

Table 11. Selected values of chemically equivalent bond distances (Å), angles and absolute value of torsion angles (°) in compounds (I)–(VII)

E.s.d.'s of single values are in parentheses; if the reported value is a mean, the number in parentheses is the larger of the r.m.s. and the mean e.s.d.'s.

	(I) ^a	(II) ^a	(III) ^a	(IV) ^a
S1—C5	1.715 (2)	1.708 (2)	1.728 (3)	1.728 (2)
C4—C5	1.371 (3)	1.369 (3)	1.366 (3)	1.364 (2)
C5—C6	1.441 (3)	1.448 (3)	1.450 (2)	1.463 (2)
S1—C5—C4	111.9 (2)	112.6 (2)	110.6 (1)	110.9 (3)
S1—C5—C6	138.9 (2)	138.4 (2)	120.6 (4)	119.5 (5)
C4—C5—C6	109.1 (2)	108.8 (2)	128.7 (4)	129.8 (8)
S1—C5—C6—S7	4.3 (10)	2.6 (5)	9.7 (20)	109.6 (1)
	(V) ^a	(VI) ^b	(VII) ^b	
S1—C5	1.728 (2)	1.734 (4)	1.733 (4)	
C4—C5	1.366 (3)	1.363 (4)	1.365 (6)	
C5—C6	1.468 (2)	1.467 (3)	1.461 (5)	
S1—C5—C4	111.2 (1)	111.0 (2)	110.7 (3)	
S1—C5—C6	119.0 (2)	119.1 (2)	120.3 (3)	
C4—C5—C6	129.7 (2)	129.9 (2)	129.0 (3)	
S1—C5—C6—S7	56.8 (2)	45.1 (3)	61.1 (6)	

Notes: (a) This work. (b) Zimmer *et al.* (1993).

Data collection: *SDP* (Frenz, 1983). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *MULTAN* (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

We thank Servizio Italiano di Diffusione Dati Cristallografici del CNR (Parma) for access to the Cambridge Data Files.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Preparation and Structural Characterization of the Charge-Transfer Complex (12[ane]S₄.I₂)_∞ (12[ane]S₄ = 1,4,7,10-Tetrathiacyclododecane)

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Abstract

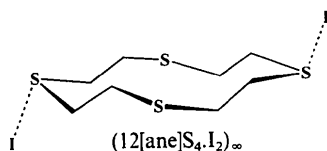
The X-ray crystal structure of the new addition compound (12[ane]S₄.I₂)_∞, C₈H₁₆S₄.I₂, is reported. The I₂ moieties bridge symmetrically between thioether groups; the I—I and S··I bond lengths of 2.736(1) and 3.220(3) Å, respectively, indicate relatively weak charge transfer. The nature of the interaction has been probed by semi-empirical molecular-orbital calculations using the PM3 method.

Comment

The interaction of thioethers with diiodine constitutes a textbook example of charge-transfer (CT) complexation (Downs & Adams, 1973); the nature of the S··I₂ interaction was first characterized in the 1960s by X-ray structural analyses of (PhCH₂)₂S.I₂ (Rømming, 1960) and 6[ane]S₂.(I₂)₂ (Chao & McCullough, 1960) (6[ane]S₂ = 1,4-dithiane), and other examples of such complexes have appeared from time to time (Herbstein *et al.*, 1986; Tipton, Lonergan, Stern & Shriver, 1992). Very recently, interest in this area has been rekindled by the structural characterization of complexes of diiodine with the macrocyclic thioether 1,4,7-trithiacyclononane, *viz.* (9[ane]S₃)₂.(I₂)₄ (Blake, Gould, Radek & Schröder, 1993) and 9[ane]S₃.(I₂)₃ (Cristiani *et al.*, 1993).

In this paper we describe the preparation and X-ray crystal structure of a complex of a larger macrocycle, (12[ane]S₄.I₂)_∞ (12[ane]S₄ = 1,4,7,10-tetrathiacyclododecane). This complex differs from previous examples in that the diiodine bridges symmetrically between two macrocycles in an unusually weak CT interaction. In order to probe the differences in electronic structures in going from terminal R₂S··I—I to bridging R₂S··I—I··SR₂, we have carried out semi-empirical molecular-orbital calculations on Me₂S.I₂ and

$(Me_2S)_2 \cdot I_2$ using the recently developed PM3 method (Stewart, 1989).



