> (25·Br<sub>2</sub>TCNQ) and a Siemens P4 four-circle diffractometer (33), all using graphite monochromators. Analytical absorption corrections were applied for a pinacoidal crystal of 25·Br<sub>2</sub>TCNQ (TEXSAN software<sup>40</sup>) and for 33 (ABSPSI program<sup>41</sup>), which crystallised as well-shaped, truncated tetragonal pyramids with the ( $\pm 111$ ), ( $1 \pm 11$ ), ( $00 \pm 1$ ) faces. In both cases the results were in good agreement with empirical  $\psi$ -curves. The structures were solved by direct methods (SHELXS-86 programs<sup>42</sup>) and refined by full-matrix least-squares against *F*<sup>2</sup> of all data with variance-based weighting scheme (SHELXL-93 software<sup>43</sup>). All non-H atoms were refined with anisotropic displacement parameters; H atoms were refined isotropically in 25 and treated as 'riding' in 33. The absolute structure (and enantiomorph space group) of 33 was determined by refining the Flack parameter,<sup>44</sup> which converged at -0.05(2). Crystal data and experimental details are listed in Table 3; atomic coordinates, thermal parameters and bond distances and angles have been deposited at the



Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/49.

It is noteworthy that the unit cell parameters of **33** slightly differ from those reported earlier,<sup>16a</sup> viz.  $a = 14.149(3)$ ,  $c = 21.651(7)$  Å. As the Cu-K $\alpha$  radiation (giving  $\mu = 81.5$  cm<sup>-1</sup> for **33**) was used in that study, the difference may be due to absorption effects, as well as to the crystal quality, reported<sup>16a</sup> to be very poor.

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