

Dispiro[adamantane-2,2'-1',3',6',9',-11',14'-hexathiacyclohexadecane-10',2''-adamantane]

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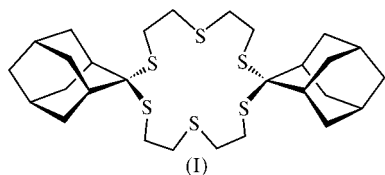
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The conformational features of the title compound, $C_{28}H_{44}S_6$, are compared with previously reported analogous macrocycles. The type of substituent affects considerably the conformation of the macrocycle. A 1H NMR titration of the title compound with $AgBF_4$ indicated the formation of the 1:1 complex, which was not crystallized.

Comment

Macrocyclic thioethers have been a topic of interest because of their moderately low σ -donating and π -accepting properties. They also possess increased thermodynamic stability over open-chain analogues as a result of the macrocyclic effect (Blake & Schroeder, 1990). These crown-like molecules have been extensively used as chelators for specific metal ions and phase-transfer catalysts. Recently, a series of cage-annulated sulfur-containing crown ethers and cryptands were synthesized and their complexation properties evaluated (Williams *et al.*, 2002). As a possible specific metal host system, we have designed and prepared an adamantylidene-derived thioether, (I) (Mlinarić-Majerski *et al.*, 2002). The C—C bonds inside the 16-membered macrocycle [range 1.490 (13)–1.520 (15) Å] are considerably shorter than expected for Csp^3 — Csp^3 linkages (Allen *et al.*, 1987; Allen, 2002). This phenomenon has already been observed in numerous macrocyclic structures (Hill & Feller, 2000; Maverick *et al.*, 1980; Dunitz & Seiler, 1974).



Generally, the conformation of a macrocyclic thioether is determined by the torsion angles along the $[-S-CH_2-CH_2]-S-[CH_2-CH_2-S-]$ moieties designated as brackets according to De Groot & Loeb (1989). These brackets are formed because S—C bonds tend to adopt a *gauche* confor-

mation and C—C bonds tend to favour an *anti* conformation inside the bracket. The molecule of (I) consists of two brackets (S11—C12—C13—S14—C15—C16—S1 and S3—C4—C5—S6—C7—C8—S9) joined by two methylene bridges at atoms C2 and C10 in a spiro junction to the two adamantane moieties (Fig. 1). According to DeSimone & Glick (1976), the orientations of the S atoms in macrocyclic thioethers can be described as endo- or exodentate. In the structure of (I), atoms S6 and S14 are exodentate, whereas atoms S1, S3, S9 and S11 are endodentate. Four endocyclic C—C bonds (C4—C5, C7—C8, C12—C13 and C15—C16) strictly obey the above-quoted rule, with an *anti* conformation about four S—C—C—S units, resulting in the exodentate orientation of atoms S6 and S14. Four of the eight S—C bonds inside the brackets (involving bonds with the two central S atoms, *viz.* S6—C5, S6—C7,

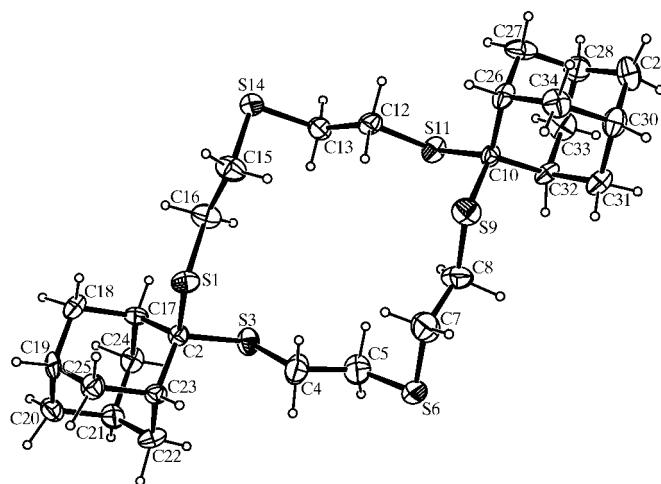


Figure 1
The molecular structure of (I), with displacement ellipsoids shown at the 50% probability level.

