The radical ions of acenaphtho[1,2-*b*][1,4]dithiine derivatives and acenaphtho[1,2-*b*][1,4]oxathiine: Solution EPR and ENDOR studies. The X-ray crystal structures of 8,9-bis(methylsulfanyl)-acenaphtho[1,2-*b*][1,4]dithiine and its complexes with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), 2,5-dibromo-TCNQ and iodine

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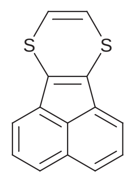
Received (in Cambridge) 18th December 1998, Accepted 17th February 1999

Syntheses of acenaphtho[1,2-*b*][1,4]oxathiine **4** and 8,9-bis(methylsulfanyl)acenaphtho[1,2-*b*][1,4]dithiine **5** are reported. The fairly persistent radical ions of acenaphtho[1,2-*b*][1,4]dithiine **1**, acenaphtho[1,2-*b*][1,4]benzodithiine **2**, acenaphtho[1,2-*b*]thieno[3,4-*e*][1,4]dithiine **3**, and **4**, *i.e.* **1**$^{\cdot+}$–**4**$^{\cdot+}$ and **1**$^{\cdot-}$–**4**$^{\cdot-}$, were generated from their neutral precursors and their EPR and ENDOR spectra are reported. Oxidation to the radical cations implies an electron removal from the heteroatoms of the donor dithiine or oxathiine moiety which houses the bulk of the spin population. Accordingly, in the EPR spectra of **1**$^{\cdot+}$–**4**$^{\cdot+}$, the ^{1}H-hyperfine pattern is only 0.25–0.70 mT wide, while the ^{33}S satellites extend over 2–3 mT. Upon reduction of **1**–**4** to their radical anions, the extra electron resides in the acenaphthylene π-system. Thus, the EPR spectra of **1**$^{\cdot-}$–**4**$^{\cdot-}$ have a total width of *ca.* 2.2 mT with no observable ^{33}S satellites. The *g* factors of the radical cations comply with the values for oxidised S-donors, whereas those of the corresponding anions are typical of reduced π-systems without heteroatoms. The crystal structure of **5** is characterised by pseudo-dimers of molecules folded by 54° along the S $\cdots$ S vector of the 1,4-dithiine ring. The structural motif of both **5**:TCNQ and **5**:Br$_2$TCNQ comprises mixed stacks of donor and acceptor moieties. The bond lengths in **5**:TCNQ and **5**:Br$_2$TCNQ show minor perturbation compared with pure **5**, which can be attributed to a small degree of charge transfer. The asymmetric unit of **5**:(I$_7^-$) comprises one radical cation **5**$^{\cdot+}$, two I$_2$ molecules and one I$_3^-$ anion. The radical cation, in contrast with the structures of **5**, **5**:TCNQ and **5**:Br$_2$TCNQ, shows only a minor boat-like distortion, and the radical cations form a stepwise stack, parallel to the *b* axis. Iodine species form an infinite zig-zag chain, running in the general direction of the *c* axis, *i.e.* normal to the stacks. The conductivity values of these complexes are low ($\sigma_{rt} = \leq 10^{-8}$ S cm^{-1}).

Polycyclic arenes, *e.g.* perylene, have been widely studied in the preparation of molecular conductors, and some of their radical-cation salts display semiconducting or metallic behaviour.[1] The introduction of one or more sulfur atoms at the periphery of such systems, to form the corresponding thia-arene derivatives, generally imparts greater stability to the radical-cation salts, coupled with increased conductivity.[2] The sulfur lone pairs are close in energy to the π-orbitals which dominate the intrastack interactions (band formation) and they facilitate such interactions by overlap of S 'd' orbitals, thereby reducing anisotropy effects and increasing the dimensionality of the system. These are important topics in the design of new molecular conductors.[3]

Recently, Tani *et al.* reported the synthesis of the π-electron donor acenaphtho[1,2-*b*][1,4]dithiine **1**,[4] and we have described a substantially-modified route to **1**, along with syntheses of the benzo- and thienyl- analogues **2** and **3**.[5] For compound **1**, X-ray structural studies have been reported on the pure donor and some radical-ion salts.[4,6] For compound **2**, the structure is known for the pure donor and for its complex with 2,5-dibromo-7,7,8,8-tetracyano-*p*-quinodimethane (2,5-Br$_2$-TCNQ).[5] We now extend this family of donors by describing the synthesis of an oxathiine derivative **4** and the substituted dithiine derivative **5**. We also report solution EPR studies on the radical cations and radical anions of compounds **1**–**4**, and the X-ray crystal structures of **5**, **5**:TCNQ, **5**:Br$_2$TCNQ and **5**:(I$_7^-$).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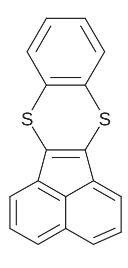
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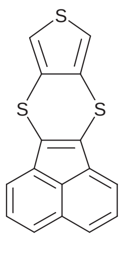
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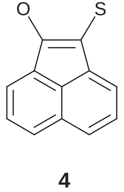
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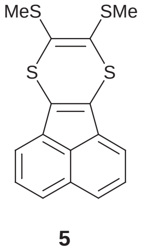
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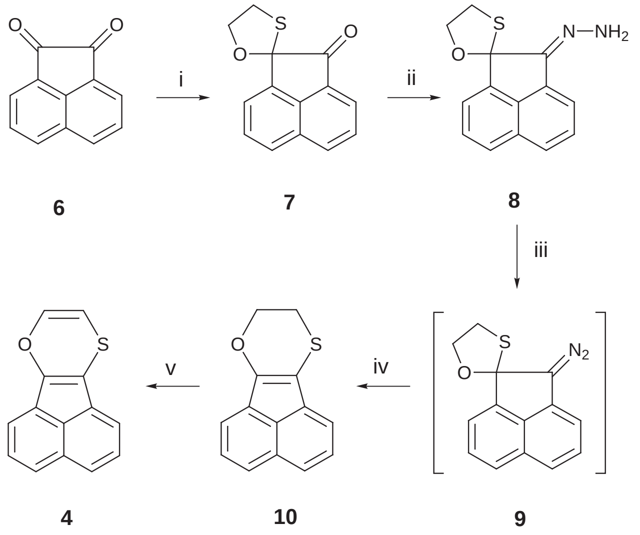
Results and discussion