Addition of a purple solution of diiodine in dichloromethane to a solution of 12[ane] S_4 in the same solvent, in 1:1 stoichiometry, immediately gave a dark-brown solution with a characteristic CT band at 305 nm. Upon standing, $(12[ane]S_4 \cdot I_2)_\infty$ precipitated out as a crystalline brown solid. The IR spectrum of $(12[ane]S_4 \cdot I_2)_\infty$ is much the same as that of free 12[ane] S_4 , showing only minor differences in the positions and intensities of some bands.

The molecular structure of 12[ane] $S_4 \cdot I_2$ is shown with the atom-numbering scheme in Fig. 1. The crystal structure of $(12[ane]S_4 \cdot I_2)_\infty$ is comprised of infinite chains in which the diiodine molecules connect the crown thioether moieties such that there is inversion symmetry about the I—I bond (Fig. 2). The 12[ane] S_4 rings also lie about centres of symmetry but are disordered with each of the bridging S—C—C—S groups taking up one of two possible orientations.

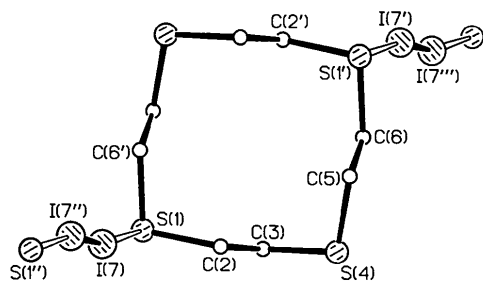


Fig. 1. View of the 12[ane] S_4 molecule and adjoining I_2 molecules in crystals of $(12[ane]S_4 \cdot I_2)_\infty$. The major conformation of the thioether ring is shown, with the atom-labelling scheme.

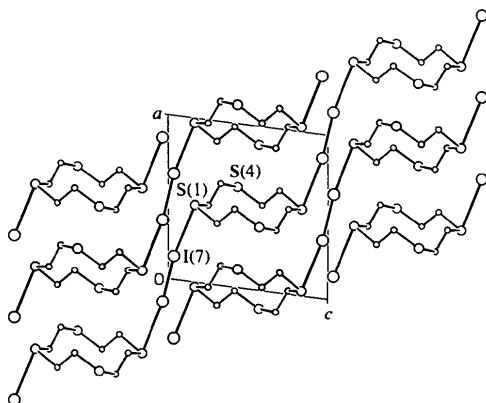


Fig. 2. Extended structure of the CT complex $(12[ane]S_4 \cdot I_2)_\infty$.

The predominant form has approximately C_{2h} ($2/m$) symmetry (Figs. 1 and 3a) but there are significant numbers of molecules with different conformations and symmetries when one or more of the ethylene groups takes the alternative orientation (*e.g.* Fig. 3b). Free 12[ane] S_4 has approximately D_4 (422) symmetry (Fig. 3c), a minor conformation in the crystals of the diiodine CT complex.

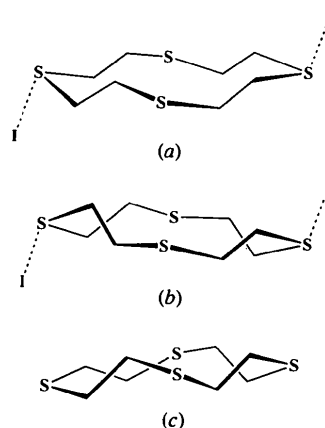


Fig. 3. Schematic diagrams of the conformations of (a) the major and (b) one of the minor conformers found in $(12[ane]S_4 \cdot I_2)_\infty$, and of free 12[ane] S_4 (c).

To the best of our knowledge, the present complex is the first example of a thioether–diiodine CT complex containing symmetrical S—I—I—S bridges, although symmetrical O—Br—Br—O bridging has been demonstrated in $(1,4\text{-dioxane} \cdot Br_2)_\infty$ (Hassel & Hvostef, 1954). There are some notable differences between $(12[ane]S_4 \cdot I_2)_\infty$ and terminal thioether–diiodine complexes in which the diiodine is coordinated through one end only. For example, although the I—I bond length of 2.736 (1) Å for $(12[ane]S_4 \cdot I_2)_\infty$ is significantly greater than that of solid diiodine [2.715 (6) Å] (van Bolhuis, Koster & Migchelsen, 1967), it is shorter than the range observed for the terminal cases (2.77–2.82 Å). Conversely, the S—I distance of 3.220 (3) Å, though a good deal smaller than the sum of the van der Waals radii (4.0 Å), is larger than the range observed for the terminal complexes (2.76–2.90 Å). It may be noted that the asymmetric S...I—I...S bridge in $(9[ane]S_3)_2 \cdot (I_2)_4$ has bond lengths intermediate between those for the terminal complexes and $(12[ane]S_4 \cdot I_2)_\infty$.

We have investigated these differences by carrying out semi-empirical molecular-orbital calculations on $Me_2S \cdot I_2$ and $(Me_2S)_2 \cdot I_2$. It is well known that the principal interaction is between the thioether HOMO (the *p*-type non-bonding 'lone-pair' orbital) and the diiodine LUMO (*i.e.* the σ_u^* antibonding orbital), with a consequent weakening of the I—I bond. There may also be a secondary interaction between the two occupied antibonding π_g^* orbitals of the diiodine and the unoccupied

σ C—S antibonding orbitals and/or sulfur d orbitals. In practice, the results of the calculations were rather more complicated than this idealized picture, with extensive mixing of the Me_2S and I_2 valence orbitals. Nevertheless, for both $\text{Me}_2\text{S}\cdot\text{I}_2$ and $(\text{Me}_2\text{S})_2\cdot\text{I}_2$ the primary bonding interaction is between the thioether HOMO and diiodine LUMO, as expected. The results of the calculations are summarized in Table 3.

The most obvious difference between the two complexes is in the polarization of the diiodine moiety in $\text{Me}_2\text{S}\cdot\text{I}_2$, viz. $\text{Me}_2\text{S}^{\delta+}\cdots\text{I}^{\delta-}$. Obviously, this is ruled out for the symmetrical $(\text{Me}_2\text{S})_2\cdot\text{I}_2$, where both I atoms carry equal negative charge. Notwithstanding this, the effects at diiodine are predicted to be quite similar. While the single S atom in $\text{Me}_2\text{S}\cdot\text{I}_2$ supplies 0.2 electrons to diiodine, the two S atoms in $(\text{Me}_2\text{S})_2\cdot\text{I}_2$ each supply about half this amount. The S—I bond order in $\text{Me}_2\text{S}\cdot\text{I}_2$ is consequently twice that in $(\text{Me}_2\text{S})_2\cdot\text{I}_2$, and the associated increase in the S—I distance is consistent with the observed pattern discussed above.

There is poorer agreement, however, between the observed and calculated trends in I—I distances; in both cases, the calculations predict an I—I bond order of *ca* 0.75, with very similar I—I separations for $\text{Me}_2\text{S}\cdot\text{I}_2$ and $(\text{Me}_2\text{S})_2\cdot\text{I}_2$, in contrast to the foregoing crystallographic results. It remains to be seen whether this discrepancy is due to a deficiency in the calculations or whether it is a consequence of crystal packing effects; given the relatively weak nature of CT interactions the latter seems quite possible.

In both cases there appears to be very little back-donation from diiodine to the C—S σ^* antibonding orbitals, since the C—S bond orders are only slightly reduced compared with free Me_2S . This is consistent with the crystallographic results and supports the view that simple aliphatic thioethers are moderate σ -donors and weak π -acceptors (Kraatz, Jacobsen, Ziegler & Boorman, 1993).

Experimental

Crystal data

$\text{C}_8\text{H}_{16}\text{S}_4\cdot\text{I}_2$

$M_r = 494.3$

Monoclinic

$P2_1/a$

$a = 9.475(1) \text{ \AA}$

$b = 8.570(1) \text{ \AA}$

$c = 9.194(1) \text{ \AA}$

$\beta = 97.430(9)^\circ$

$V = 740.3 \text{ \AA}^3$

$Z = 2$

$D_x = 2.217 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 10\text{--}11^\circ$

$\mu = 4.72 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Small almost-square plate

$0.24 \times 0.21 \times 0.05 \text{ mm}$

Very dark brown

Crystal source: recrystallized from CH_2Cl_2

Data collection

Enraf-Nonius CAD-4 diffractometer

$R_{\text{int}} = 0.047$

$\theta_{\text{max}} = 22.5^\circ$

ω - θ scans

Absorption correction:

empirical

$T_{\text{min}} = 0.82$, $T_{\text{max}} = 1.00$

1119 measured reflections

961 independent reflections

750 observed reflections

$[I > 2\sigma(I)]$

$h = -10 \rightarrow 10$

$k = 0 \rightarrow 9$

$l = 0 \rightarrow 9$

2 standard reflections

frequency: 166 min

intensity decay: -14.8%

Refinement

Refinement on F

$R = 0.047$

$wR = 0.061$

$S = 0.66$

863 $[I > \sigma(I)]$ reflections

90 parameters

Only H-atom U 's refined

$w = 1/[\sigma^2(F) + 0.002F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.017$

$\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.07 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

U_{iso} for disordered C(2x), C(3x), C(5x), C(6x); for other atoms					
$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$					
	Occupancy	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
S(1)	1.0	0.4705 (3)	0.0832 (3)	0.1645 (3)	0.059 (1)
C(2)	0.85 (3)	0.4799 (13)	-0.1141 (14)	0.2498 (15)	0.053 (5)
C(3)	0.85 (3)	0.6200 (13)	-0.1559 (17)	0.3271 (14)	0.063 (5)
C(2x)	0.15 (3)	0.587 (5)	-0.035 (6)	0.266 (5)	0.019 (16)
C(3x)	0.15 (3)	0.498 (5)	-0.199 (6)	0.324 (6)	0.018 (16)
S(4)	1.0	0.6128 (3)	-0.3310 (3)	0.4319 (3)	0.056 (1)
C(5)	0.65 (3)	0.5221 (16)	-0.268 (2)	0.5863 (19)	0.058 (7)
C(6)	0.65 (3)	0.6240 (18)	-0.189 (2)	0.696 (2)	0.060 (7)
C(5x)	0.35 (3)	0.644 (3)	-0.220 (3)	0.614 (3)	0.029 (8)
C(6x)	0.35 (3)	0.494 (3)	-0.201 (3)	0.673 (3)	0.032 (9)
I(7)	1.0	0.14402 (8)	0.01665 (9)	0.03457 (8)	0.0654 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

In the 12[ane] S_4 molecule

S(1)—C(2)	1.861 (13)	S(1)—C(2x)	1.69 (5)
C(2)—C(3)	1.467 (18)	C(2x)—C(3x)	1.75 (7)
C(3)—S(4)	1.789 (14)	C(3x)—S(4)	1.78 (6)
S(4)—C(5)	1.833 (18)	S(4)—C(5x)	1.91 (3)
C(5)—C(6)	1.47 (3)	C(5x)—C(6x)	1.60 (4)
C(6)—S(1 ¹)	1.887 (19)	C(6x)—S(1 ¹)	1.80 (3)
S(1)—C(2)—C(3)	114.6 (9)	C(2x)—C(3x)—S(4)	113 (3)
C(2)—C(3)—S(4)	111.8 (9)	C(3x)—S(4)—C(5x)	100.7 (16)
C(3)—S(4)—C(5)	103.0 (7)	S(4)—C(5x)—C(6x)	108.0 (17)
S(4)—C(5)—C(6)	109.6 (12)	C(5x)—C(6x)—S(1 ¹)	105.2 (18)
C(5)—C(6)—S(1 ¹)	111.1 (12)	C(6x ¹)—S(1)—C(2x)	80.7 (18)
C(6 ¹)—S(1)—C(2)	98.6 (7)	C(3)—S(4)—C(5x)	92.4 (9)
C(6 ¹)—S(1)—C(2x)	104.3 (17)	C(3x)—S(4)—C(5)	86.1 (16)
C(6x ¹)—S(1)—C(2)	99.6 (9)		
S(1)—C(2x)—C(3x)	110 (3)		

Torsion angles in the 12[ane] S_4 ring

S(1)—C(2)—C(3)—S(4)	169.9 (6)
C(2)—C(3)—S(4)—C(5)	-73.0 (11)
C(3)—S(4)—C(5)—C(6)	-79.9 (13)
S(4)—C(5)—C(6)—S(1 ¹)	167.4 (9)
C(5)—C(6)—S(1 ¹)—C(2 ¹)	-95.3 (13)
C(6 ¹)—S(1)—C(2)—C(3)	-103.1 (11)
S(1)—C(2x)—C(3x)—S(4)	-180.0 (25)
C(2)—C(3)—S(4)—C(5x)	-109.7 (12)
C(2x)—C(3x)—S(4)—C(5)	110 (3)
C(2x)—C(3x)—S(4)—C(5x)	75 (3)
C(3)—S(4)—C(5x)—C(6x)	101.1 (17)
C(3x)—S(4)—C(5)—C(6)	-115.9 (20)
C(3x)—S(4)—C(5x)—C(6x)	62.1 (24)

S(4)—C(5x)—C(6x)—S(1 ⁱ)	-175.5 (12)
C(5)—C(6x)—S(1 ⁱ)—C(2x ⁱ)	-55.3 (21)
C(5x)—C(6)—S(1 ⁱ)—C(2 ⁱ)	84.1 (16)
C(5x)—C(6x)—S(1 ⁱ)—C(2x ⁱ)	119.0 (23)
C(6 ⁱ)—S(1)—C(2x)—C(3x)	78 (3)
C(6x ⁱ)—S(1)—C(2)—C(3)	-63.7 (13)
C(6x ⁱ)—S(1)—C(2x)—C(3x)	109 (3)

In the iodine molecule

I(7)—I(7ⁱⁱ) 2.736 (1)

Between the molecules

S(1)—I(7) 3.220 (3)

S(1)—I(7)—I(7ⁱⁱ) 170.5 (1) C(2x)—S(1)—I(7) 128.8 (16)C(2)—S(1)—I(7) 89.2 (4) C(6xⁱ)—S(1)—I(7) 118.5 (8)C(6ⁱ)—S(1)—I(7) 79.6 (6)

Symmetry codes: (i) 1 - x, -y, 1 - z; (ii) -x, -y, -z.

Table 3. Calculated bonding parameters for Me₂S, I₂ and their CT complexes

	Bond orders			Net electron transfer (e)	Bond lengths (Å)		
	I—I	S—I	C—S		I—I	S—I	C—S
I ₂	1.00	—	—	—	2.668	—	—
Me ₂ S	—	—	1.00	—	—	—	1.801
Me ₂ S·I ₂	0.76	0.23	0.98	0.20	2.690	2.707	1.810
(Me ₂ S) ₂ ·I ₂	0.74	0.12	0.99	0.25	2.696	2.767	1.808

The ethylene bridges are disordered, each in two possible orientations. In the final cycles of refinement, the C atoms of the more populated arrangements were refined anisotropically, those of the minor sites isotropically. For the major ethylene groups, H atoms were included in calculated positions but with freely refined U_{iso} 's. The site occupancy factors of the disordered groups were refined, in one bridge to 0.85/0.15 (3) and in the other bridge to 0.65/0.35 (3).

The structure was determined by a combination of heavy-atom, direct and trial-and-error methods with the *SHELX76* (Sheldrick, 1976) and *SHELXS86* (Sheldrick, 1985) programs. Refinement was by full-matrix least-squares methods in *SHELX76*.

Computer programs, noted above and by Anderson, Richards & Hughes (1986) were run on a MicroVAXII computer.

We thank the SERC for a CASE award to SDH.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Highly Substituted Methylenecyclopropanes

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Abstract

The relative stereochemistries of the two title compounds, (*R*,R**)- α -(1-methoxy-2-methylenecyclopropyl)-cyclohexanemethanol (*2b*), C₁₂H₂₀O₂, and (*R*,R**)- α -(1-methyl-2-methylenecyclopropyl)cyclohexanemethanol (*3a*), C₁₂H₂₀O, have been established. Each structure has a different mode of hydrogen bonding; compound (*2b*) forms infinite chains [O··O 2.862 (3) Å], while compound (*3a*) forms centrosymmetric tetramers [O··O 2.782 (4) and 2.835 (4) Å].

Comment

Methylenecyclopropanes are among the most highly strained carbocyclic molecules (Greenberg & Liebman, 1978) and have attracted attention from the synthetic (Ohta & Takaya, 1991), mechanistic (Dewar & Wasson, 1971) and biological perspectives (Baldwin & Widdison, 1992). We have recently reported a novel highly regioselective cyclopropanation of α -allenic alcohols (1) using samarium/dihalomethane to provide a variety of methylene- and alkylidenecyclopropane carbinols [compounds (2) and (3)] in good yields (Lautens & Delanghe, 1993, 1994). The diastereoselectivity varies from 1:1 to 50:1 and depends on the substituents on the carbinol side chain (*R* group) and on the substitution of the allene (*R'* group).