Acta Cryst. (1998). C**54**, 245–247

1,4,8,11-Tetrathiacyclotetradecan-6-one

Alexander J. Blake, Wan-Sheung Li, Liam R. Sutton and Martin Schröder

Department of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England. E-mail: a.j.blake@nottingham.ac.uk

(*Received 15 October 1997; accepted 21 November 1997*)

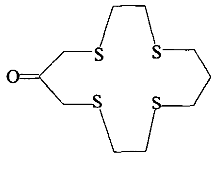
Abstract

Molecules of the title compound, $C_{10}H_{18}OS_4$, adopt the same [3434] conformation as the parent macrocycle 1,4,8,11-tetrathiacyclotetradecane, supporting our conjecture concerning the steric influence of the hydrazone H atoms in some related derivatives. The closest intermolecular contacts are C—H···O distances of 2.61–2.73 Å, which link molecules in linear chains.

Comment

Homoleptic thioether crown macrocycles have been the subject of a large body of work in the field of coordination chemistry by virtue of the propensity of such molecules to act as binding agents for late transition metal ions (Blake & Schröder, 1990; Cooper & Rawle, 1990). Because sulfur is divalent in these moieties, any peripheral alterations must occur on the carbon backbone. The most common method of achieving this is to incorporate functional groups during ring synthesis: these groups can then be transformed as required. Several examples of precursor functional groups have been incorporated into thioether crowns: ketones were introduced independently by the groups of Kellogg (Buter *et al.*, 1991) and Setzer (Setzer *et al.*, 1990). Our work in this field has concentrated on dihydroxy derivatives of thioether crowns and their subsequent functionalization to yield thermotropic mesogens and metallomesogens (Blake *et al.*, 1994, 1996).

Some of our recent work involves the functionalization of the title compound, 1,4,8,11-tetrathiacyclotetradecan-6-one (keto[14]aneS_4), with phenyl hydrazines to form hydrazones (Sutton *et al.*, 1998). One feature of these products is that the macrocyclic cores are highly distorted by comparison with the parent macrocycle 1,4,8,11-tetrathiacyclotetradecane ([14]aneS_4). We argued that the H atom of the hydrazone function was critical in causing these distortions as the ketone derivatives of other sulfur macrocycles (*e.g.* [13]aneS_4) were almost identical in ring conformation to their parent macrocycles (Buter *et al.*, 1991), so the role of sp^2 hybridization was negligible. In order to allow more precise arguments, we undertook a structure determination on keto[14]aneS_4 itself.



keto[14]aneS_4

This determination (Fig. 1) reveals normal bond lengths within the [14]aneS_4 core (Blake & Schröder, 1990) and a C=O distance of 1.205 (3) Å. Atoms C5, C6, O6 and C7 all lie within 0.002 (2) Å of their least-squares plane: this plane forms a dihedral angle of 95.05 (6)° with the S_4 mean plane. Overall, the molecule adopts (Table 1) the same [3434] conformation (Dale, 1973) as the parent macrocycle [14]aneS_4 (DeSimone & Glick, 1976), supporting our conjecture concerning the steric influence of the hydrazone H atoms. The atoms of the macrocyclic ring (*i.e.* all non-H atoms with the exception of O6) are related by a non-crystallographic inversion centre located at (0.755,0.680,0.257). Atoms C6, O6 and C13 define a non-crystallographic mirror plane (equation: $0.186x + 3.670y + 8.814z = 1.049$), which is markedly inclined to all three pairs of principal faces.

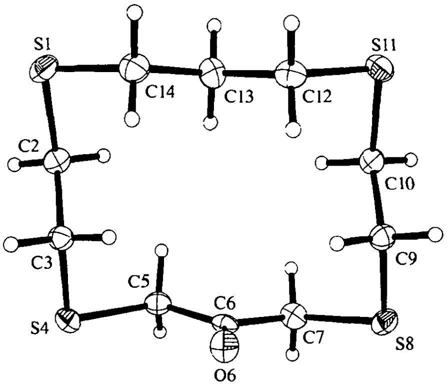


Fig. 1. A view of a molecule of the title compound with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii.

Molecules form stacks parallel to the *a* axis of the unit cell (Fig. 2): the shortest intermolecular contacts within these stacks are three C—H···O distances of 2.61–2.73 Å. The distribution of these contacts does not coincide with the molecular mirror plane in that $H7A^i$ lies 2.73 Å from O6, whereas the pseudo-related $H5B^i$ is only 2.61 Å away. More strikingly, the O6···$H10A^i$ contact of 2.66 Å is much shorter than the O6···$H2B^i$ distance of 3.07 Å [symmetry code: (i) $1 + x, y, z$].