Synthesis

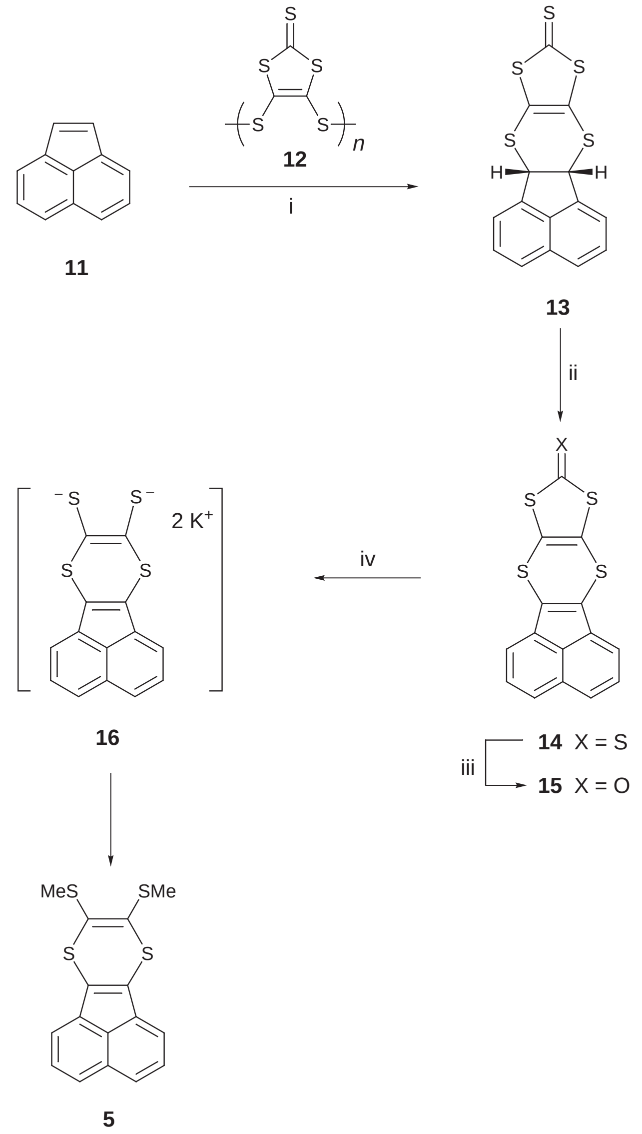


Scheme 1 *Reagents and conditions*: i, $HOCH_2CH_2SH$, PhH, reflux, 85%; ii, H_2NNH_2, MeOH, reflux, 68%; iii, MnO_2, KOH, EtOH, Et_2O, 20 °C; iv, HCl, 72% (based on **8**); v, DDQ, 1,4-dioxane, reflux, 6%.

The synthesis of compound **4**, which is shown in Scheme 1, utilises 2-mercaptoethanol in the diazo-mediated ring expansion protocol which we had previously used for the synthesis of **1**.[5] A mixture of 2-mercaptoethanol and acenaphthenequinone **6** was refluxed in benzene with azeotropic removal of water, to produce the oxothioketal **7** in 85% yield. Compound **7** reacted with hydrazine hydrate in methanol to afford the hydrazone derivative **8** in 68% yield, which was then treated with activated manganese dioxide to give a solution of the unstable diazo compound **9**. On addition of dilute hydrochloric acid, this solution rapidly changed colour from orange to bright red, and compound **10** was isolated in 72% yield (based on **8**). Dehydrogenation of **10** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing benzene gave the target compound **4**, as a purple solid, albeit in very low yield (6%). Despite the poor yield of the final step, the ease and high yields of the previous steps make compound **4** available in reasonable quantities (>200 mg). Compound **4** is highly soluble in all common organic solvents, *e.g.* methanol, chloroform and hexane.

We had established previously that functionalisation of the dithiine ring of **1** could not be achieved by lithiation/electrophilic substitution methodology.[5] We, therefore, sought an alternative protocol. Thermally-induced depolymerisation of oligo(1,3-dithiole-2,4,5-trithione) **12**[7] in refluxing toluene in the presence of acenaphthylene **11** gave the cycloaddition product **13** in 79% yield (Scheme 2).[8] Dehydrogenation of **13** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) readily afforded compound **14** (94% yield) which was converted into the corresponding ketone derivative **15** (76% yield) under standard conditions[9] (mercuric acetate in chloroform–glacial acetic acid).

It is known that 1,3-dithiol-2-ones are sensitive to nucleophilic ring opening,[7b] and treatment of compound **15** with two equivalents of potassium *tert*-butoxide in THF produced the dithiolate intermediate **16** which was reacted *in situ* with an excess of methyl iodide to give the desired product **5** in 80% yield as red plates.



Scheme 2 *Reagents and conditions:* i, PhMe, reflux, 79%; ii, DDQ, PhMe, 94%; iii, $Hg(OAc)_2$, $CHCl_3$, AcOH, 20 °C, 76%; iv, $KOBu^t$, THF, 20 °C, then MeI, 80%.

Electrochemical redox properties and formation of charge-transfer complexes and radical ion salts

The electrochemical redox properties of the new donors **4** and **5** were studied by cyclic voltammetry in acetonitrile solution. Compound **4** undergoes a reversible one-electron oxidation to form the radical cation at $E_1^{1/2} = +\ 0.72$ V (*vs.* Ag/AgCl) (*cf.* + 0.68 V for compound **1**) and a second irreversible oxidation at $E_2^{ox} = ca.\ +1.5$ V. For compound **5** the first oxidation occurs at a very similar potential ($E_1^{1/2} = +\ 0.75$ V) but the second oxidation is cathodically shifted and is reversible ($E_2^{1/2} = +\ 1.07$ V), probably due to the dication being stabilised by the methylthio substituents.

Attempts to isolate crystalline complexes of **4** with either TCNQ, 2,5-Br_2TCNQ or iodine were unsuccessful, possibly because of the high solubility of compound **4**. Donor **5** formed crystalline complexes with TCNQ and with 2,5-Br_2TCNQ (both 1 : 1 stoichiometry) and a crystalline radical-cation salt with iodine of stoichiometry **5**:(I_7^-). Both **5**:TCNQ and **5**:Br_2TCNQ are insulators, and **5**:(I_7^-) showed a very low conductance ($\sigma_{rt} = ca.\ 10^{-8}$ S cm^{-1}) by two-probe compressed pellet measurements.

EPR and ENDOR spectra

The fairly persistent radical ions $\mathbf{1}^{\cdot+}$–$\mathbf{4}^{\cdot+}$ and $\mathbf{1}^{\cdot-}$–$\mathbf{4}^{\cdot-}$ were generated from their neutral precursors at 195 K, the cations with aluminium chloride in dichloromethane and the anions with potassium mirror in 1,2-dimethoxyethane (DME). They gave rise to well-resolved EPR spectra which were taken in the

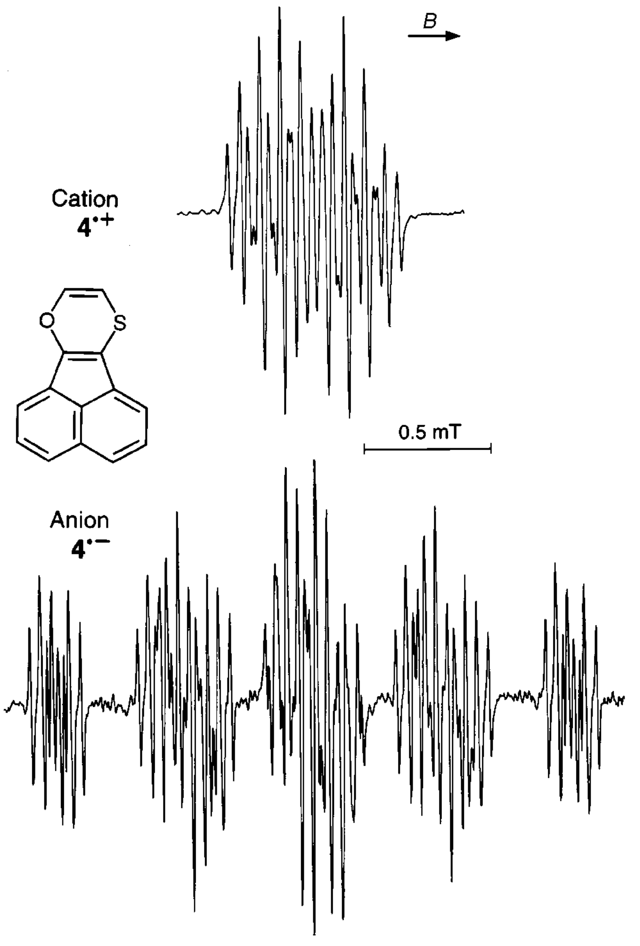


Fig. 1 EPR spectra of the radical ions **4**$^{\cdot+}$ (in CH_2Cl_2 at 200 K) and **4**$^{\cdot-}$ (in DME at 200 K; counterion K^+).

