

Structural and solution studies of diiodine charge-transfer complexes of thioether crowns

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The charge-transfer complexes 2[9]aneS₃·4I₂ ([9]aneS₃ = 1,4,7-trithiacyclononane), [12]aneS₄·I₂ ([12]aneS₄ = 1,4,7,10-tetrathiacyclododecane), [14]aneS₄·I₂, [14]aneS₄·2I₂ ([14]aneS₄ = 1,4,8,11-tetrathiacyclotetradecane), [16]aneS₄·I₂ and [16]aneS₄·4I₂ ([16]aneS₄ = 1,5,9,13-tetrathiacyclohexadecane) have been prepared by slow evaporation of solutions containing I₂ and the appropriate thioether macrocycle in CH₂Cl₂. The structure of 2[9]aneS₃·4I₂ shows two independent macrocycles in the asymmetric unit which are linked by a diiodine bridge. Asymmetric units are linked by I···I and S···I interactions to form an extended array of linked macrocycles. The single-crystal structure of [12]aneS₄·I₂ features an infinite chain structure formed by alternating [12]aneS₄ and I₂ molecules. The structure contains both symmetric and asymmetric diiodine bridges. Although the 1:1 adduct [14]aneS₄·I₂ can also be described as a one-dimensional infinite chain structure with asymmetric diiodine bridging, the structure is better visualised as alternating layers of macrocycle and iodine spanned by short contacts of 3.335(4) Å. The adduct [14]aneS₄·2I₂ shows two independent macrocycles each co-ordinated to two I₂ molecules. The charge-transfer network consists of chains of molecules with alternating orientations. The single-crystal structure of a third 1:1 adduct [16]aneS₄·I₂ contains only symmetrical diiodine bridges between neighbouring macrocycles leading to an infinite chain structure. The compound [16]aneS₄·4I₂ is the first example of a tetradentate macrocycle which incorporates I₂ bound to all four S atoms. The single-crystal structure shows four terminal I₂ molecules co-ordinated to the four S donors of the macrocycle. Molecules are linked into interwoven sheets by I···I interactions of 3.639(2) Å. The formation enthalpies (ΔH) and constants (K) of 1:1 adducts obtained by treating various thioether macrocycles with I₂ in CH₂Cl₂ have been determined by electronic spectroscopy. The Fourier-transform Raman spectra for all the charge-transfer adducts have been recorded in CH₂Cl₂ solutions at different concentrations. The Raman frequencies of the $\nu(I-I)$ vibrations show good correlation with the measured formation enthalpies ΔH .

Many examples of charge-transfer complexes between halogens and interhalogens, particularly ICl, Br₂ and I₂, and donors such as amines,¹ phosphines,² ethers,³ thioketones,^{4,5} thioethers,⁶⁻¹¹ selenoketones⁵ and selenoethers¹² have been reported. Donation of electron density from non-bonding orbitals of the donor atom into the LUMO (lowest unoccupied molecular orbital) of the dihalogen molecule, which is an antibonding σ_u^* orbital lying along the main axis of the dihalogen, decreases the bond order thus increasing the bond lengths in the halogen molecule. Solid I₂ forms a layered structure where iodine molecules form a distorted honeycomb structure in each layer. The I–I bond length [2.715(6) Å]¹³ is elongated compared to that in the gas phase [2.667(2) Å]¹⁴ and this deviation can be attributed directly to donation of electron density from filled non-bonding p orbitals to the antibonding LUMO of a neighbouring I₂ molecule. The elongation of the I–I bond and the angle between the I₂ molecule and the donor atom, which should be approximately linear, can therefore be used as a sensitive probe in the investigation of co-ordinative bonding in solution and the solid state.

The electronic features of donor–acceptor complexes containing I₂ are in general well established, although few adducts between I₂ and small organic molecules containing more than one donor atom have been investigated. We argued that adducts of I₂ with polydentate organic molecules should be

capable of forming a number of structurally diverse assemblies in the solid state. We report herein a study on charge-transfer adducts of homoleptic thioether macrocycles with varying I₂ concentrations, and describe the synthesis, single-crystal structures and solution data for charge-transfer complexes of the tridentate macrocycle [9]aneS₃ and the tetradentate macrocycles [12]-, [14]- and [16]-aneS₄.†

Results and Discussion

Solid-state studies

All compounds described were prepared by allowing a solution of the appropriate macrocycle and I₂ in CH₂Cl₂ to evaporate slowly. Crystals suitable for single-crystal X-ray diffraction studies deposited slowly, usually near the bottom of the reaction vessel, and were collected. The adduct 2[9]aneS₃·4I₂ can be prepared either as described above by slow evaporation of a solution of I₂ and [9]aneS₃ in CH₂Cl₂ or by reaction of 2 molar equivalents of ICl with 1 molar equivalent of [9]aneS₃ in CH₂Cl₂.^{8,9} The initial yellow precipitate [9]aneS₃·2ICl converts slowly over a few months *via* sublimation into red-

† [9]aneS₃ = 1,4,7-Trithiacyclononane, [12]aneS₄ = 1,4,7,10-tetrathiacyclododecane, [14]aneS₄ = 1,4,8,11-tetrathiacyclotetradecane and [16]aneS₄ = 1,5,9,13-tetrathiacyclohexadecane.

Table 1 Selected bond lengths (Å), angles (°) and torsion angles (°) with estimated standard deviations (e.s.d.s) in parentheses for 2[9]aneS₃·4I₂ **1**

| | | | |
|-------------------------|------------|--------------------|------------|
| I(14)–I(14') | 2.785(2) | I(24)–I(11) | 2.754(2) |
| I(14)–S(14) | 2.870(6) | I(24)–S(24) | 3.054(6) |
| I(17)–I(17') | 2.816(2) | I(27')–I(27) | 2.799(2) |
| I(17)–S(17) | 2.760(6) | I(27)–S(27) | 2.862(6) |
| I(11)–S(11) | 3.017(6) | | |
| I(14')–I(14)–S(14) | 178.35(14) | I(11)–S(11)–C(12) | 101.5(8) |
| I(14)–S(14)–C(13) | 95.2(7) | I(11)–I(24)–S(24) | 168.39(13) |
| I(14)–S(14)–C(15) | 99.2(8) | I(24)–S(24)–C(23) | 93.8(8) |
| I(17')–I(17)–S(17) | 174.86(14) | I(24)–S(24)–C(25) | 99.0(8) |
| I(17)–S(17)–C(16) | 94.0(7) | I(27')–I(27)–S(27) | 177.27(14) |
| I(17)–S(17)–C(18) | 96.8(8) | I(27)–S(27)–C(26) | 99.7(7) |
| I(24)–I(11)–S(11) | 176.18(12) | I(27)–S(27)–C(28) | 98.8(7) |
| I(11)–S(11)–C(19) | 87.9(7) | | |
| S(11)–C(12)–C(13)–S(14) | –86.7(18) | | |
| C(12)–C(13)–S(14)–C(15) | 71.6(18) | | |
| C(13)–S(14)–C(15)–C(16) | –123.6(17) | | |
| S(14)–C(15)–C(16)–S(17) | 60(2) | | |
| C(15)–C(16)–S(17)–C(18) | 75.3(18) | | |
| C(16)–S(17)–C(18)–C(19) | –113.9(16) | | |
| S(17)–C(18)–C(19)–S(11) | 77.4(18) | | |
| C(18)–C(19)–S(11)–C(12) | –97.5(17) | | |
| C(19)–S(11)–C(12)–C(13) | 132.2(17) | | |
| S(21)–C(22)–C(23)–S(24) | 55(2) | | |
| C(22)–C(23)–S(24)–C(25) | –132.2(17) | | |
| C(23)–S(24)–C(25)–C(26) | 57.8(19) | | |
| S(24)–C(25)–C(26)–S(27) | 56(2) | | |
| C(25)–C(26)–S(27)–C(28) | –132.9(16) | | |
| C(26)–S(27)–C(28)–C(29) | 59.0(19) | | |
| S(27)–C(28)–C(29)–S(21) | 55(2) | | |
| C(28)–C(29)–S(21)–C(22) | –131.9(18) | | |
| C(29)–S(21)–C(22)–C(23) | 58(2) | | |