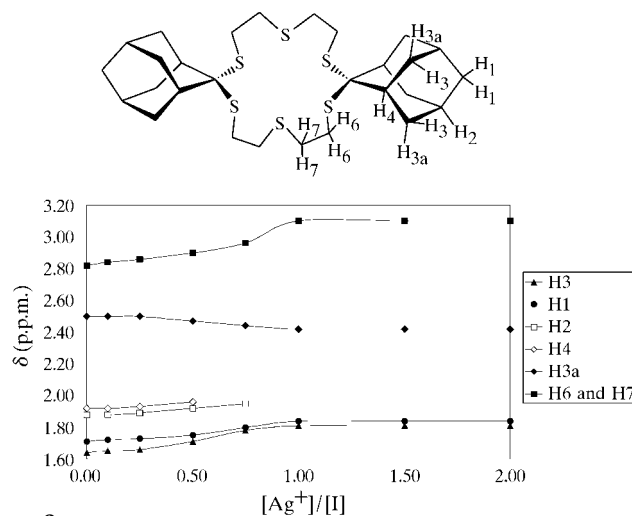


Figure 2
 1H NMR chemical shifts during the titration of (I) with $AgBF_4$. The chemical shifts of atoms H2 and H4 were only partially observable because of overlap with the CD_3CN signal. H atoms are labelled according to the chemical diagram.

S14—C13 and S14—C15) adopt the *gauche* conformation. The remaining four S—C bonds (involving bonds with the side S atoms, *viz.* S1—C16, S3—C4, S9—C8 and S11—C12) adopt an *anti* conformation; these S atoms are endodentate. The conformations about the four S—C bonds involving two bridging methylene groups (C2—S1, C2—S3, C10—S11 and C10—S9) are all *gauche*. This arrangement generates a rectangular projection of the 16-macrocyclic ring having approximate D_2 symmetry (with S6, S14, C2 and C10 at the corners). The approximate D_2 symmetry is also valid for the complete molecule. The average length of the 'square' edge is 5.570 (15) Å and the lengths of the diagonals are 8.240 (12) (C2··C10) and 7.514 (11) Å (S6··S14). The opposite endodentate S atoms are separated by 6.449 (10) (S1··S9) and 6.257 (13) Å (S3··S11). Thus, the cavity of (I) might be suitable for complexation of Ag^+ or Cu^+ .

The presence of the adamantane cages at the 2- and 10-positions greatly affects the conformation of the [16]ane-S₆ macrocycle. In order to evaluate its structural characteristics and to analyze its conformation and complexation properties, an inspection of the Cambridge Structural Database (CSD; Version 5.23 of April 2002; Allen, 2002) was performed. This search revealed the structures of four 1,3,6,9,11,14-hexathiacyclohexadecane derivatives and two of their metal complexes with Cu^+ and Ag^+ . The structure of 7,10,13,20,23,26-hexathiadispiro[5.7.5.7]hexacosane (CSD refcode WEKXIT; Xianming *et al.*, 1994) is the only spiro derivative of 1,3,6,9,11,14-hexathiacyclohexadecane reported so far. The overall conformation of WEKXIT shows remarkable similarity with (I). WEKXIT also possesses two exodentate S atoms at the 'square' corners, and the *gauche-anti* arrangements are similar to those in (I). The C—C endocyclic linkages show discrepancies from the values expected for $\text{Csp}^3-\text{Csp}^3$ bond lengths that are even larger than the discrepancies seen in (I). In contrast to these two spiro derivatives, the structure of unsubstituted 1,3,6,9,11,14-hexathiacyclohexadecane (CSD refcode KAVYIP; De Groot & Loeb, 1989) has two crystallographically independent half molecules in the asymmetric unit, located around crystallographic inversion centres. Thus, the molecular symmetry is C_i in contrast to (I) and WEKXIT, where C_1 symmetry was observed. The conformational features of *trans*-2,10-diphenyl-1,3,6,9,11,14-hexathiacyclohexadecane (CSD refcode WEKWUE; Xianming *et al.*, 1994) are similar to the features of the unsubstituted KAVYIP but differ from the spiro derivatives WEKXIT and (I). The interatomic distances between the opposite endocyclic S atoms for the set of six 1,3,6,9,11,14-hexathiacyclohexadecane derivatives from the CSD and for (I) are given in Table 1. (Refcode KAVYIP has two independent halves in the asymmetric unit and hence two entries in Table 1.) Refcodes KAVYOV (De Groot & Loeb, 1989) and SOLHIK (De Groot & Loeb, 1991) correspond to the Cu^+ and Ag^+ complexes of KAVYIP, respectively. Four of the six S atoms are involved in the metal complexation in these structures, and the S··S distances are shorter than those in the ligand.

Complexation of a ligand with a metal ion causes ^1H NMR shifts (Ishikawa *et al.*, 1999). In order to prove the

complexation of (I) with Ag^+ , an NMR titration experiment was performed. Ligand (I) was dissolved in CDCl_3 and a solution of AgBF_4 in CD_3CN was added in molar amounts of 10, 25, 50, 75, 100, 150 and 200%, respectively. As depicted in Fig. 2, the NMR chemical shifts gradually changed until 100% of the molar amount of AgBF_4 was added, indicating the formation of the 1:1 complex. However, attempts to isolate and crystallize the complex were unsuccessful. In the ^1H NMR spectra of the $\text{Ag}^+[(\text{I})]$ complex, downfield shifts were observed for all H atoms except for the H3a atom (Fig. 2).

Experimental

Compound (I) was prepared according to the procedure reported by Mlinarić-Majerski *et al.* (2002). Suitable single crystals of (I) were obtained by slow evaporation from a mixture of dichloromethane and water in a 1:1 molar ratio.

Crystal data

$\text{C}_{28}\text{H}_{44}\text{S}_6$	Mo $K\alpha$ radiation
$M_r = 572.99$	Cell parameters from 28 reflections
Orthorhombic, $Pbca$	$\theta = 5.6-10.2^\circ$
$a = 15.154$ (4) Å	$\mu = 0.49 \text{ mm}^{-1}$
$b = 10.499$ (3) Å	$T = 293$ (2) K
$c = 36.743$ (8) Å	Prism, colourless
$V = 5846$ (3) Å ³	$0.36 \times 0.25 \times 0.18 \text{ mm}$
$Z = 8$	
$D_x = 1.302 \text{ Mg m}^{-3}$	

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.014$
Non-profiled $\omega/2\theta$ scans	$\theta_{\text{max}} = 26.3^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -18 \rightarrow 0$
$T_{\text{min}} = 0.765$, $T_{\text{max}} = 0.915$	$k = -13 \rightarrow 0$
5907 measured reflections	$l = 0 \rightarrow 45$
5907 independent reflections	3 standard reflections
1913 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 3%

Refinement

Refinement on F^2	H-atom parameters constrained
$R(F) = 0.063$	$w = 1/[\sigma^2(F_o^2) + (0.0826P)^2]$
$wR(F^2) = 0.204$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.92$	$(\Delta/\sigma)_{\text{max}} = 0.001$
5907 reflections	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
307 parameters	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$

Table 1

Interatomic distances (Å) for the opposite endocyclic S atoms in the set of 1,3,6,9,11,14-hexathiacyclohexadecane derivatives from the CSD (Allen, 2002) and in (I).

CSD refcode	S6··S14	S1··S9	S3··S11
(I)	7.51	6.45	6.26
KAVYIP	8.07	4.47	8.85
KAVYIP	6.75	4.85	8.20
KAVYOV	3.99	3.86	6.56
SOLHIK	4.26	4.39	6.69
WEKWUE	7.20	8.71	7.09
WEKXIT	7.17	6.72	6.76

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1053). Services for accessing these data are described at the back of the journal.

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