Acta Crystallographica Section C
ISSN 0108-2701 © 1998

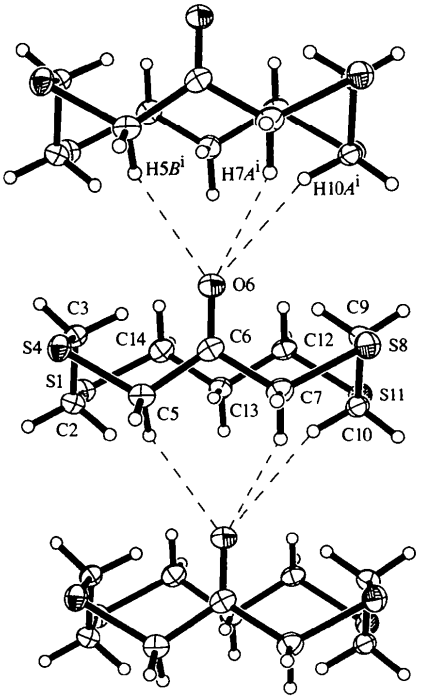


Fig. 2. Part of a chain of molecules running parallel to the *a* axis; O6···H5B^{i} 2.61, O6···H7A^{i} 2.73 and O6···H10A^{i} 2.66 Å. [Symmetry code: (i) $1+x, y, z$.]

Experimental

The title compound was synthesized according to literature methods (Buter *et al.*, 1991). A very large plate (8 × 8 × 0.34 mm) was obtained by slow evaporation from a $CHCl_3$ solution of the product, and a colourless block suitable for diffraction studies was cut from this plate and mounted in a film of RS3000 perfluoropolyether oil (Hoechst).

Crystal data

$C_{10}H_{18}OS_4$
$M_r = 282.48$
Monoclinic
$P2_1$
$a = 4.8789\,(10)$ Å
$b = 15.011\,(3)$ Å
$c = 9.2835\,(19)$ Å
$\beta = 99.46\,(3)^\circ$
$V = 670.7\,(2)$ Å^3
$Z = 2$
$D_x = 1.399$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 12.5$–16.6°
$\mu = 0.682$ mm^{-1}
$T = 150\,(2)$ K
Colourless
0.39 × 0.35 × 0.34 mm
Block

Data collection

Stoe Stadi-4 four-circle diffractometer with Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)
ω–θ scans
Absorption correction: none
3190 measured reflections
1227 independent reflections (1130 Friedel pairs)
1193 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\rm max} = 25.01^\circ$
$h = -5 \rightarrow 5$
$k = -17 \rightarrow 17$
$l = -11 \rightarrow 11$
3 standard reflections frequency: 60 min intensity variation: random ±4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.052$
$S = 1.111$
2357 reflections
137 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 0.22P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.13 (8)

Table 1. *Selected torsion angles (Å)*

C14—S1—C2—C3	58.14 (17)	C6—C7—S8—C9	−60.4 (2)
S1—C2—C3—S4	176.70 (11)	C7—S8—C9—C10	−62.37 (18)
C2—C3—S4—C5	69.20 (17)	S8—C9—C10—S11	−174.53 (11)
C3—S4—C5—C6	73.43 (19)	C9—C10—S11—C12	−63.53 (17)
S4—C5—C6—O6	−5.8 (3)	C10—S11—C12—C13	−66.8 (2)
S4—C5—C6—C7	174.53 (17)	S11—C12—C13—C14	−173.12 (17)
O6—C6—C7—S8	−11.2 (3)	C12—C13—C14—S1	−178.78 (17)
C5—C6—C7—S8	168.47 (16)	C2—S1—C14—C13	58.1 (2)

Each member of a Friedel pair was treated as an independent observation in the least-squares refinement. H atoms were introduced at geometrically calculated positions and thereafter constrained to ride on their parent C atoms with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$. The presence of four S atoms in the molecule was sufficient to allow reliable estimation of the Flack parameter. The s.u.'s on C—C distances do not exceed 0.003 Å.

Data collection: *STADI4* (Stoe & Cie, 1996*a*). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXL97*.

We thank EPSRC for support and Professor R. M. Kellogg for helpful discussion.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1526). Services for accessing these data are described at the back of the journal.

References

Blake, A. J., Bruce, D. W., Fallis, I. A., Parsons, S., Richtzenhain, H., Ross, S. A. & Schröder, M. (1996). *Philos. Trans. R. Soc. London Ser. A*, **354**, 395–414.

Blake, A. J., Bruce, D. W., Fallis, I. A., Parsons, S. & Schröder, M. (1994). *J. Chem. Soc. Chem. Commun.* pp. 2471–2473.

Blake, A. J. & Schröder, M. (1990). *Adv. Inorg. Chem.* **35**, 1–80.

Buter, J., Kellogg, R. M. & van Bolhuis, F. (1991). *J. Chem. Soc. Chem. Commun.* pp. 910–912.

Cooper, S. R. & Rawle, S. C. (1990). *Struct. Bonding (Berlin)*, **72**, 1–72.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Dale, J. (1973). *Acta Chem. Scand.* **27**, 1115–1129.