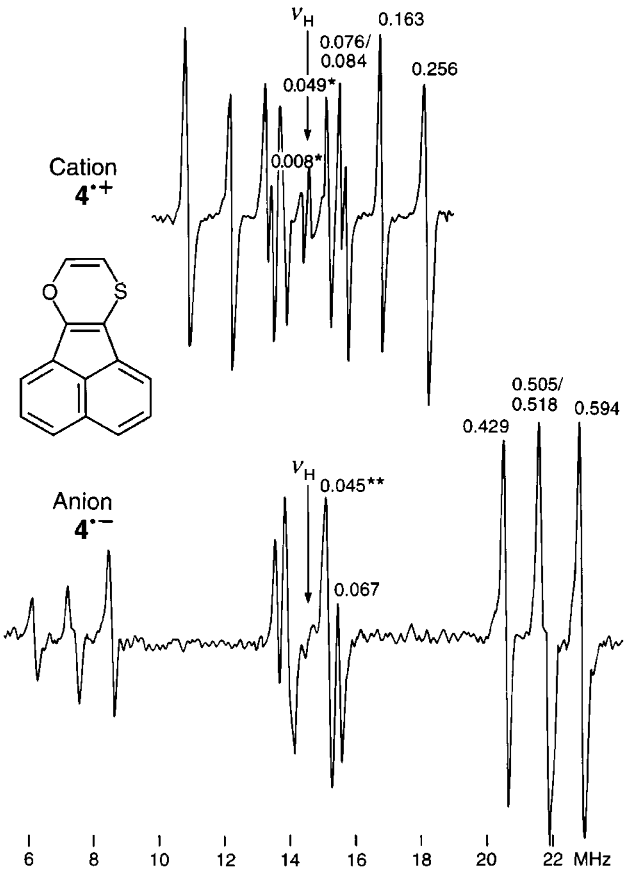


Fig. 2 ENDOR spectra of the radical ions **4**$^{\cdot+}$ and **4**$^{\cdot-}$ (taken at the same conditions as the EPR spectra in Fig. 1). The numbers above the ENDOR signals are the ^{1}H-coupling constants (absolute values) in mT. Each of them refers to a single proton, except those marked by asterisks which are due to two (*) or three protons (**).

range 200–260 K. Analysis of their hyperfine patterns was carried out with the use of ^{1}H-coupling constants derived from the corresponding ENDOR spectra and optimised by a fitting procedure.[10] For illustration, Figs. 1 and 2 show the EPR and ENDOR spectra of the least symmetric radical ions **4**$^{\cdot+}$ and **4**$^{\cdot-}$ which exhibited hyperfine interaction with eight nonequivalent single protons. The large coupling constants of the ^{33}S isotopes in the radical cations were determined from the pertinent satellite lines. The hyperfine data and the *g* factors for all radical ions, **1**$^{\cdot+}$–**4**$^{\cdot+}$ and **1**$^{\cdot-}$–**4**$^{\cdot-}$, are assembled in Fig. 3. Assignments of the ^{1}H-coupling constants are based on analogy with structurally related radical ions (see below) and on internal consistency of the data. They agree with the results of calculations in the frame of the Hückel–McLachlan procedure[11] ($\alpha_S = \alpha + \beta$,[12] $\alpha_O = \alpha + 2\beta$, $\beta_{CS} = 0.7\beta$[12] and $\beta_{CO} = 0.8\beta$). Their absolute signs are those required by theory; the relative ones were verified by a general-TRIPLE-resonance experiment carried out on the ENDOR signals.[13]

The compounds **1**–**4** consist of an electron-donor moiety, 1,4-dithiine in **1**, benzo-1,4-dithiine in **2**, thieno-1,4-dithiine in **3** and 1,4-oxathiine in **4**, which is fused to a nonalternant π-system of acenaphthylene as an acceptor. Oxidation of **1**–**4** to their radical cations implies an electron removal from the heteroatoms of the donor moiety which houses the bulk of the spin population. Accordingly, in the EPR spectra of **1**$^{\cdot+}$–**4**$^{\cdot+}$, the ^{1}H-hyperfine pattern is only 0.25–0.70 mT wide, while the ^{33}S satellites extend over 2–3 mT. On the other hand, upon reduction of **1**–**4** to their radical anions, the extra electron is accepted by the acenaphthylene π-system which accomodates almost the entire spin population. Thus, the EPR spectra of **1**$^{\cdot-}$–**4**$^{\cdot-}$ have a total width of *ca.* 2.2 mT with no observable ^{33}S satellites. The *g* factors of the radical cations comply with the values for oxidised S-donors, whereas those of the corresponding anions are typical of reduced π-systems without heteroatoms.

The hyperfine data for **1**$^{\cdot+}$–**4**$^{\cdot+}$ and **1**$^{\cdot-}$–**4**$^{\cdot-}$ reflect the shape of the relevant frontier orbitals which are schematically presented for **1** in Fig. 4, together with the HOMO of 1,4-dithiine and the LUMO of acenaphthylene. Obviously, the HOMO of **1** at the six π-centres of the heterocyclic ring closely resembles that of the dithiine, particularly in the large coefficient at the S atoms, while the LUMO of **1** at the twelve π-centres of the acenaphthylene moiety is almost identical with that of acenaphthylene itself. The hyperfine data for **1**$^{\cdot+}$ compare favourably with corresponding values for the radical cation of 1,4-dithiine[14] and an analogous statement holds for **1**$^{\cdot-}$ with respect to the radical anion of acenaphthylene[15] (Fig. 4).

X-Ray crystal structures of 5, 5:TCNQ, 5:Br$_2$TCNQ and 5:(I$_7^-$)

We have recently analysed the structural features of the 1,4-dithiine derivatives in the October 1995 release of the Cambridge Structural Database,[5] so the discussion here will be brief. The general trend is that a neutral dithiine ring is folded along the S···S vector in a boat conformation, whereas charge-transfer interactions lead to a more planar structure. The crystal structure of **5** is characterised by pseudo-dimers of folded molecules [by 54° along the S(1)···S(2) vector (*cf.* 48° in pure **2**)[5]] with overlapping parallel acenaphtho moieties (interplanar separation 3.58 Å) (Figs. 5 and 6).

The structural motif of **5**:TCNQ is a mixed stack of **5** and TCNQ molecules (Fig. 7). Both components lie on a crystallographic mirror plane, passing in the donor moiety through the C(5), C(6) atoms and the midpoints of the C(7)–C(7′) and C(8)–C(8′) bonds, and in the TCNQ moiety through the mid-

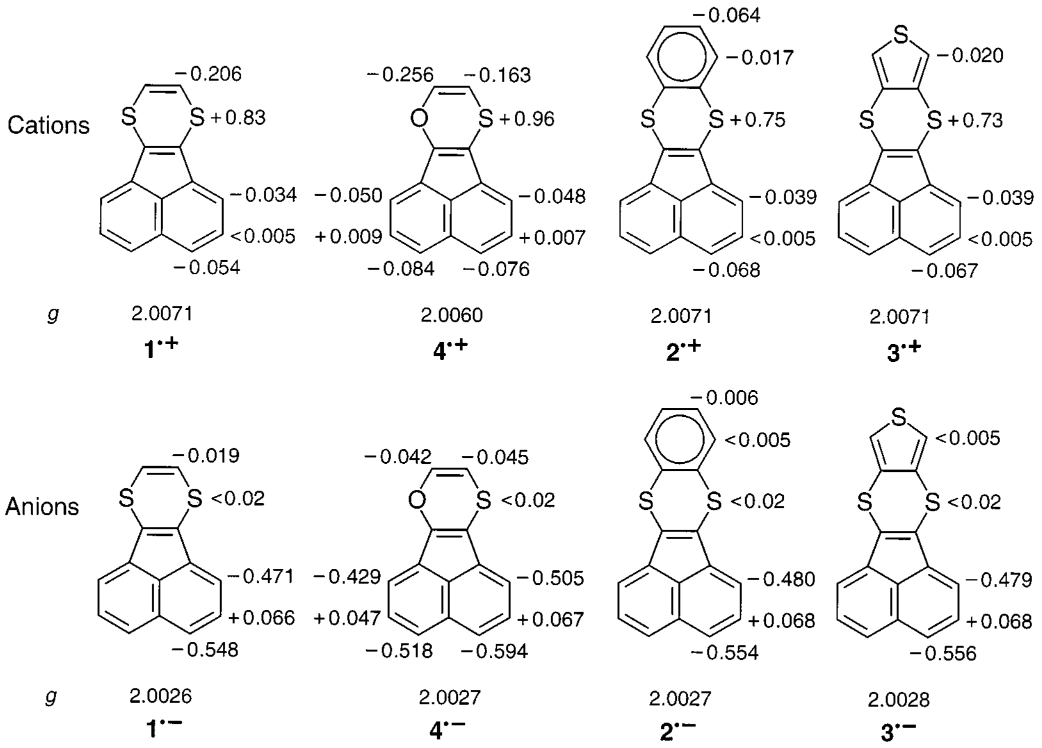


Fig. 3 ^{1}H- and ^{33}S-coupling constants in mT (experimental error ± 1%) and *g* factors (experimental error ± 0.0001) for the radical ions $\mathbf{1}^{\bullet +}$–$\mathbf{4}^{\bullet +}$ and $\mathbf{1}^{\bullet -}$–$\mathbf{4}^{\bullet -}$.

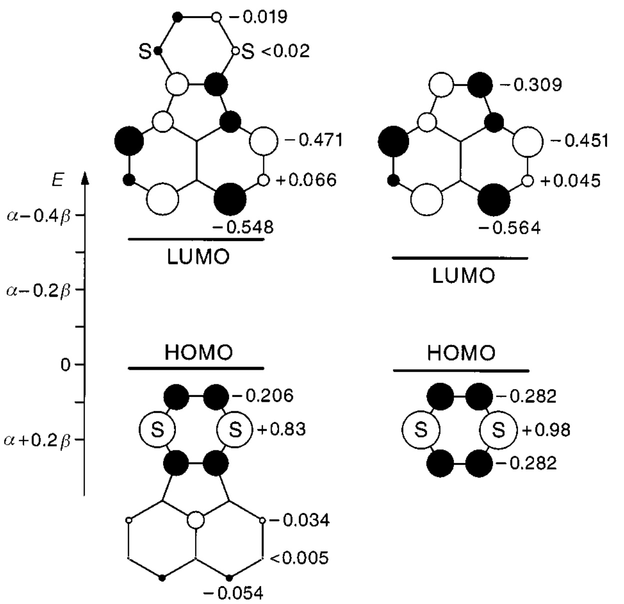


Fig. 4 Schematic presentation of the frontier orbitals of **1**, as compared with the HOMO of 1,4-dithiine and the LUMO of acenaphthylene. The numbers are the ^{1}H- and ^{33}S-coupling constants in mT for the radical ions: $\mathbf{1}^{\bullet +}$ (left, bottom), $\mathbf{1}^{\bullet -}$ (left, top), 1,4-dithiine$^{\bullet +}$ (right, bottom) and acenaphthylene$^{\bullet -}$ (right, top).

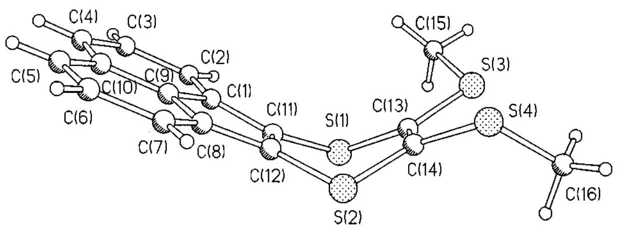


Fig. 5 Molecular structure of compound **5**.

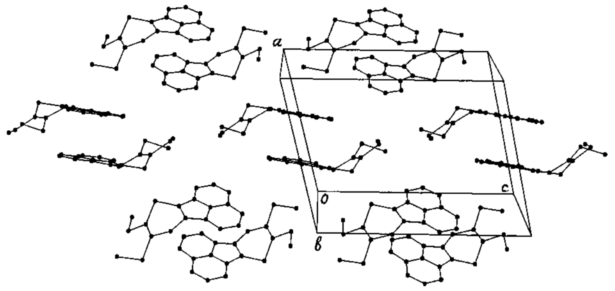


Fig. 6 Crystal packing of compound **5** (H atoms are omitted).

points of the C(11)–C(11′) and C(12)–C(12′) bonds. The donor molecule is folded in the same way as in pure **5** so that only its acenaphtho part is actually participating in the stack (Fig. 8). This moiety and the two adjacent TCNQ molecules are parallel within 5.4°; the mean interplanar separations between them are 3.26 and 3.44 Å.

The structure of **5**:Br_2TCNQ also contains mixed stacks, running parallel to the crystal axis *a*, and comprising the acenaphtho moieties of folded molecule **5** and Br_2TCNQ (Fig. 9). However, the relative orientations between donor and acceptor in a stack are quite different from that in **5**:TCNQ. In **5**:Br_2TCNQ, the principal axis of Br_2TCNQ (*i.e.* the C(07)···C(08) vector) and the (local) *m* plain of the donor molecule form an angle of *ca.* 16°, while in **5**:TCNQ they are perpendicular. The folding of the donor molecule along the S(1)···S(2) vector is nearly the same (48.1°). The Br_2TCNQ molecule is planar within ±0.03 Å, except for the C(71)N(71) and C(81)N(81) cyano groups, which are tilted out of the plane by 7.6 and 9.0°, respectively. The acenaphtho moiety and two adjacent Br_2TCNQ planes in a stack (Fig. 10) are parallel within 2.4°, with interplanar separations of 3.27 and 3.36 Å. The bond distances in the acenaphtho systems in **5**:TCNQ and **5**:Br_2TCNQ show small (in fact, on the limits of statistical significance) perturbation compared with pure **5**, which can be attributed to a small degree of charge transfer.

Aquisition of a negative charge by a neutral TCNQ molecule is known[16] to cause lengthening of the C–C bonds a and c (see the scheme in Table 1) and shortening of the b and d bonds.

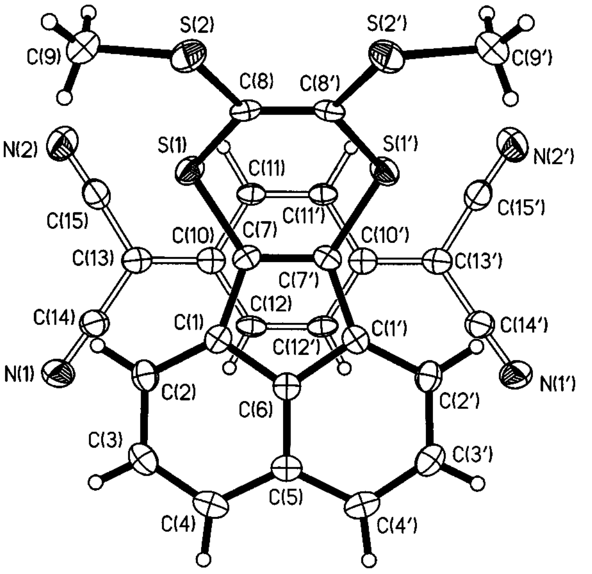


Fig. 7 Molecular structure of complex **5**:TCNQ (50% thermal ellipsoids); primed atoms are symmetry related *via* the mirror plane.

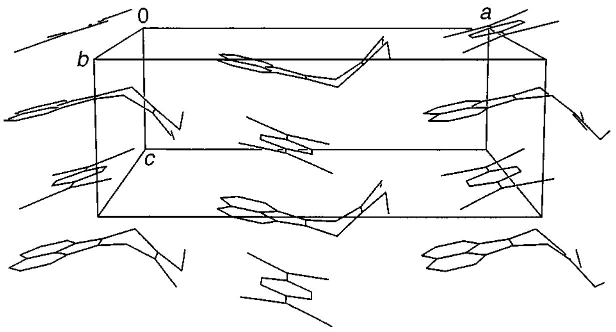


Fig. 8 Crystal packing of **5**:TCNQ.

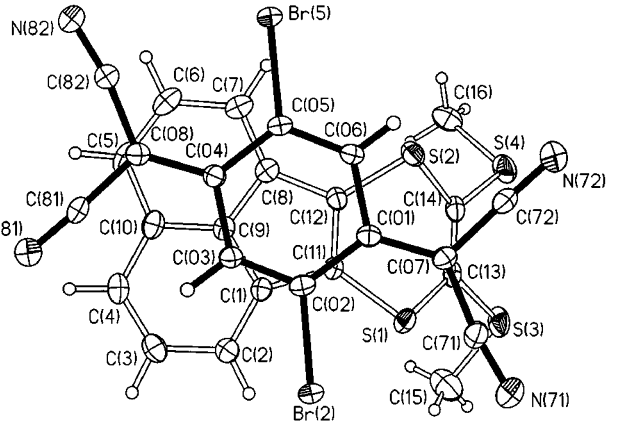


Fig. 9 Molecular structure of complex **5**:Br_2TCNQ (50% thermal ellipsoids).

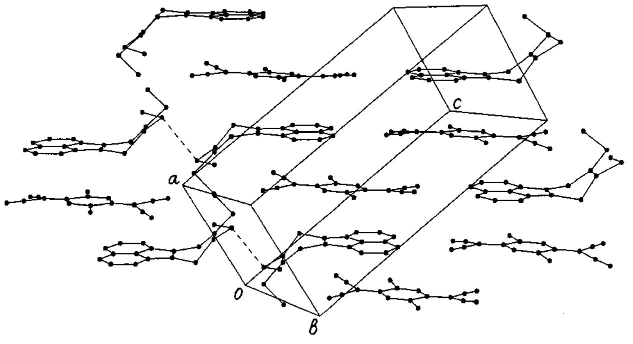


Fig. 10 Crystal packing of **5**:Br_2TCNQ.

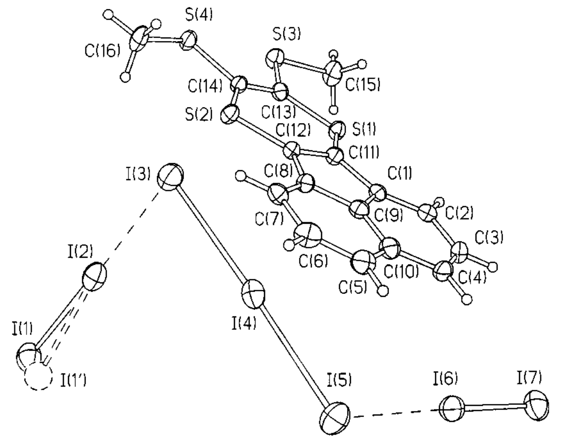


Fig. 11 Molecular structure of **5**:(I_7^-), showing 50% thermal ellipsoids and 2 positions of the disordered I(1) atom. Selected distances (Å): I(1)–I(2) 2.780(1), I(1′)–I(2) 2.789(7), I(2)···I(3) 3.162(1), I(3)–I(4) 2.965(1), I(4)–I(5) 2.881(1), I(5)···I(6) 3.313(1), I(6)–I(7) 2.745(1).

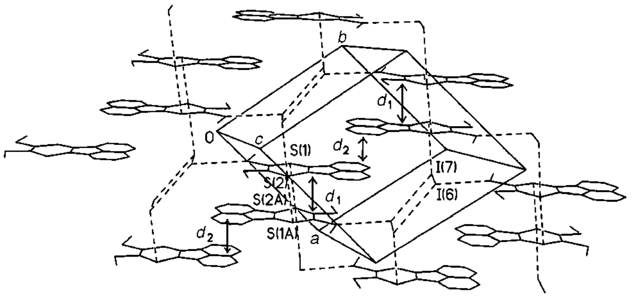


Fig. 12 Crystal packing of **5**:(I_7^-), projection on the (0 0 1) plane, showing contacts equal or less the sums of covalent radii. Iodine atoms are omitted, except the I(6)I(7) molecule.

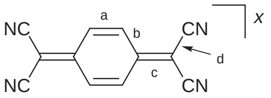
However, the changes are not very large and can be further obscured by systematic errors in bond lengths caused by thermal motion. Table 1 quotes more accurate structures of pristine TCNQ[17] and its salts,[18,19] determined at low temperatures and/or corrected for thermal vibration, and in which the charge of the TCNQ is certain. Comparison with the structure of **5**:TCNQ indicates no appreciable charge transfer in the latter, while **5**:Br_2TCNQ (like **2**:Br_2TCNQ[5]) shows marginal changes from the neutral Br_2TCNQ geometry[20] in the direction of the anionic structure.

The nitrile absorption frequencies in the solid state IR spectra of the TCNQ and Br_2TCNQ complexes (2219 cm^{-1} and 2210 cm^{-1}, respectively) also suggest very little charge transfer in the former complex, and an increased degree of charge transfer in the latter complex,[22] consistent with the increased electron affinity of Br_2TCNQ.[23]

The mixed stacking motifs of **5**:TCNQ and **5**:Br_2TCNQ explain the insulating behaviour of these complexes.

The asymmetric unit of **5**:(I_7^-) comprises one radical cation of $\mathbf{5}^{\cdot+}$, two I_2 molecules and one I_3^- anion (Fig. 11). The radical cation, in contrast with the structures of **5**, **5**:TCNQ and **5**:Br_2TCNQ, is nearly planar: non-H atoms deviate from the mean plane by 0.05 Å on average (0.1 Å maximum). The dithiine ring is folded by only 4° and bond distances in it are changed from the pattern of localised C=C and single C–S bonds to a substantially conjugated structure (see Table 2). The radical cations, which lie nearly parallel to the crystallographic (1 $\bar{1}$ 0) plane, form a stair-like stack (Fig. 12) in which two different modes of overlap alternate. In one case (d_1 in Fig. 12), the dithiine rings of the two cation radicals are eclipsed and exocyclic sulfur atoms of each overlap with the acenaphtho moiety of the other. The separation between the *mean* molecular planes is 3.40 Å, but the dithiine sulfur atoms are shifted

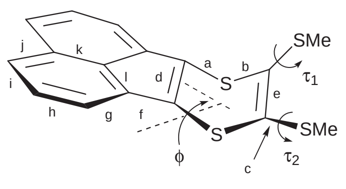
Table 1 Geometry *vs.* charge (x) of TCNQ moiety



Compound	x	a/Å	b/Å	c/Å	d/Å	T/K	Ref.
TCNQ	0	1.346(3)	1.448(4)	1.374(3)	1.441(4)	293[a]	17*a*
TCNQ	0	1.351	1.439	1.372	1.436	110	17*b*
TTF:TCNQ	-0.6[b]	1.352(4)	1.435(3)	1.395(3)	1.434(3)	110[c]	18*a*
TTF:TCNQ		1.343(3)	1.444(4)	1.393(3)	1.430(3)	45[a]	18*b*
RbTCNQ	-1	1.373(4)	1.423(4)	1.420(4)	1.416(4)	113	19*a*
$(C_5Et_5)_2Fe$:TCNQ	-1	1.368(3)	1.417(3)	1.427(3)	1.413(3)	110	19*b*
$(C_5Et_5)_2Fe$:TCNQ	-1	1.370(2)	1.416(3)	1.423(2)	1.416(3)	203[c]	19*c*
$(C_5HEt_4)_2Fe$:TCNQ	-1	1.364(3)	1.428(3)	1.422(3)	1.418(3)	110	19*b*
$(C_5Me_5)_2Mn$:TCNQ	-1	1.368	1.418	1.419	1.419	153	19*d*
5:TCNQ		1.340(8)	1.447(5)	1.373(5)	1.437(6)	150	This work
2,5-Br_2TCNQ	0	1.344(6)	1.453(6)	1.378(6)	1.436(6)	295	20
2:2,5-Br_2TCNQ		1.350(6)	1.452(6)	1.389(6)	1.434(6)	150	5
5:2,5-Br_2TCNQ		1.352(4)	1.453(3)	1.386(4)	1.444(4)	150	This work

[a] Corrected for libration. [b] Determined from the superstructure X-ray scattering.[21] [c] Incorrectly recorded at the Cambridge Structural Database as studied at $T = 295$ K.

Table 2 Selected bond distances (Å; average) and dihedral angles (°)



	Compound			
	5	**5**:TCNQ	**5**:Br_2TCNQ	**5**(I_7^-)
a	1.751(3)	1.749(4)	1.748(3)	1.719(6)
b	1.781(3)	1.787(4)	1.788(3)	1.736(6)
c	1.766(3)	1.753(4)	1.763(3)	1.757(6)
d	1.364(4)	1.365(7)	1.369(4)	1.388(8)
e	1.341(4)	1.355(7)	1.338(4)	1.371(8)
f	1.475(4)	1.470(5)	1.474(4)	1.465(8)
g	1.373(4)	1.381(5)	1.377(4)	1.387(8)
h	1.423(5)	1.415(6)	1.426(4)	1.422(9)
i	1.367(5)	1.376(6)	1.378(5)	1.386(10)
j	1.425(5)	1.429(4)	1.432(4)	1.430(9)
k	1.397(4)	1.387(8)	1.395(4)	1.391(8)
l	1.416(4)	1.417(5)	1.420(4)	1.418(8)
φ	50.4	54.6	48.1	4.0
τ_1	-156.7	164.7	-142.6	176.5
τ_2	-58.4	-164.7	127.5	-179.2

out of these planes to form contacts S(1)···S(2A) and S(2)···S(1A) of only 3.24 Å, much shorter than the standard intermolecular distance of 3.60 Å.[24]

The other type of overlap (d_2 in Fig.12) is between naphthalene moieties only, with interplanar separation of 3.45 Å and such a slip that a carbon atom is located over the centre of a ring. Thus the stack in fact comprises relatively strongly bound dimers rather than individual radical cations. A comparison can be made with a number of substituted dithiadiazolyl radicals,[25] which usually couple in the solid state into diamagnetic dimers through S···S contacts of 2.99–3.14 Å. This feature of the structure can explain the low conductivity of **5**:(I_7^-).

Iodine species form an infinite zig-zag chain, running in the general direction of the *c* axis, *i.e.* normal to the stacks (Fig. 13). The shortest intermolecular I···I contacts (or 'secondary' donor–acceptor bonds) are practically colinear to the I_2 molecules but normal to the direction of the I_3^- anion (which is itself linear) in a pattern usual for polyiodide structures (Fig. 13).

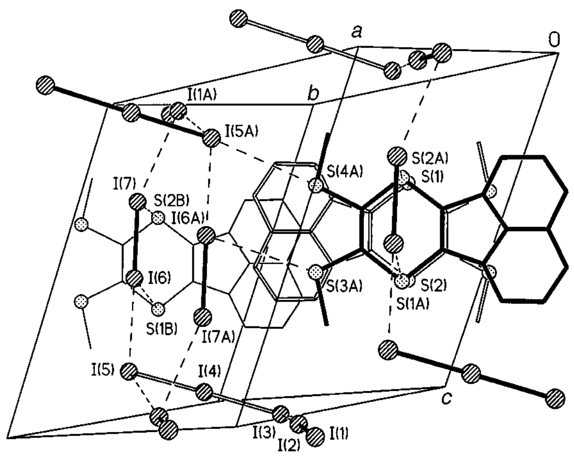


Fig. 13 Crystal packing of **5**:(I_7^-), projection on the (1 $\bar{1}$ 0) plane. Intermolecular contacts (Å): I(7)···I(1A) 3.630(1), I(1A)···I(5A) 3.924(1), I(6)···S(1B) 3.993(2), I(7)···S(2B) 3.819(2), I(5A)···S(4A) 3.901(2), I(6A)···S(3A) 3.915(2), S(1A)···S(2) 3.240(3).

Conclusions

The radical cations and radical anions generated from acenaphtho[1,2-*b*][1,4]dithiine derivatives and acenaphtho-[1,2-*b*][1,4]oxathiine have been characterised by EPR and ENDOR studies. The new derivative 8,9-bis(methylsulfanyl)-acenaphtho[1,2-*b*][1,4]dithiine **5** has emerged as a promising electron donor for the formation of crystalline charge-transfer complexes and radical ion salts, and the X-ray crystal structures have been obtained for its 1:1 complexes with TCNQ and Br_2TCNQ, and a salt **5**:(I_7^-). The mixed stacking motifs of **5**:TCNQ and **5**:Br_2TCNQ explain the insulating behaviour of these complexes, while the low conductivity of **5**:(I_7^-) is probably a consequence of the dimerisation of the radical cations in the stacks. Further studies on charge-transfer complexes and radical ion salts of **5** and related acenaphtho[1,2-*b*][1,4]dithiine derivatives may yield mixed-valence salts with higher conductivity values. We note that further reactions of the readily-available dithiolate species **16** should provide access to new π-electron donors in this family, and interesting metal dithiolate coordination species.[26]

Experimental

^{1}H NMR Spectra were obtained on a Bruker AC 250 spectrometer operating at 250.134 MHz. δ Values are given in ppm and *J* values 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. EPR spectra were taken on a Varian-E9-instrument, while a Bruker-ESP-300-system served for ENDOR and general-TRIPLE resonance. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. All reagents were of commercial quality and dried where necessary, using standard procedures.

Spiro[1,2-dihydroacenaphthylene-1,2′-(1′,3′-oxathiolane)]-2-one 7

Acenaphthenequinone **6** (15.0 g, 82.3 mmol) and 2-mercaptoethanol (5.75 cm^3, 82.0 mmol) were azeotroped in benzene (500 cm^3) at reflux until all the suspended solid had dissolved; the reaction was then continued for a further 1 h. The solution was then cooled and the solvent evaporated *in vacuo*. The residue was dissolved in the minimum amount of boiling methanol, left to cool, and the fine colloidal precipitate was removed by filtration. The yellow solid, which crystallised from the cooled solution, was recrystallised from methanol to give **7** (16.8 g, 85%) as large yellow crystals, mp 83–85 °C (Found: C, 69.1; H, 4.0. $C_{14}H_{10}O_2S$ requires C, 69.4; H, 4.2%); ν_{max} (thin solid film)/cm^{-1} 2951, 2884, 1715 (C=O), 1605, 1433, 1261, 1063, 1015, 994, 919, 829, 775, 707, 677, 625, 594, 539; δ_H(200 MHz; $CDCl_3$) 3.44 (1 H, m, SCH*H*CH_2), 3.65 (1 H, m, SC*H*HCH_2), 4.57 (1 H, m, OCH*H*CH_2), 4.81 (1 H, m, OC*H*HCH_2) and 7.54–7.97 (6H, m, Ar-*H*); δ_C(50 MHz; $CDCl_3$) 31.34, 73.64, 92.83, 122.26, 122.83, 126.64, 128.90, 129.35, 129.96, 130.68, 132.23, 136.56, 141.40 and 201.25; *m*/*z* (CI) 243 (M^+ + H, 7%), 200 (9).

Spiro[1,2-dihydroacenaphthylene-1,2′-(1′,3′-oxathiolane)]-2-hydrazone 8

Hydrazine hydrate (15 cm^3 of 80% aqueous solution) and **7** (2.50 g, 10.3 mmol) were stirred in methanol (50 cm^3) at reflux for 3 h. The solution was cooled at 5 °C for 16 h, the resulting crystalline precipitate filtered and washed with cold methanol (50 cm^3) and then recrystallised from ethanol to give **8** (1.80 g, 68%) as yellow crystals, mp 164–167 °C. (Found: C, 65.5; H, 4.65; N, 10.90. $C_{14}H_{12}N_2OS$ requires C, 65.6; H, 4.70 N, 10.90%); ν_{max} (KBr)/cm^{-1} 3355, 3286, 3202, 3044, 2945, 1636, 1488, 1175, 1037, 927; δ_H(200 MHz; $CDCl_3$) 3.57 (2 H, m, SCH_2CH_2), 4.58 (1 H, m, OC*H*HCH_2), 4.75 (1 H, m, OCH*H*CH_2), 6.09 (2 H, br s, NNH_2), 7.66 (3 H, m, Ar-*H*) and 7.86 (3 H, m, Ar-*H*); δ_C(50 MHz; $CDCl_3$; Me_4Si) 35.03, 71.94, 95.43, 121.19, 121.96, 125.78, 126.79, 127.90, 128.54, 128.99, 130.58, 136.43, 141.31 and 153.45; *m*/*z* (CI) 257 (M^+ + H, 81%), 197 (90).

8,9-Dihydroacenaphtho[1,2-*b*][1,4]oxathiine 10

Compound **8** (0.26 g, 1.00 mmol), activated manganese dioxide (0.87 g, 10.0 mmol) and ethanol saturated with potassium hydroxide (0.15 cm^3) were stirred for 1 h in diethyl ether (125 cm^3). The mixture was filtered to give a bright orange solution which was shaken with aqueous hydrochloric acid (2 M, 2 cm^3), washed with water (3 × 50 cm^3) and dried ($MgSO_4$). The organic solvent was evaporated *in vacuo* to yield a red oil which was purified by column chromatography [silica, eluent hexane–dichloromethane (1 : 1 v/v)] to afford **10** (0.16 g, 72%) as a bright red crystalline solid, mp 62–64 °C (from hexane–dichloromethane) (Found: C, 74.1; H, 4.5. $C_{14}H_{10}OS$ requires C, 74.3; H, 4.5%); ν_{max}(KBr)/cm^{-1} 3039, 2967, 2928, 2871, 1541, 1475, 1461, 1433, 1309, 1105, 818, 760; δ_H(200 MHz; $CDCl_3$) 3.20 (2 H, t, *J* 4.2, OCH_2CH_2), 4.62 (2 H, t, *J* 4.2, SCH_2CH_2), 7.45 (4 H, m, Ar-*H*) and 7.67 (2 H, m, Ar-*H*); δ_C(50 MHz; $CDCl_3$) 25.51, 67.80, 104.58, 119.22, 119.83, 125.31, 126.12, 127.31, 127.76, 127.87, 128.25, 134.27, 137.30 and 150.91; *m*/*z* (CI) 257 (M^+ + H, 61%), 227 (35), 197 (78).

Acenaphtho[1,2-*b*][1,4]oxathiine 4

Compound **10** (4.00 g, 17.7 mmol) and DDQ (6.00 g, 26.5 mmol) were stirred in dry dioxane (150 cm^3) at reflux under argon for 24 h. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography [silica, eluent hexane–dichloromethane (9 : 1 v/v)]. The first purple band was collected and the solvent evaporated *in vacuo* to yield **4** (0.23 g, 6%) as a purple microcrystalline solid, mp 96–98 °C (from hexane–dichloromethane) (Found: C, 75.0; H, 3.6. $C_{14}H_8OS$ requires C, 75.0; H, 3.6%); ν_{max}(KBr)/cm^{-1} 3075, 2924, 2853, 1631, 1537, 1459, 1433, 1344, 1289, 1218, 1096, 1004, 969, 817, 766, 712, 702; λ_{max}(CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}) 530 (510), 311 (10 676), 240 (14 300), 212 (2724); δ_H(200 MHz; $CDCl_3$) 5.11 (1 H, d, *J* 6.3, SC*H*CH), 6.43 (1 H, d, *J* 6.3, OC*H*CH), 7.33 (1 H, m, Ar-*H*), 7.47 (3 H, m, Ar-*H*) and 7.72 (2 H, m, Ar-*H*); δ_C(200 MHz; $CDCl_3$) 94.48, 103.85, 119.90, 120.81, 124.41, 126.82, 126.90, 127.23, 127.53, 127.60, 131.27, 134.25, 139.11 and 147.70; *m*/*z* (EI) 224 (M^+, 100%), 196 (28), 170 (99).

6b,11a-Dihydroacenaphtho[1,2-*b*][1,3]dithiolo[4,5-*e*][1,4]-dithiine-9-thione 13

Compound **12**[7] (10.0 g, 50.9 mmol) and acenaphthylene **11** (10.0 g, 65.7 mmol) were stirred in toluene (250 cm^3) at reflux for 0.5 h. During this time **12** was gradually consumed and a yellow precipitate formed. The suspension was cooled to room temperature, filtered and washed with hot ethanol (150 cm^3) to yield **13** (14.0 g, 79%) as yellow needles, mp 235–240 °C (Found: C, 51.6; H, 2.2. $C_{15}H_8S_5$ requires C, 51.7; H, 2.3%); ν_{max}(KBr)/cm^{-1} 1065, 1041, 821, 775, 505; δ_H(400 MHz; CS_2–$CDCl_3$ 5 : 1 v/v) 5.74 (2 H, s, *benzylic H*), 7.45 (2 H, d, *J* 6.8, Ar-*H*), 7.57 (2 H, m, Ar-*H*) and 7.72 (2 H, d, *J* 8.4, Ar-*H*); *m*/*z* (EI) 348 (M^+, 100%), 152 (89).

Acenaphtho[1,2-*b*][1,3]dithiolo[4,5-*e*][1,4]dithiine-9-thione 14

Compound **13** (5.00 g, 14.4 mmol) and DDQ (6.50 g, 28.6 mmol) were refluxed in toluene (200 cm^3) under dry argon for 16 h. The mixture was cooled to room temperature and the resultant precipitate was filtered and washed with 25 cm^3 portions of hot toluene and hot acetone until the solvent remained colourless. The orange solid, which did not dissolve in these solvents, was recrystallised from hot chlorobenzene to afford **14** (4.65 g, 94%) as orange microcrystals, mp > 250 °C (Found: C, 51.7; H, 1.8. $C_{15}H_6S_5$ requires C, 52.0; H, 1.75%); ν_{max} (KBr)/cm^{-1} 1423, 1073, 1032, 816, 763; δ_H(400 MHz; CS_2–$CDCl_3$ 5 : 1 v/v) 7.61 (4 H, m, Ar-*H*) and 7.86 (2 H, d, *J* 7.6, Ar-*H*); *m*/*z* (EI) 347 (M^+ + H, 6%), 185 (100).

Acenaphtho[1,2-*b*][1,3]dithiolo[4,5-*e*][1,4]dithiine-9-one 15

A suspension of mercuric acetate (5.50 g, 17.3 mmol) and **14** (2.00 g, 5.77 mmol) in a mixture of chloroform and acetic acid (200 cm^3, 3 : 1 v/v), was stirred for 15 h under dry argon at 20 °C. The resultant pale pink suspension was filtered through a bed of Celite and eluted with hot chloroform. The eluent was washed with sodium bicarbonate solution until neutral and then with brine (100 cm^3). The organic solution was dried ($MgSO_4$) and evaporated *in vacuo* to afford **15** (1.45 g, 76%) as salmon pink needles, mp 222 °C (decomp.) (from toluene) (Found: C, 54.75; H, 1.8. $C_{15}H_6OS_4$ requires C, 54.5; H, 1.8%); ν_{max} (KBr)/cm^{-1} 1687 (C=O), 1659, 1423, 816, 765; δ_H(400 MHz; $CDCl_3$) 7.58 (2 H, m, Ar-*H*), 7.66 (2 H, d, *J* 7.7, Ar-*H*) and 7.86 (2 H, d, *J* 8.0, Ar-*H*); *m*/*z* (CI) 331 (M^+ + H, 39%), 185 (100).

8,9-Bis(methylsulfanyl)acenaphtho[1,2-*b*][1,4]dithiine 5

Under a positive pressure of argon, potassium *tert*-butoxide

Table 3 Crystal data

Compound	**5**	**5**:TCNQ	**5**:Br$_2$TCNQ	**5**(I$_7^-$)
Formula	$C_{16}H_{12}S_4$	$C_{28}H_{16}N_4S_4$	$C_{28}H_{14}N_4Br_2S_4$	$C_{16}H_{12}S_4I_7$
M	332.5	536.7	694.5	1220.8
T/K	295	150	150	150
Symmetry	monoclinic	orthorhombic	triclinic	triclinic
a/Å	11.928(1)	19.451(1)	7.848(1)	10.420(1)
b/Å	8.302(1)	18.738(1)	10.295(1)	11.263(1)
c/Å	15.736(1)	6.883(1)	17.309(1)	13.087(1)
α/°	90	90	77.29(1)	64.76(1)
β/°	103.34(1)	90	83.47(1)	78.80(1)
γ/°	90	90	89.59(1)	79.74(1)
U/Å^3	1516.2(2)	2508.7(4)	1355.1(2)	1354.9(2)
Space group	$P2_1/n$	$Pnma$	$P\bar{1}$	$P\bar{1}$
Z	4	4	2	2
μ/cm^{-1}	6.1	4.1	33.3	83.3
D_x/g cm^{-3}	1.457	1.421	1.702	2.992
Crystal size/mm	0.08 × 0.18 × 0.40	0.06 × 0.16 × 0.44	0.08 × 0.13 × 0.36	0.15 × 0.17 × 0.30
$2\theta_{max}$/°	55	50	61	60.5
Data total	9795	8339	13741	17175
Data unique	3382	2153	7121	7262
Data observed, $I > 2\sigma(I)$	2533	1693	5664	5770
R_{int} [a]	0.043, 0.036	0.078, 0.055	0.086, 0.029	0.139, 0.035
Transmission min, max	0.832, 0.958	0.759, 0.978	0.591, 0.907	0.259, 0.419
No. of least-squares (refined) variables	230	198	400	252
$wR(F^2)$, all data	0.105	0.144	0.081	0.099
Goodness-of-fit	1.11	1.13	1.11	1.10
$R(F)$, obs. data	0.047	0.058	0.034	0.040
max, min $\Delta\rho$/e Å^{-3}	0.25, −0.38	0.61, −0.42	0.49, −0.52	1.15, −1.89

[a] Before and after absorption correction.

(510 mg, 4.54 mmol) was added in one portion to a stirred suspension of **15** (500 mg, 1.51 mmol) in dry tetrahydrofuran (100 cm^3). This mixture was stirred at room temperature for a further 0.5 h, during which time the solution (presumably containing dithiolate salt **16**) became a milky-brown colour. Iodomethane (0.29 cm^3, 4.66 mmol) was added dropwise causing the solution quickly to turn milky red. The solution was stirred for a further 0.5 h whereupon the solvent was evaporated *in vacuo*. The residue was dissolved in dichloromethane and filtered through a short plug of silica gel eluting with dichloromethane to afford **5** (0.40 g, 80%) as red plates, mp 102–104 °C (from methanol) (Found: C, 57.6; H, 3.5. $C_{16}H_{12}S_4$ requires C, 57.8; H, 3.6%); ν_{max} (KBr)/cm^{-1} 2918, 1456, 1422, 1176, 1135, 1061, 841, 818, 767, 615; λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}) 496 (260), 328 (11 900), 238 (25 500); δ_H(400 MHz; $CDCl_3$) 2.5 (6 H, s, CH_3), 7.54 (2 H, dd, J 7.2 and 7.2, Ar-H), 7.63 (2 H, d, J 6.8, Ar-H) and 7.80 (2 H, d, J 8.0, Ar-H); δ_C(100 MHz; $CDCl_3$) 135.8, 133.2, 129.6, 128.8, 128.0, 127.9, 127.8, 121.4 and 18.1; m/z (EI) 332 (M$^+$, 41%), 285 (100).

Complex of 5 and TCNQ. A complex was prepared by mixing hot solutions of **5** (0.05 mmol) and TCNQ (0.05 mmol) each dissolved in anhydrous acetonitrile (15 cm^3) and filtering the black needles which formed upon cooling [Found: C, 61.6; H, 2.8; N, 10.5. $C_{28}H_{16}N_4S_4$ (a 1 : 1 complex) requires C, 62.7; H, 3.0; N, 10.4%]; ν_{max} (KBr)/cm^{-1} 2219.

Complex of 5 and 2,5-dibromo-TCNQ. A complex was prepared by the same method described above for **5**:TCNQ, using 2,5-dibromo-TCNQ[20] [Found: C, 48.2; H, 1.9; N, 8.25. $C_{28}H_{14}Br_2N_4S_4$ (a 1 : 1 complex) requires C, 48.4; H, 2.0; N, 8.1%)]; ν_{max}(KBr)/cm^{-1} 2210.

Salt of 5 and iodine. A salt was prepared by slow diffusion of iodine vapour into a solution of **5** (12.5 mg) in dry dichloromethane (5 cm^3) at room temperature. Black prisms formed over a period of 4 days and were subsequently filtered and washed with a small amount of dichloromethane [Found: C, 15.9; H, 0.9. $C_{16}H_{12}I_7S_4$ (*i.e.* stoichiometry **5**:I$_7$) requires C, 15.7; H, 1.0%].

X-Ray structure determinations

X-Ray single-crystal diffraction experiments (see Table 3) were carried out on a Siemens SMART 3-circle diffractometer equipped with a 1 K CCD area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N$_2$ gas cryostat. Diffraction intensities were measured by ω scans (in steps of 0.3° ω each), nominally covering over a hemisphere of reciprocal space, and integrated using SAINT software.[27] The absorption correction for **5** was performed by numerical integration (SHELXTL program[28]), based on measurements of the real shape of the crystal and face indexing. For other compounds, a semi-empirical absorption correction (using SADABS program[29]) was applied, based on multiple measurements of identical reflections and Laue equivalents. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[28] All non-H atoms were refined with anisotropic displacement parameters. All H atoms were refined freely in isotropic approximation, except in **5**:(I$_7^-$) where methyl groups were refined as rigid bodies, other H atoms treated as 'riding'. In **5**:(I$_7^-$), one iodine atom is disordered over two positions, I(1) and I(1′), with the occupancies of 90 and 10%, respectively. The minor position was refined in an isotropic approximation.†

Acknowledgements

We are grateful to the UK Engineering and Physical Sciences Research Council for funding the work in Durham, and Dr J. N. Heaton for the synthesis of Br$_2$TCNQ. We thank the

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† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available *via* the RSC web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/158. See http://www.rsc.org/suppdata/p2/1999/755/ for crystallographic files in .cif format.

University of Durham and the Leverhulme Trust for funding (to A. S. B.) and the Royal Society for a Leverhulme Senior Research Fellowship (to J. A. K. H.). The work in Basel was supported by the Swiss National Science Foundation.

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Paper 8/09872G