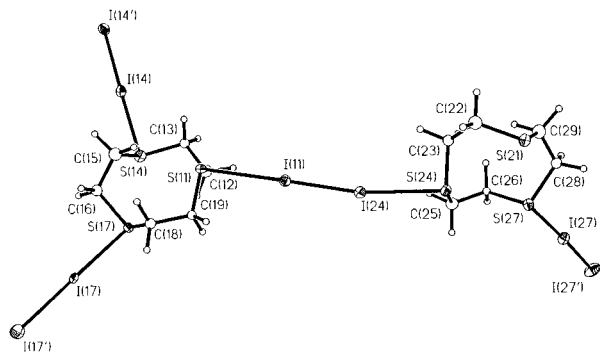


Fig. 1 Single-crystal structure of 2[9]aneS₃·4I₂ **1** with the numbering scheme adopted

brown crystals of composition 2[9]aneS₃·4I₂.⁸ The single-crystal structures of the compounds obtained following those two routes are identical and show two independent [9]aneS₃ molecules which are bridged by an I₂ molecule [S(11)–I(11) 3.017(6), S(24)–I(24) 3.054(6) and I(11)–I(24) 2.754(2) Å; S(11)–I(11)–I(24) 176.18(12), S(24)–I(24)–I(11) 168.39(13)°] (Fig. 1, Table 1). One macrocycle is co-ordinated to another I₂ molecule [S(27)–I(27) 2.862(6), I(27)–I(27') 2.799(2) Å; S(27)–I(27)–I(27') 177.27(14)°] whereas the second macrocycle interacts with two I₂ molecules [S(14)–I(14) 2.870(6), I(14)–I(14') 2.785(2), S(17)–I(17) 2.760(6) and I(17)–I(17') 2.816(2) Å; S(14)–I(14)–I(14') 178.35(14) and S(17)–I(17)–I(17') 174.86(14)°]. The compound may therefore be regarded formally as an adduct between [9]aneS₃·I₂ and [9]aneS₃·3I₂⁹ rather than being simply the dimer of [9]aneS₃·2I₂. However, the packing in **1** (Fig. 2) is complicated revealing extensive additional I⋯I and I⋯S contacts throughout the structure to give an extended network of interlinking macrocycles. One of the [9]aneS₃ molecules [S(21)–C(29)] adopts the same general

Table 2 Selected bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.s in parentheses for [12]aneS₄·I₂ **2b** (I 1 – x, –y, 2 – z, II –x, –y, –z)

| | | | |
|--|------------|----------------------------------|-----------|
| I(21)–I(1) | 2.7549(8) | I(7)–S(7) | 3.203(2) |
| I(7)–I(7') | 2.7500(10) | I(21)–S(21) | 3.148(2) |
| I(1)–S(1) | 3.174(2) | | |
| S(1)–I(1)–I(21) | 174.99(4) | C(8')–S(7)–I(7) | 85.1(7) |
| C(12)–S(1)–I(1) | 106.9(5) | C(6)–S(7)–I(7) | 84.0(4) |
| C(2)–S(1)–I(1) | 88.0(4) | S(21)–I(21)–I(1) | 170.28(4) |
| S(7)–I(7)–I(7') | 165.00(4) | C(26 ^{II})–S(21)–I(21) | 91.9(4) |
| C(8)–S(7)–I(7) | 119.5(5) | C(22)–S(21)–I(21) | 85.2(4) |
| C(2)–S(1)–C(12)–C(11) | –73.7(6) | | |
| C(12)–S(1)–C(2)–C(3) | –72.3(6) | | |
| S(1)–C(2)–C(3)–S(4) | 173.2(4) | | |
| C(2)–C(3)–S(4)–C(5) | –76.0(6) | | |
| C(3)–S(4)–C(5)–C(6) | –76.3(6) | | |
| S(4)–C(5)–C(6)–S(7) | 171.6(4) | | |
| C(5)–C(6)–S(7)–C(8) | –60.5(6) | | |
| C(6)–S(7)–C(8)–C(9) | –71.3(7) | | |
| S(7)–C(8)–C(9)–S(10) | 173.9(5) | | |
| C(8)–C(9)–S(10)–C(11) | –81.0(7) | | |
| C(9)–S(10)–C(11)–C(12) | –64.4(7) | | |
| S(10)–C(11)–C(12)–S(1) | 172.0(4) | | |
| S(21)–C(22)–C(23)–S(24) | 172.0(4) | | |
| C(22)–C(23)–S(24)–C(25) | –79.3(6) | | |
| C(23)–S(24)–C(25)–C(26) | –82.3(6) | | |
| S(24)–C(25)–C(26)–S(21 ^{II}) | 167.0(4) | | |
| C(25)–C(26)–S(21 ^{II})–C(22 ^{II}) | –90.7(6) | | |
| C(26)–S(21 ^{II})–C(22 ^{II})–C(23 ^{II}) | 94.8(6) | | |

[333] conformation, which is found in the solid-state structure of free [9]aneS₃ with the S atoms adopting *exo* orientations.¹⁵ However, the [9]aneS₃ moiety S(11)–C(19) adopts an unusual distorted [234] conformation. With a 1:3 molar ratio of [9]aneS₃·I₂, crystals of [9]aneS₃·3I₂, in which all the thioether donors are bound to I₂, can be obtained.⁹ In this adduct the S–I [2.865(6)–2.933(4) Å] and I–I [2.772(1)–2.751(2) Å] distances are similar to those in 2[9]aneS₃·4I₂.

The single-crystal structure of [12]aneS₄·I₂ **2a** has been reported recently by Baker *et al.*¹⁰ It consists of independent [12]aneS₄ molecules bridged symmetrically by I₂ molecules [S–I 3.220(3) and I–I 2.736(1) Å; S–I–I 170.5(1)°]. We were able to prepare¹¹ a similar compound with the same stoichiometry [12]aneS₄·I₂ **2b** but a different solid-state structure. Compounds **2a** and **2b** both crystallise in the monoclinic crystal system (*P*₂₁/*a* and *P*₂₁/*c* respectively) but the unit-cell volume for **2b** (2190 Å³) is approximately three times that for **2a** (740 Å³). The asymmetric unit of **2b** therefore contains three times the number of atoms compared with **2a** (1.5 [12]aneS₄ and 1.5 I₂ molecules, Fig. 3). One macrocycle and one I₂ molecule lie on crystallographic inversion centres and the structure therefore contains a symmetric [S(7)–I(7) 3.203(2) and I(7)–I(7') 2.7500(10) Å; S(7)–I(7)–I(7') 165.00(4)°; I 1 – x, –y, 2 – z] as well as an asymmetric [S(1)–I(1) 3.174(2), S(21)–I(21) 3.148(2) and I(1)–I(21) 2.7549(8) Å; S(1)–I(1)–I(21) 174.99(4) and S(21)–I(21)–I(1) 170.28(4)°] bridging I₂ moieties within the same structure (Table 2). The macrocycles in **2a** and S(21)–C(26) in **2b** adopt the typical [3333] conformation with *exo*-oriented S atoms which has also been found in the structure of free [12]aneS₄,¹⁶ although the macrocycle S(1)–C(12) in **2b** adopts a distorted [2334] conformation. The alternating sequence of [12]aneS₄ and I₂ molecules results in infinite one-dimensional chains running in the [102] direction in the packing diagram (Fig. 4).

In [14]aneS₄·I₂ **3** (Fig. 5, Table 3) the macrocycle retains the [3434] conformation of free [14]aneS₄¹⁷ and the I₂ molecules [I(1)–I(1') 2.8095(11) Å; S(1)–I(1)–I(1') 178.57(7)°] bridge asymmetrically between two independent [14]aneS₄ molecules [S(1)–I(1) 2.859(3) and S(8')–I(1') 3.640(3) Å; S(8')–I(1')–I(1) 168.38(5); I –½ + x, y, ½ – z] thus forming an infinite one-

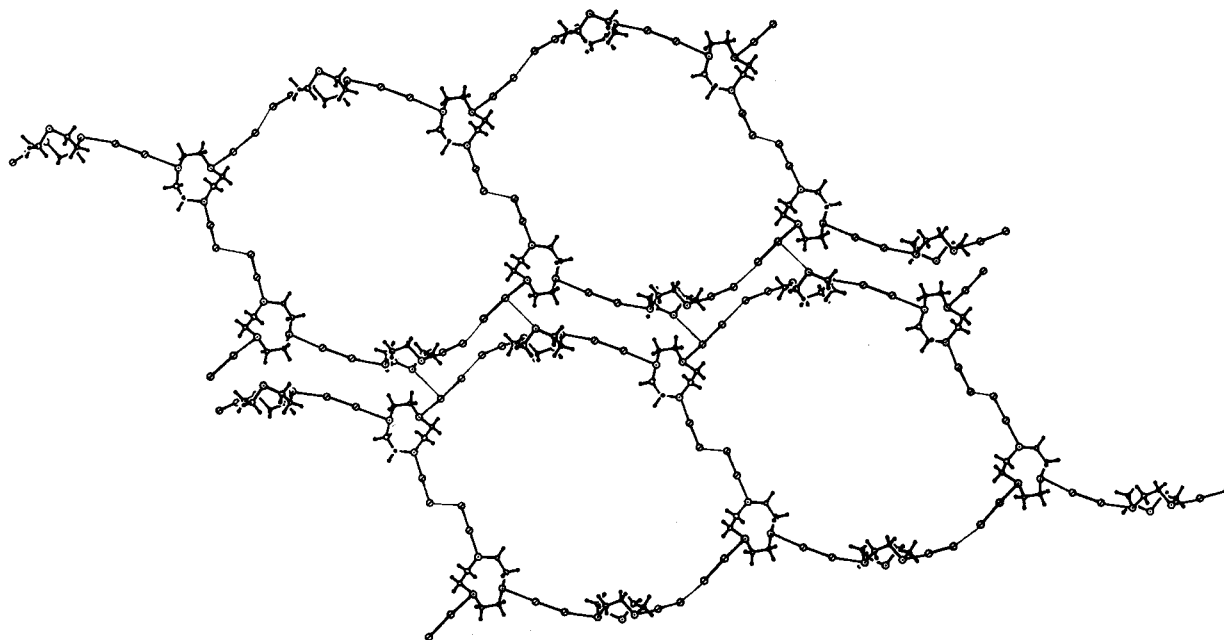


Fig. 2 Packing diagram of compound 1

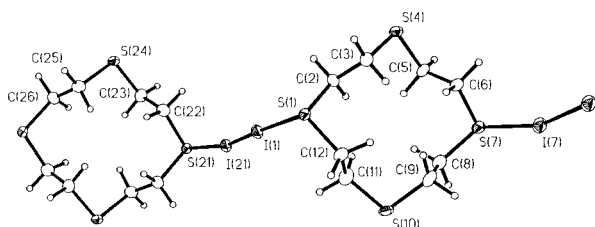


Fig. 3 Single-crystal structure of [12]aneS₄·I₂ **2b** with the numbering scheme adopted

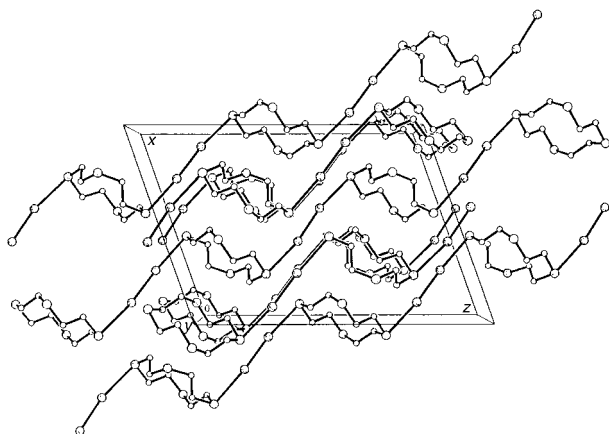


Fig. 4 Packing in [12]aneS₄·I₂ **2b** showing the infinite one-dimensional chain structure formed by alternating I₂ and [12]aneS₄ molecules

dimensional chain structure. However, the structure can also be visualised as having alternating layers of macrocycle and I₂ spanned by S···S contacts of 3.335(4) Å (Fig. 6).

The asymmetric unit of [14]aneS₄·2I₂ **4** comprises two independent half-macrocycles and two I₂ molecules (Fig. 7, Table 4). The S–I [S(11)–I(11) 2.800(4), S(21)–I(21) 2.841(4) Å] and I–I distances [I(11)–I(11') 2.821(2), I(21)–I(21') 2.808(2) Å] are very similar to those found for compound **3**. The S–I–I geometry is, as expected, essentially linear [S(11)–I(11)–I(11') 177.58(8) and S(21)–I(21)–I(21') 177.86(8)°]. Both macrocycles again adopt the [3434] conformation found in the solid-state structure of **3** and free [14]aneS₄.¹⁷ The least-squares planes through the S atoms of the two macrocycles are tilted against

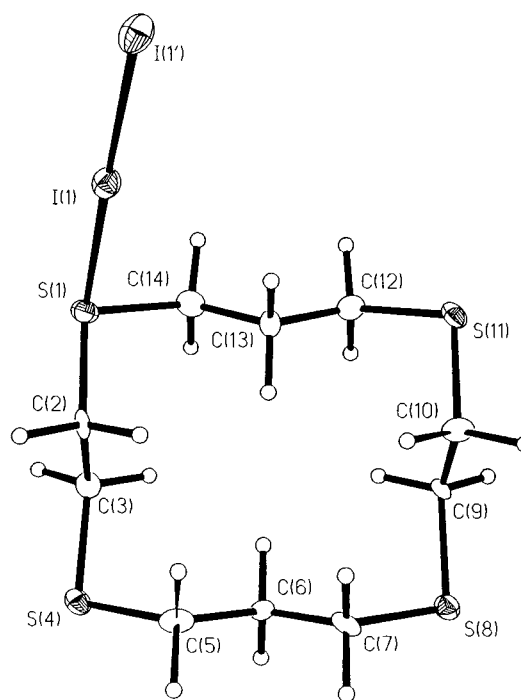


Fig. 5 Single-crystal structure of [14]aneS₄·I₂ **3** with the numbering scheme adopted

each other by about 47° leading to stacks of [14]aneS₄·2I₂ molecules in two different orientations in the packing diagram (Fig. 8). The presence of alternating sheets of macrocycle and I₂ is a feature also found in **3**. The arrangements within each stack are nevertheless very similar and this is reflected in the conformation of the macrocycles and the I–I and I–S distances. A view approximately along the *a* lattice direction showing the packing motif in **4** in which S···I interactions link molecules into a three-dimensional, infinite network is shown in Fig. 8. The network can be visualised as chains of molecules with alternating orientations running in the [011] direction and linked by S···I contacts of 3.699 Å (shown as thin dashed lines). These chains are cross-linked by longer S···I contacts of 3.931 Å (shown as dotted lines) to form layers. The I₂ centres involved in these contacts are derived exclusively from one of the two independent molecules and its symmetry equivalents.

Table 3 Selected bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.s in parentheses for [14]aneS₄·I₂ **3** ($I - \frac{1}{2} + x, y, \frac{1}{2} - z$)

| | | | |
|-------------------------|------------|-----------------|----------|
| I(1)–I(1') | 2.8095(11) | I(1)–S(1) | 2.859(3) |
| I(1')–S(8') | 3.640(3) | | |
| S(8')–I(1')–I(1) | 168.38(5) | I(1)–S(1)–C(2) | 108.3(4) |
| I(1')–I(1)–S(1) | 178.57(7) | I(1)–S(1)–C(14) | 99.7(4) |
| S(1)–C(2)–C(3)–S(4) | –175.2(5) | | |
| C(2)–C(3)–S(4)–C(5) | –63.5(8) | | |
| C(3)–S(4)–C(5)–C(6) | –67.4(8) | | |
| S(4)–C(5)–C(6)–C(7) | 177.8(7) | | |
| C(5)–C(6)–C(7)–S(8) | –176.8(7) | | |
| C(6)–C(7)–S(8)–C(9) | 67.5(8) | | |
| C(7)–S(8)–C(9)–C(10) | 69.7(8) | | |
| S(8)–C(9)–C(10)–S(11) | 178.6(5) | | |
| C(9)–C(10)–S(11)–C(12) | 54.5(9) | | |
| C(10)–S(11)–C(12)–C(13) | 61.0(9) | | |
| S(11)–C(12)–C(13)–C(14) | 172.4(7) | | |
| C(12)–C(13)–C(14)–S(1) | –175.6(7) | | |
| C(13)–C(14)–S(1)–C(2) | –55.0(9) | | |
| C(14)–S(1)–C(2)–C(3) | –64.8(8) | | |

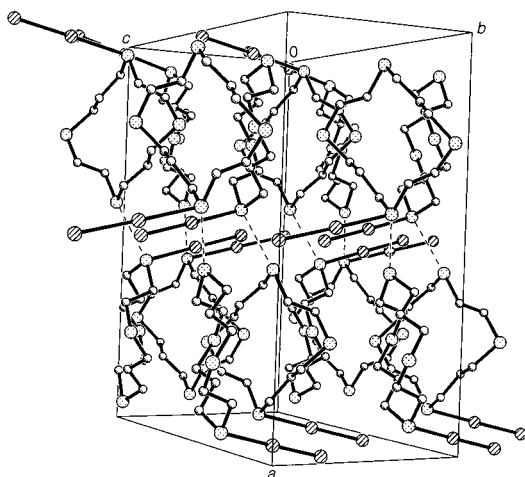


Fig. 6 Packing in [14]aneS₄·I₂ **3** showing alternating zones of macrocycle and I₂ along the *a* direction; S···S contacts link the macrocyclic layers across the I₂ sheets

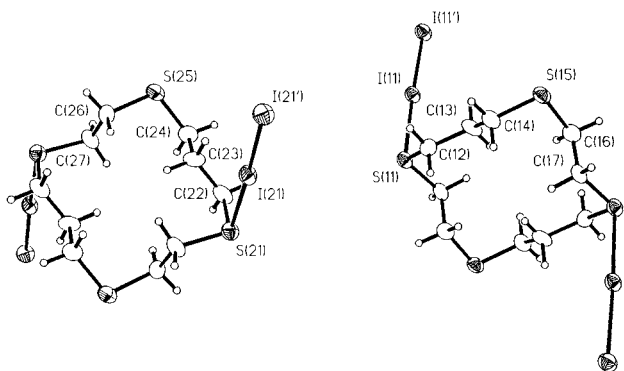


Fig. 7 Single-crystal structure of [14]aneS₄·2I₂ **4** with the numbering scheme adopted

Diiodine moieties from the other type of molecule participate in S···I contacts of 3.699 Å to molecules in layers above and below: these interactions are depicted as thick dashed lines in Fig. 8 and the three molecules representing an upper layer are identified by the letter A at their centre.

The 1:1 adduct [16]aneS₄·I₂ **5** exhibits features similar to those seen in **2a**, **2b** and **3**. Molecules of [16]aneS₄ lie on crystallographic inversion centres with a [233233] macrocyclic conformation (Fig. 9, Table 5) which is unexpectedly different

Table 4 Selected bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.s in parentheses for [14]aneS₄·2I₂ **4** ($I - x, -y, 3 - z, II - x, 1 - y, 2 - z$)

| | | | |
|--|------------|--------------------|-----------|
| I(11)–I(11') | 2.821(2) | I(21)–I(21') | 2.808(2) |
| I(11)–S(11) | 2.800(4) | I(21)–S(21) | 2.841(4) |
| S(11)–I(11)–I(11') | 177.58(8) | S(21)–I(21)–I(21') | 177.86(8) |
| C(12)–S(11)–I(11) | 104.9(5) | C(22)–S(21)–I(21) | 101.2(4) |
| C(17)–S(11)–I(11) | 101.0(5) | C(27)–S(21)–I(21) | 101.1(5) |
| S(11)–C(12)–C(13)–C(14) | –177.2(10) | | |
| C(12)–C(13)–C(14)–S(15) | –178.5(9) | | |
| C(13)–C(14)–S(15)–C(16) | –61.8(12) | | |
| C(14)–S(15)–C(16)–C(17) | –67.5(10) | | |
| S(15)–C(16)–C(17)–S(11 ^I) | –171.6(6) | | |
| C(16)–C(17)–S(11 ^I)–C(12 ^I) | –66.2(10) | | |
| C(17)–S(11 ^I)–C(12 ^I)–C(13 ^I) | 56.2(11) | | |
| S(21)–C(22)–C(23)–C(24) | –174.8(10) | | |
| C(22)–C(23)–C(24)–S(25) | –178.3(10) | | |
| C(23)–C(24)–S(25)–C(26) | –60.3(11) | | |
| C(24)–S(25)–C(26)–C(27) | –67.2(11) | | |
| S(25)–C(26)–C(27)–S(21 ^{II}) | –167.5(7) | | |
| C(26)–C(27)–S(21 ^{II})–C(22 ^{II}) | –66.6(11) | | |
| C(27)–S(21 ^{II})–C(22 ^{II})–C(23 ^{II}) | 54.5(11) | | |

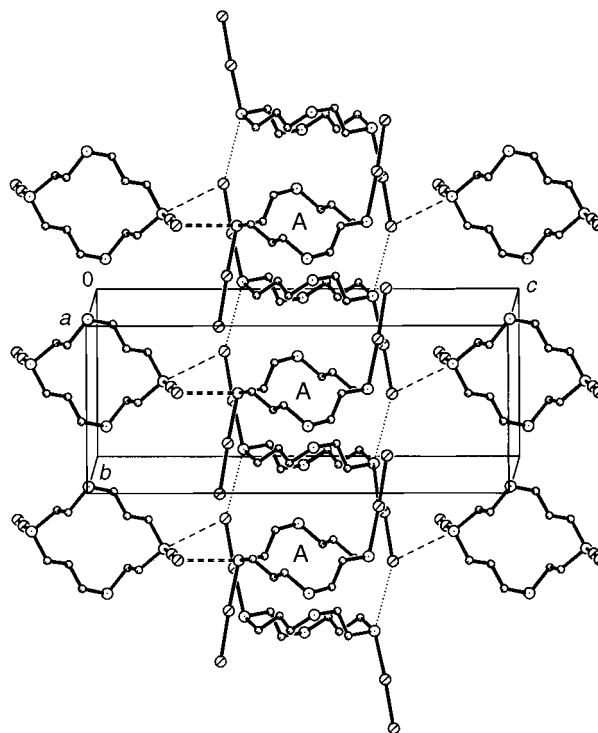


Fig. 8 Packing in [14]aneS₄·2I₂ **4** showing stacks in two distinct orientations within the crystal lattice

from the [3535] conformation of the uncomplexed macrocycle.¹⁸ Nevertheless a common feature in both **5** and [16]aneS₄ is the presence of two *endo*-oriented S atoms, contrasting with the other tetradentate macrocycles [12]aneS₄ and [14]aneS₄. In **5** alternating [16]aneS₄ and I₂ molecules form infinite, one-dimensional chains running in the [111] direction as shown in Fig. 10. The I₂ bridges between independent macrocycles are symmetrical [I(1)–I(1^I) 2.773(12) and S(1)–I(1) 3.114(14) Å; S(1)–I(1)–I(1^I) 173.02(8)°; $I = -x, -y, -z$].

The compound [16]aneS₄·4I₂ **6** is the only example in the present investigation where all four S-donor atoms co-ordinate to I₂ molecules (Fig. 11, Table 6). The I(1)–I(1') and I(5)–I(5') distances of 2.8108(9) and 2.7916(8) Å and I(1)–S(1) and I(5)–S(5) distances of 2.756(2) and 2.848(2) Å are typical and very similar to those in **4**: the S–I–I moieties, as expected, are

Table 5 Selected bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.s in parentheses for [16]aneS₄I₂ **5** (I -x, -y, -z, II 1 - x, 1 - y, 1 - z)

| | | | |
|--|-----------|-------------------------------|-----------|
| I(1)–I(1 ^I) | 2.773(12) | S(1)–I(1) | 3.114(14) |
| I(1 ^I)–I(1)–S(1) | 173.02(8) | I(1)–S(1)–C(8 ^{II}) | 92.6(5) |
| I(1)–S(1)–C(2) | 92.9(6) | | |
| S(1)–C(2)–C(3)–C(4) | –156.4(9) | | |
| C(2)–C(3)–C(4)–C(5) | 74.7(13) | | |
| C(3)–C(4)–S(5)–C(6) | 81.4(11) | | |
| C(4)–S(5)–C(6)–C(7) | –172.0(9) | | |
| S(5)–C(6)–C(7)–C(8) | 82.7(12) | | |
| C(6)–C(7)–C(8)–S(1 ^{II}) | 173.8(9) | | |
| C(7)–C(8)–S(1 ^{II})–C(2 ^{II}) | –165.1(9) | | |
| C(8)–S(1 ^{II})–C(2 ^{II})–C(3 ^{II}) | 78.6(10) | | |

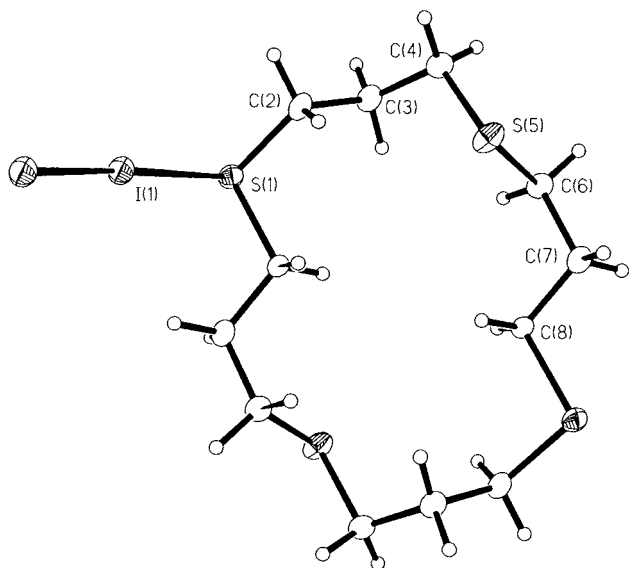


Fig. 9 Single-crystal structure of [16]aneS₄I₂ **5** with the numbering scheme adopted

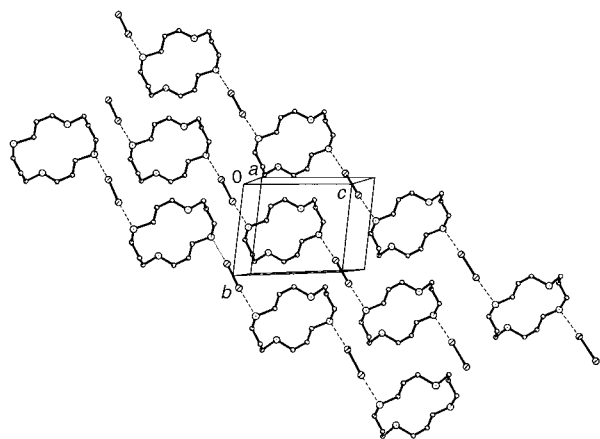


Fig. 10 Packing in [16]aneS₄I₂ **5** which has a one-dimensional chain structure similar to that of compound **2b**

quasi-linear [S(1)–I(1)–I(1^I) 174.74(5) and S(5)–I(5)–I(5^I) 171.71(5)°]. Although the macrocycle lies on a crystallographic two-fold axis passing through C(15) and C(7) it adopts a [233233] conformation similar to that found in the structure of **5**, where the molecules lie on inversion centres. However, the conformations of the [16]aneS₄ macrocycle in **5** and **6** (Figs. 9 and 11, respectively) are different with respect to the orientation of the S atoms. The packing diagram of **6** reveals a stacked arrangement of the macrocycles embedded in a matrix of I₂. The most significant intermolecular interactions are I⋯I con-

Table 6 Selected bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.s in parentheses for [16]aneS₄·4I₂ **6** (I -x, y, ½ - z)

| | | | |
|--------------------------------------|-----------|------------------------------|-----------|
| I(1)–I(1 ^I) | 2.8108(9) | I(5)–I(5 ^I) | 2.7916(8) |
| I(1)–S(1) | 2.756(2) | I(5)–S(5) | 2.848(2) |
| I(1 ^I)–I(1)–S(1) | 174.74(5) | I(5 ^I)–I(5)–S(5) | 171.71(5) |
| I(1)–S(1)–C(16) | 95.8(3) | I(5)–S(5)–C(4) | 107.4(3) |
| I(1)–S(1)–C(2) | 108.6(3) | I(5)–S(5)–C(6) | 93.7(3) |
| C(16 ^I)–C(15)–C(16)–S(1) | 68.9(7) | | |
| C(15)–C(16)–S(1)–C(2) | –166.1(5) | | |
| C(16)–S(1)–C(2)–C(3) | 73.3(6) | | |
| S(1)–C(2)–C(3)–C(4) | 166.4(6) | | |
| C(2)–C(3)–C(4)–S(5) | –177.6(6) | | |
| C(3)–C(4)–S(5)–C(6) | 81.8(7) | | |
| C(4)–S(5)–C(6)–C(7) | –162.5(6) | | |
| S(5)–C(6)–C(7)–C(6 ^I) | 76.1(7) | | |

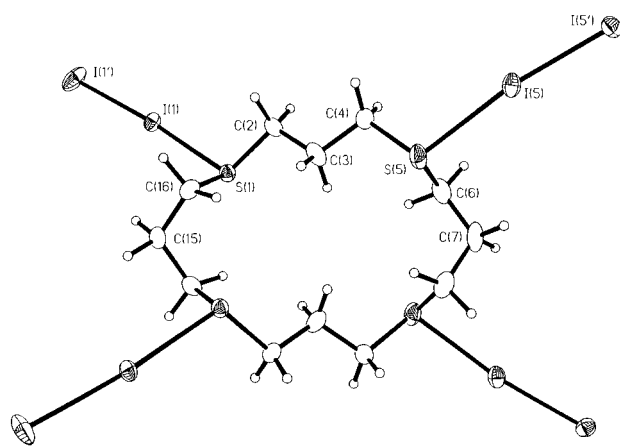


Fig. 11 Single-crystal structure of [16]aneS₄·4I₂ **6** with the numbering scheme adopted

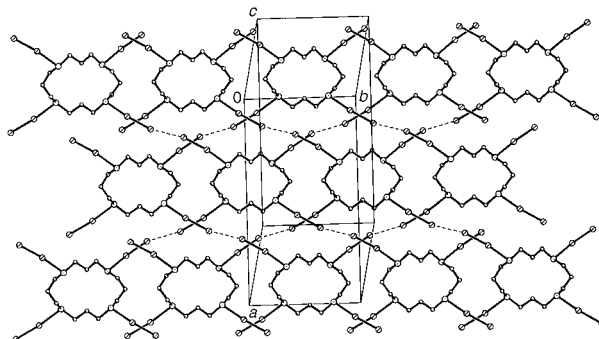


Fig. 12 Packing in [16]aneS₄·4I₂ **6**. Molecules are linked by I⋯I contacts into infinite chains which are interwoven to form a corrugated bilayer

tacts of 3.639(2) Å, which link molecules into two-dimensional, interwoven corrugated sheets lying in the *ab* plane (Fig. 12). Each molecule is linked to four of its neighbours *via* their terminal I₂ atoms: two of these neighbours lie in the upper part of the bilayer and two in the lower. Chains of molecules are nearly linear with I–I⋯I angles of 153.7(1) and 165.9(1)°. Any chain has its I₂⋯I₂ bridges consistently above or below those of the chains it crosses, and this relationship applies to each set of parallel chains (Fig. 12).

Fig. 13 shows a plot of S–I vs. I–I distances for solid-state structures of diiodine adducts of thioether crowns and related thioethers. It is clear that there is, as expected, a general inverse relationship between these distances, with S–I distances of greater than 3 Å being associated with bridging S⋯I₂⋯S fragments.

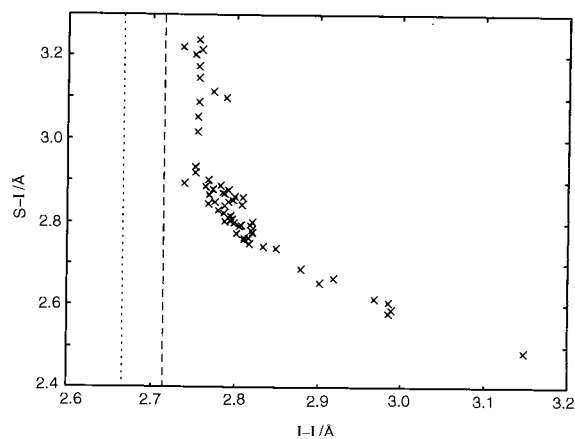
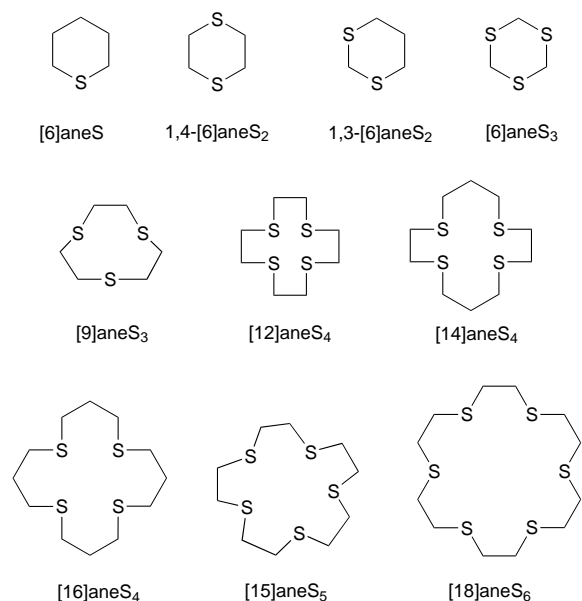


Fig. 13 Plot of $S-I$ vs. $I-I$ for structurally characterised adducts of thioethers and I_2 . Dotted and dashed vertical lines denote the $I-I$ distance in I_2 in the gas phase and solid state respectively



Solution studies

Electronic spectroscopic studies in solution allow measurement of the formation constants (K) and the thermodynamic parameters for the formation of charge-transfer adducts, equation (1).



Except for [6]aneS, all the thioether compounds under consideration contain two or more sulfur atoms capable of binding molecular I_2 and consequently molecular adducts having ligand: I_2 molar ratios different from 1:1 are to be expected in solution. Solutions containing both I_2 and suitable donors such as homoleptic thioether macrocycles in CH_2Cl_2 are dark brown in contrast to the violet colour of I_2 in CH_2Cl_2 . The change from violet to brown ($\lambda_{max} = 490$ nm) upon addition of the thioether macrocycle indicates the formation of charge-transfer adducts in solution. It is important to establish the stoichiometry of the dissolved species and initially Job's method¹⁹ of constant concentration variation was used to study the I_2 -[9]aneS₃ system in CH_2Cl_2 . The data (Table 7) strongly suggest that the predominant species under high dilution conditions has a 1:1 I_2 :[9]aneS₃ composition. For all the macrocycles investigated, the electronic spectra of different solutions containing a constant amount of macrocycle and an increasing amount of I_2 up to a macrocycle: I_2 molar ratio of 1:5 were recorded. Only one isosbestic point was observed with each

Table 7 Absorbances at 308 ± 3 nm for $0.993 \text{ mmol dm}^{-3}$ mixtures of diiodine and [9]aneS₃ in CH_2Cl_2

| I_2 :[9]aneS ₃ ratio | Absorbance |
|-----------------------------------|------------|
| 0:10 | 0.000 |
| 1:9 | 0.056 |
| 2:8 | 0.097 |
| 3:7 | 0.129 |
| 4:6 | 0.150 |
| 5:5 | 0.164 |
| 6:4 | 0.142 |
| 7:3 | 0.130 |
| 8:2 | 0.103 |
| 9:1 | 0.070 |
| 10:0 | 0.000 |

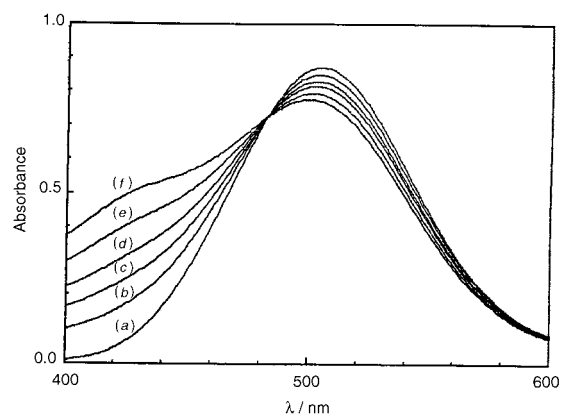


Fig. 14 Electronic spectra for addition of [18]aneS₆ to I_2 . $[I_2] = 9.3 \times 10^{-4} \text{ mol dm}^{-3}$ and $[18]aneS_6] = 1.792 \times 10^{-4}, 3.584 \times 10^{-4}, 6.272 \times 10^{-4}, 8.96 \times 10^{-4}, 1.254 \times 10^{-3}$ and $1.613 \times 10^{-3} \text{ mol dm}^{-3}$ for (a), (b), (c), (d), (e) and (f) respectively

macrocycle. Fig. 14 illustrates the isosbestic formation of the I_2 adduct of [18]aneS₆ up to a 1:5 [18]aneS₆: I_2 molar ratio. However, in order to avoid the formation of adducts different from 1:1, all the solutions used for the calculation of the stability constants of equilibrium (1) were prepared with macrocycle concentration always higher than that of I_2 . Thus, under the conditions of the experimental spectrophotometric measurements, only the formation of the 1:1 adduct is relevant as confirmed by the presence of isosbestic points (Table 8) for all the compounds.

The formation constants K at 25 °C together with the ΔH values, calculated from plots of $\ln(K\varepsilon)$ versus $1/T$, are reported in Table 9.†¹ Values previously reported for [6]aneS₃ and [9]aneS₃ are also included.⁹ The correlation coefficient ($r \geq 0.999$ for all compounds) for the plots of $\ln(K\varepsilon)$ versus $1/T$ indicate a good reliability for the ΔH values. It should be emphasised that it has not always been possible to explore the whole range of the saturation fraction(s) with these substrates, which should spread from 0 to 1 for each set of solutions in order to have the best confidence in the calculated K and ε values.^{21,22} In many cases either low solubility of the substrate or of the charge-transfer adduct prevented measurements throughout the full range of saturation fractions, s . For [6]aneS and [16]aneS₄ the accessible ranges of s were 0.11–0.95 and 0.21–0.91 (at 25 °C) respectively; for 1,4-[6]aneS₂, 1,3-[6]aneS₂, [14]aneS₄, [15]aneS₅ and [18]aneS₆ they were

† The molar absorption coefficients (ε) at six different wavelengths used for the calculation, the K values at temperatures of 15, 20, 25, 30 and 35 °C, the range of the saturation fraction experimentally realised for the sets of the solutions, the sum of the squared deviations between the calculated and observed absorbances, the ΔH values, calculated from the plots of $\ln(K\varepsilon)$ versus $1/T$ and the correlation coefficients for the compounds are available from the authors.

Table 8 Charge-transfer band (λ_{CT}) molar absorption coefficients (ϵ_{CT}) and isosbestic points obtained between the I_2 visible band and its blue-shifted band (CH_2Cl_2 solutions, 25 °C) for thioether crowns

| Compound | λ_{CT}/nm | $\epsilon_{CT}/dm^3 mol^{-1} cm^{-1}$ | Isosbestic point/nm |
|--------------------------|-------------------|---------------------------------------|---------------------|
| [6]aneS | 305 | 27 300 | 474 |
| 1,4-[6]aneS ₂ | 305 | 38 600 | 480 |
| 1,3-[6]aneS ₂ | 310 | 26 500 | 480 |
| [6]aneS ₃ | 310 | 35 900 | 479 |
| [9]aneS ₃ | 310 | 26 200 | 480 |
| [12]aneS ₄ | 310 | 17 900 | 492 |
| [14]aneS ₄ | 310 | 30 900 | 482 |
| [16]aneS ₄ | 310 | 31 400 | 479 |
| [15]aneS ₅ | 310 | 25 800 | 490 |
| [18]aneS ₆ | 310 | 27 400 | 485 |

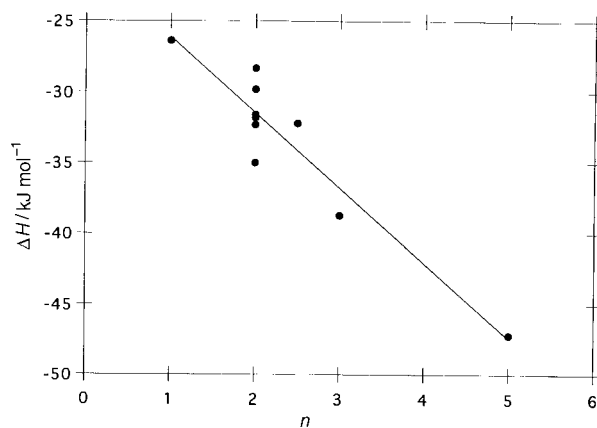


Fig. 15 Plot of ΔH vs. n (n = average number of CH_2 groups per sulfur atom) for I_2 adducts with thioether crowns

0.2–0.7, whereas those for [6]aneS₃, [9]aneS₃⁹ and [12]aneS₄ were narrower at 0.05–0.25. Obviously, the narrower the range of s explored the less reliable are the values for K . For this reason, more reliable values of ΔH were obtained from plots of $\ln(K\epsilon)$ versus $1/T$ in place of van't Hoff plots.^{§2}

Some preliminary conclusions can be drawn from inspection of the K values in Table 9. For rings of the same size the value of K decreases as the number of sulfur atoms increases. Otherwise, in the presence of the same number of sulfur atoms, K increases with increasing size of the ring (see for example the K values in Table 9 for the adducts of [6]aneS₃, [9]aneS₃ and [12]aneS₄, [14]aneS₄, [16]aneS₄). These trends can be explained in terms of inductive effects of the thioether atoms (–I) or *vice versa* in terms of the +I effect of the methylene groups. A convenient parameter that might take into account both these factors is the mean number of CH_2 groups (n) per sulfur atom. A rough correlation is found between the K values and n ; compare for example the K value of [6]aneS₃ (13 $dm^3 mol^{-1}$, $n = 1$) with that of [9]aneS₃ (169 $dm^3 mol^{-1}$, $n = 2$) or the K values of [12]aneS₄ (74 $dm^3 mol^{-1}$), [14]aneS₄ (151 $dm^3 mol^{-1}$) and [16]aneS₄ (519 $dm^3 mol^{-1}$) for which $n = 2, 2.5$ and 3 respectively. However, since the values obtained for ΔH are more reliable than those for K , a plot of ΔH vs. n should be considered (Fig. 15). As can be seen, the values of ΔH do appear to depend upon n . However, all the compounds for which $n = 2$ show a high spread of ΔH values, indicating

[§] As reported in the Experimental section, the formation constants K for the adduct of I_2 with 1,4-dithiacyclohexane were also calculated using SUPERSPEC.²⁰ The best values of K and ϵ obtained which minimise χ^2 are quite different from those reported in Table 9 [25 °C, $K = 104(18) dm^3 mol^{-1}$]. However the value of ΔH obtained from a normal van't Hoff plot ($31.8 \pm 0.06 kJ mol^{-1}$) is very similar to that in Table 9, thus supporting our choice of the method used in calculating ΔH .

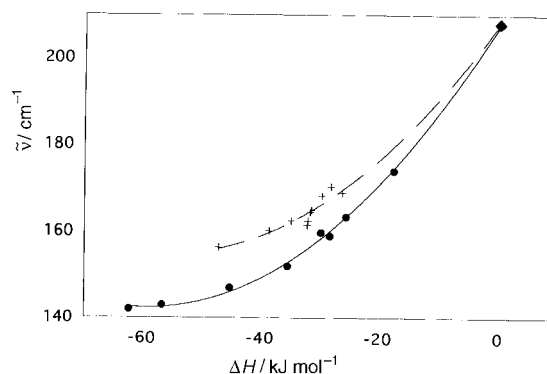


Fig. 16 Plot of $\nu(I-I)$ Raman vs. ΔH values. the lower curve (●) refers to diiodine-thioether crown adducts, the upper (+) to the diiodine-thioether crown adducts. The value of $208 cm^{-1}$ ($\Delta H = 0$) (◆) refers to free I_2

that other factors such as solvation must inevitably affect the strength of the S– I_2 interaction. The existence of several potential conformers for each charge-transfer adduct in solution also appears likely, and may play an important role in the observed K and ΔH values. The presence of a range of possible conformers for these compounds is underlined clearly by X-ray studies on crystalline adducts with I_2 as described above.

In order to monitor further diiodine-thioether crown interactions, the Fourier-transform Raman spectra of CH_2Cl_2 solutions of a range of thioether crowns and I_2 have been recorded in the characteristic $\nu(I-I)$ region, and the Raman shifts and the band half-widths, $\Delta\nu_{1/2}$, are reported in Table 9. Although the band half-widths are affected by some uncertainty, they generally increase with the size of the ring, presumably reflecting an increased number of adduct conformers present in solution each with very slightly different I_2 –S (thioether) bond strengths.

Fig. 16 shows a plot of the $\nu(I-I)$ Raman frequencies vs. ΔH values, together with data previously reported for the adducts obtained from compounds containing the C=S group.²³ The two sets of data do not fit the same curve and all the points corresponding to the thioether crowns lie above the curve obtained for the thioketones. This can be ascribed to the different hybridisation of the sulfur atoms in the two sets of compounds.

Conclusion

We have shown that diiodine charge-transfer adducts with homoleptic thioether macrocycles exhibit a range of different assemblies in the solid state and we have been able to identify and correlate those assemblies with the diiodine contents of the complex. Interestingly, regardless of ligand: I_2 ratios there is a tendency to obtain only certain adduct stoichiometries in the solid state. This reflects the solubility and packing behaviour of these isolated products. In particular, 1:1 adducts of I_2 and homoleptic S-donor macrocycles feature largely in this work and incorporate I_2 -bridged chain structures. The overall conformation of these chains depends, however, very much on the conformational preferences of the macrocycles which accounts for instance for the differences in the structures of **2a**, **2b**, **3** and **5**. It is also interesting that the macrocycles in complexes with low diiodine content adopt similar conformations compared with the solid-state structure of the uncomplexed macrocycle.

In solution our findings strongly suggest that the 1:1 adduct is the predominant species. Electronic spectroscopy has been used to obtain formation constant data, and from the ΔH vs. $\nu(I-I)$ correlation it has been possible to evaluate the enthalpy of the $S \cdots I_2$ donor-acceptor interaction.

A future paper will describe work on adducts of I_2 with penta-, hexa- and octa-dentate thioether macrocycles.

Table 9 Formation constants (K) at 25 °C, ΔH values, Raman frequencies $\nu(\text{I-I})$ and their band half-width for adducts of I_2 with thioether crowns (standard deviations in parentheses)

| Compound | n^a | $K/\text{dm}^3 \text{ mol}^{-1}$ | $-\Delta H/\text{kJ mol}^{-1}$ | $\nu(\text{I-I})/\text{cm}^{-1}$ | $\Delta\nu/\text{cm}^{-1}$ |
|--------------------------|-------|----------------------------------|--------------------------------|----------------------------------|----------------------------|
| [6]aneS | 5 | 827(26) | 47.2(0.1) | 156 | 17 |
| 1,4-[6]aneS ₂ | 2 | 40(1) | 31.8(0.1) | 164 | 19 |
| 1,3-[6]aneS ₂ | 2 | 94(3) | 32.3(0.3) | 162 | 20 |
| [6]aneS ₃ | 1 | 13(1) | 26.4(0.1) | 169 | 21 |
| [9]aneS ₃ | 2 | 169(4) | 35.0(0.1) | 162 | 22 |
| [12]aneS ₄ | 2 | 74(7) | 28.3(0.2) | 170 | b |
| [14]aneS ₄ | 2.5 | 151(4) | 32.2(0.1) | 162 | 21 |
| [16]aneS ₄ | 3 | 519(9) | 38.7(0.1) | 160 | 19 |
| [15]aneS ₅ | 2 | 94(1) | 29.8(0.1) | 168 | 22 |
| [18]aneS ₆ | 2 | 151(2) | 31.6(0.1) | 165 | 23 |

^a Number of methylene groups per sulfur atom. ^b Not reported since the low solubility of the adduct prevented the same precision as that for the other compounds.

Experimental

Spectrophotometric measurements were carried out using a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. Diiodine was purified by sublimation from KI and stored in a desiccator. A typical preparation consisted of mixing solutions of I_2 and the appropriate macrocycle in HPLC-grade CH_2Cl_2 affording about 15 cm^3 of a dark brown mixture. Slow evaporation at room temperature over a few weeks afforded products on the glass walls and the bottom of the reaction vessel. The products appeared in bands which could be distinguished by colour and morphology. It should be noted that most of these deposits were thin films covering the glass walls. Crystalline material suitable for single-crystal X-ray diffraction studies could in general only be recovered from near the bottom of the reaction vessel. The crystallisation products were collected and initially characterised by microanalysis. Larger deviations between observed and calculated values are commonly found for compounds with high diiodine contents, where loss of I_2 was apparent (Found: C, 11.25; H, 1.8. Calc. for $\text{C}_{12}\text{H}_{24}\text{I}_8\text{S}_6$ **1**: C, 10.5; H, 1.75. Found: C, 19.4; H, 3.3. Calc. for $\text{C}_8\text{H}_{16}\text{I}_2\text{S}_4$ **2b**: C, 19.45; H, 3.25. Found: C, 23.0; H, 3.95. Calc. for $\text{C}_{10}\text{H}_{20}\text{I}_2\text{S}_4$ **3**: C, 23.0; H, 3.85. Found: C, 13.05; H, 2.2. Calc. for $\text{C}_{12}\text{H}_{20}\text{I}_8\text{S}_4$ **6**: C, 11.0; H, 1.85%).

The relatively weak nature of the charge-transfer interaction in these compounds is reflected in mass spectral measurements which do not show molecular ion peaks for the adducts themselves but peaks assigned to I_2 and free macrocycle.

Crystallography

The following procedure is typical. A single crystal suitable for X-ray diffraction studies was mounted in the cold dinitrogen stream of an Oxford Cryosystems low-temperature device²⁴ on a Stoë Stadi-4 four-circle diffractometer [graphite-monochromated Mo-K α X-radiation ($\lambda = 0.71073 \text{ \AA}$); data acquisition by ω -2 θ scan mode]. Other details of crystal data, data collection and processing and structure analysis are given in Table 10. The single-crystal structures of compounds **1**, **2b** and **6** were solved by direct methods using SHELXS 86.²⁵ A Patterson synthesis revealed the positions of the I atoms in the structures of **4** and **5** using SHELXS 86²⁵ and in **3** using SHELX 76.²⁶ The structures were developed by iterative cycles of least-squares refinement and ΔF synthesis. Excessive residual electron density in close proximity to I atoms at isotropic convergence warranted a further empirical absorption correction (DIFABS²⁷) in the case of compounds **1**, **3** and **5**. All non-hydrogen atoms were refined anisotropically, except in the structure of **2b** where the minor components of the C atom disorder were allowed only thermal isotropic motion. Hydrogen atoms were included in calculated positions riding on the parent C atom. Their thermal parameters were either refined to a common U_{eq} (0.0236, 0.0312, 0.0342 and 0.0497 \AA^2 in

compounds **1**, **2b**, **3** and **6** respectively) or assigned 1.2 times the isotropic U_{eq} value of the parent C atom (in **4** and **5**). In Figs. 1, 3, 5, 7, 9 and 11 displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by small spheres of arbitrary radii. Illustrations were generated using SHELXTL-PC,²⁸ and molecular geometry calculations utilised CALC,²⁹ SHELXTL-PC and SHELXL 93.³⁰

The S(7)C(8)C(9)S(10) region in [12]aneS₄· I_2 **2b** was affected by disorder which was successfully modelled by allowing alternative positions for C(8) and C(9) with site occupancy factors of 0.75 and 0.25. All C–C and C–S distances in this region were restrained to 1.52 and 1.82 \AA respectively and the minor components C(8') and C(9') were refined isotropically.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/325.

Solution studies

Two solutions of I_2 ($0.993 \text{ mmol dm}^{-3}$) and [9]aneS₃ ($0.993 \text{ mmol dm}^{-3}$) in CH_2Cl_2 were made up and the absorbance of 11 mixtures ranging from 0:10 to 10:0 ratio were measured at $\lambda_{\text{max}} = 308 \pm 3 \text{ nm}$ in 0.3 mm cuvettes using a Perkin-Elmer Lambda 9 spectrophotometer. A plot of the measured absorbances against the I_2 :[9]aneS₃ ratio gave a curve with a maximum of 0.98:1.02 I_2 :[9]aneS₃ determined by the intersection of two linear regression tangents on either side of the curve. The 11 spectra recorded showed an isosbestic point at 480 nm.

Spectrophotometric measurements and data treatment. The spectrophotometric measurements for the determination of formation constants were carried out in CH_2Cl_2 solutions by using a Varian Cary 5 spectrophotometer having a temperature-controller accessory and connected to an IBM PS2 computer. The spectra of 12 different solutions were recorded in the range 250–600 nm at temperatures 15, 20, 25, 30 and 35 °C. The concentrations of the reagents were chosen according to criteria outlined in ref. 31 and discussed in previous papers.^{21,22} In all the solutions the macrocycle concentrations were always higher than that of I_2 in order to avoid or at least minimise the formation of higher adducts. The sets of data for all thioether-diiodine solutions were analysed using a factor-analysis program³² to determine the number of species present in solution. In all cases the presence of only two species, namely I_2 and the 1:1 L: I_2 adduct, has been confirmed. Data analysis was carried out with a program based on a non-linear least-squares method,³³ assuming that the best values of K and ϵ are those which minimise the sum of the function $\chi^2 = \sum (A_c - A_s)^2 / (N - 2)$, where A_c and A_s are the calculated and experimental absorbances and N is the number of data points. The optimis-

Table 10 Experimental data for single-crystal structure determinations of [2]janeS₃-4I₂ **1**, [12]janeS₄-I₂ **3**, [14]janeS₄-I₂ **3**, [14]janeS₄-2I₂ **4**, [16]janeS₄-I₂ **5** and [16]janeS₄-4I₂ **6**

| Compound | 1 | 2b | 3 | 4 | 5 | 6 |
|---|---|--|---|---|---|---|
| Formula | C ₁₂ H ₂₄ I ₈ S ₆ | C ₈ H ₁₆ I ₂ S ₄ | C ₁₀ H ₂₀ I ₂ S ₄ | C ₁₀ H ₂₀ I ₄ S ₄ | C ₁₂ H ₂₄ I ₂ S ₄ | C ₁₂ H ₂₄ I ₈ S ₄ |
| M | 1375.88 | 494.25 | 522.31 | 776.10 | 550.39 | 1311.76 |
| Crystal size/mm | 0.70 × 0.08 × 0.04 | 0.35 × 0.33 × 0.12 | 0.30 × 0.25 × 0.05 | 0.62 × 0.62 × 0.54 | 0.31 × 0.15 × 0.04 | 0.25 × 0.20 × 0.10 |
| Crystal system | Triclinic | Monoclinic | Orthorhombic | Monoclinic | Triclinic | Monoclinic |
| Space group | P $\bar{1}$ (no. 2) | P2 ₁ /c (no. 14) | Pbca (no. 61) | P2 ₁ /a (alt. P2 ₁ /c no. 14) | P $\bar{1}$ (no. 2) | C2/c (no. 15) |
| a/Å | 8.437(7) | 13.882(4) | 19.445(2) | 9.362(3) | 5.420(14) | 21.236(8) |
| b/Å | 13.82(2) | 8.550(3) | 17.509(2) | 9.295(3) | 8.05(4) | 11.693(6) |
| c/Å | 14.752(10) | 19.563(6) | 9.7030(11) | 23.016(9) | 10.74(3) | 14.771(6) |
| a/° | 65.95(5) | 109.44(3) | | 92.38(7) | 97.4(3) | |
| β/° | 89.31(4) | | | 95.1(2) | 95.1(2) | 123.710 (14) |
| γ/° | 81.08(4) | | | 94.9(3) | 94.9(3) | |
| U/Å ³ | 1549 | 2190 | 3304 | 2001 | 461 | 3051 |
| Z | 2 | 6 | 8 | 4 | 1 | 4 |
| D _c /g cm ⁻³ | 2.949 | 2.249 | 2.100 | 2.576 | 1.984 | 2.855 |
| μ/mm ⁻¹ | 8.32 | 4.78 | 4.23 | 6.63 | 3.80 | 8.32 |
| F(000) | 1232 | 1404 | 2000 | 1424 | 266 | 2336 |
| 2θ _{max} /° | 40 | 45 | 45 | 50 | 45 | 45 |
| hkl Ranges | -8 to 8, -11 to 13, 0-14 | -14 to 14, 0-9, 0-21 | 0-20, 0-18, 0-10 | -11 to 11, 0-11, 0-27 | -5 to 5, -8 to 8, 0-11 | -22 to 15, -12 to 0, -15 to 15 |
| Measured reflections | 2897 | 3097 | 3200 | 3695 | 1204 | 2105 |
| Independent reflections, R _{int} | 2897, — | 2743, — | 1930, 0.014 | 3443, 0.0654 | 1204, — | 1827, — |
| Observed reflections | 2405 [F ≥ 4σ(F)] | 2589 [F ≥ 4σ(F)] | 1462 [F ≥ 4σ(F)] | 3370 [F ≥ 2σ(F)] | 1053 [F ≥ 2σ(F)] | 1712 [F ≥ 4σ(F)] |
| Maximum, minimum ψ-scan correction | 0.891, 0.269 | 0.411, 0.238 | 0.398, 0.198 | 0.023, 0.007 | 0.337, 0.219 | 0.906, 0.557 |
| Full-matrix least squares on using | F | F | F | F ² | F ² | F |
| Maximum, minimum DIFABS correction | SHELX 76 | SHELX 76 | SHELX 76 | SHELXL 93 | SHELXL 93 | SHELX 76 |
| Parameters refined | 1.390, 0.643 | — | 1.245, 0.811 | — | 1.236, 0.667 | — |
| SHELX 76 ^a R, R', S | 177 | 201 | 147 | 163 | 82 | 112 |
| x | 0.057, 0.073, 0.85 | 0.037, 0.056, 1.01 | 0.037, 0.041, 0.99 | — | — | 0.027, 0.032, 1.12 |
| SHELXL 93 ^b R1, wR2, S | 0.000 961 | 0.000 363 | 0.000 206 | — | — | 0.000 48 |
| A, B | — | — | — | 0.077, 0.212, 1.11 | 0.073, 0.199, 1.09 | — |
| (Δ/σ) _{max} | 0.001 | 0.001 | 0.032 | 0.085, 43.89 | 0.1647, 1.14 | — |
| Δρ _{max, min} /e Å ⁻³ | +2.23, -1.86 | +1.24, -1.37 | +0.84, -0.77 | +2.20, -1.93 | +2.93, -1.96 | +1.63, -1.30 |

^a Weighting scheme $w^{-1} = \sigma^2(F) + xF^2$, S (goodness of fit) = $[\sum w(F_o) - |F_c|]^2 / (N_o - N_p)$; ^b Weighting scheme $w^{-1} = [\sigma^2(F_o) + (AP)^2 + BP]$ where $P = [\max(F_o, 0) + 2F_c^2]/3$, $S = [\sum w(F_o^2 - F_c^2)/(n - p)]^{1/2}$.

ation of K was carried out at six different wavelengths. For some compounds the calculated K and ε values were correlated with an observed decrease in ε with increase in temperature. The value of ΔH were therefore calculated by averaging the slopes of the six straight lines obtained by plotting $\ln(K\varepsilon)$ versus $1/T$ at six different wavelengths; $\Delta H = (\sum \Delta H/\sigma) / \sum 1/\sigma$, $\sigma = \{(N-1)\sum \sigma_i^2 / [Nn(Nn-1)]\}^{1/2}$, where N and n are the numbers of the different temperatures and wavelengths respectively. This procedure provides more reliable values of ΔH than those obtainable by using a van't Hoff plot. In addition to the factor analysis,³² a new set of electronic spectra for 1,4-dithiacyclohexane were recorded. Fifteen solutions having a constant concentration of 1,4-dithiacyclohexane (3.999×10^{-3} mol dm⁻³) and increasing amounts of I₂ (I₂: donor molar ratio ranging from 0.1 to 30:1) were analysed with the SUPERSPEC program,²⁰ giving convergence of unique values for K and ε confirming the formation of the 1:1 adduct only.

Fourier-transform Raman spectra. The Fourier-transform Raman spectra were recorded on an FRA 106 FT Raman accessory mounted on a Bruker IFS 66 FT-IR vacuum instrument, operating with an excitation frequency of 1064 nm (Nd-YAG laser). No sample decomposition was observed during the experiments. The solutions used contained 0.8:1.0 molar ratios of diiodine:macrocycle, $[I_2] = 2.6 \times 10^{-2}$ mol dm⁻³.

Acknowledgements

We thank the EPSRC for support and the Comitato Nazionale per le Scienze Chimiche of Consiglio Nazionale delle Ricerche (Rome) for financial support.

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Received 5th August 1996; Paper 6/05476E