DeSimone, R. E. & Glick, M. D. (1976). *J. Am. Chem. Soc.* **98**, 762–767.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Setzer, W. N., Afshar, S., Burns, N. L., Ferrante, L. A., Hester, A. M., Meehan, E. J. Jr, Grant, G. J., Isaac, S. M., Laudemann, C. P., Lewis, C. M. & VanDerveer, D. G. (1990). *Heteroatom Chem.* **1**, 375–387.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1995). *SHELXTL/PC*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Stoe & Cie (1996*a*). *STADI4. Data Collection Program for Windows*. Version 1.06a. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1996*b*). *X-RED. Data Reduction Program for Windows*. Version 1.08. Stoe & Cie, Darmstadt, Germany.
Sutton, L. R., Blake, A. J., Li, W.-S. & Schröder, M. (1998). *J. Chem. Soc. Dalton Trans.* In the press.

Acta Cryst. (1998). C**54**, 247–249

2′-Hydroxy-3′-methoxy-5′-flavonesulfonic Acid Trihydrate: a New Zwitterion

Jean-Claude Wallet,[a] Amar Habsaoui,[a] Emile M. Gaydou,[a] Elies Molins[b] and Carlos Miravitlles[b]

[a]*Laboratoire de Phytochimie, Case 412, Faculté des Sciences et Techniques de Saint-Jérome, 13397 Marseille CEDEX 20, France, and* [b]*Institut de Ciéncia de Materials de Barcelona, CSIC, Campus Universitat de Bellaterra, 08193 Cerdanyola, Spain. E-mail: jean-claude.wallet@iut-chimie.u-3mrs.fr*

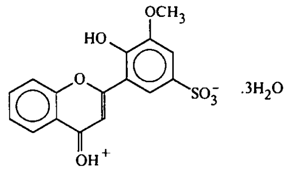
(Received 28 April 1997; accepted 21 October 1997)

Abstract

The title compound, $C_{16}H_{12}O_7S.3H_2O$, displays an anionic part, the deprotonated sulfonic acid group, and a cationic part, the protonated carbonyl group, indicative of a zwitterionic structure. These two parts in different molecules are linked by hydrogen bonding involving three water molecules.

Comment

Amino acids are well known zwitterions. Substitution of a carboxylic acid group by a sulfonic acid group gives another type of zwitterion, for example, in sulfanilic acid. Substitution of an amino group by a carbonyl group also gives zwitterions, provided that the carbonyl group is basic enough. This is the case for 2′,6′-dimethoxyflavone which can accept Brønsted (Wallet, Gaydou & Baldy, 1989; Tinant, Declercq, Wallet, Gaydou & Baldy, 1991; Wallet, Cody, Wojtczak & Blessing, 1993; Wallet, Cody & Wojtczak, 1994) as well as Lewis acids (Maniukiewicz, Molins, Miravitlles, Wallet & Gaydou, 1996). In the title compound, (I), similar S—O lengths [1.441 (2), 1.443 (2) and 1.445 (2) Å] and O—S—O bond angles [111.92 (10), 112.91 (11) and 112.96 (11)°] clearly show the deprotonation of the sulfonic acid group. An H atom (H4) was located near the carbonyl O atom as the highest peak in a difference Fourier map. To assure this assignment, its isotropic displacement was refined independently (0.077 Å^2). The structure contains an anionic part, the deprotonated sulfonic acid group, and a cationic part, the protonated carbonyl group.



(I)

Molecules are not directly bound through carbonyl and sulfonic acid groups. The bonding is mediated by hydrogen bonding in the three water molecules. Each water molecule is engaged in three hydrogen bonds. O*W*1 is bound to two sulfuryl O atoms belonging to two different flavone molecules and also to a water molecule. O*W*2 is involved in a similar hydrogen-bonding scheme. O*W*3 is bound to O*W*2 and O*W*1, and to the carbonyl O atom. The sulfonyl O atoms are engaged in different hydrogen bonds, O51 has only one bond with O*W*2, O52 is hydrogen bonded to two water molecules, and O53 is bound to the water molecule O*W*1 and to the hydroxyl group of the flavone. Hydrates of sulfonic acids form various cationic water species. In the case of trihydrates, $H_7O_3^+$ (Mootz & Fayos, 1970;

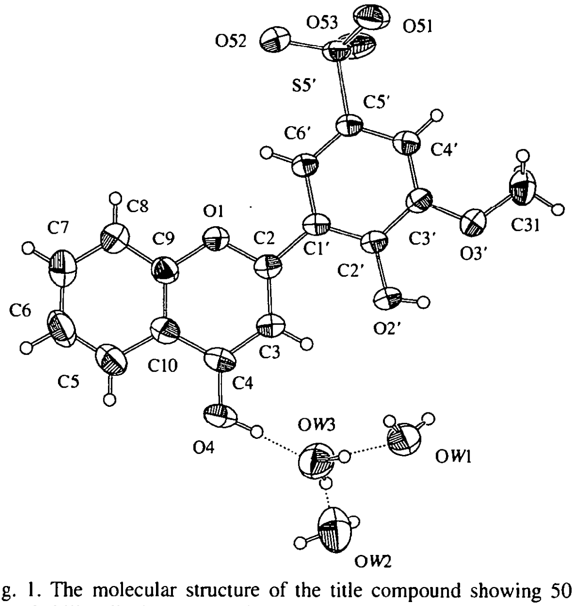


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids.