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Acta Cryst. (1995). **C51**, 2668–2671

Redetermination of the Structures of 1,4,7-Trioxa-10,13-dithiacyclopentadecane and 1,4,7,10-Tetraoxa-13,16-dithiacyclooctadecane

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Abstract

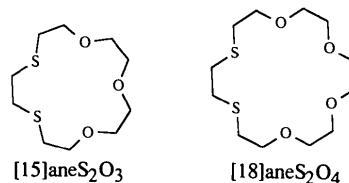
Both 1,4,7-trioxa-10,13-dithiacyclopentadecane, C₁₀H₂₀O₃S₂, and 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane, C₁₂H₂₄O₄S₂, show *exo*-oriented S and *endo*-oriented O atoms. The torsion angle of the SCH₂CH₂S moiety is *anti* [−165.93 (8)°] in the former and *gauche* [60.0 (2)°] in the latter. The latter exhibits C₂ symmetry through the midpoints of the C3—C3' and C11—C11' bonds.

Comment

We have been investigating the coordination chemistry of mixed O/S donor ionophores such as 1,4,7-trioxa-10,13-dithiacyclopentadecane (C₁₀H₂₀O₃S₂, [15]aneS₂O₃) and 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane (C₁₂H₂₄O₄S₂, [18]aneS₂O₄). Both ionophores have been found to adopt *endo* as well as *exo* coordination modes with a range of transition metal ions (Bell, 1987; Reid, 1989; Blake, Gould, Reid & Schröder, 1990; Blake, Reid & Schröder, 1990; Blake, Collison, Gould, Reid & Schröder, 1993; Blake, Gould, Radek & Schröder, 1994; Radek, 1995).

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We recently reported the single-crystal X-ray structure of 1,4,7,10,13-pentaoxa-16,19-dithiacyclohenicosane ([21]aneS₂O₅) sesquihydrate (Blake, Gould, Harris, Parsons, Radek & Schröder, 1995), which shows extended inter- and intramolecular hydrogen bonding with molecules of water of crystallization. As part of this study, we have redetermined the structures of the title compounds in order to improve on earlier structure determinations (Dalley, Larson, Smith, Matheson, Izatt & Christensen, 1981) and to establish whether hydration and similar extended hydrogen bonding are present in these structures.



The single-crystal X-ray structures of [15]aneS₂O₃ (Fig. 1) and [18]aneS₂O₄ (Fig. 2) do not exhibit any new features compared with the earlier structure determinations. The differences in bond lengths, angles and torsion angles are marginal but the estimated standard deviations were improved by a factor of up to four. A discussion of the conformation of these compounds has been given (Dalley, Larson, Smith, Matheson, Izatt & Christensen, 1975, 1981; Wolf, Hartman, Storey, Foxman & Cooper, 1987). It should be emphasized, however, that Wolf, Hartman, Storey, Foxman & Cooper (1987) consider an S—C—C—S *gauche* torsion angle to be destabilizing (repulsive *gauche* effect) whereas an O—C—C—O *gauche* torsion angle is considered to be stabilizing (attractive *gauche* effect). [15]aneS₂O₃ conforms to these conditions, while

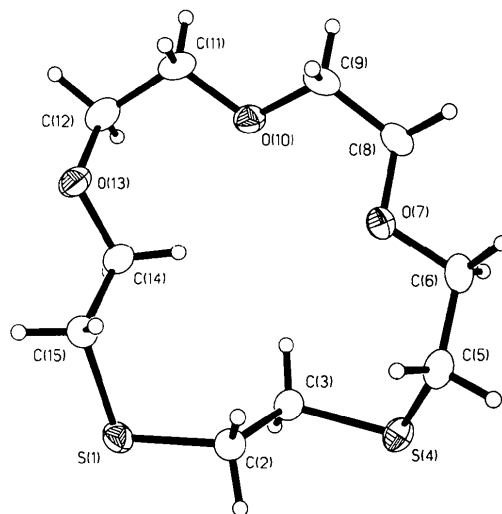


Fig. 1. The structure of the [15]aneS₂O₃ ionophore. Displacement ellipsoids enclose 50% probability surfaces.

[18]aneS₂O₄ shows an unusual *gauche* torsion angle at the SCH₂CH₂S moiety. This unexpected behaviour has to be attributed to a combined effect of all O—C—C—O moieties *endo* and the preferences of S atoms to adopt *exo* orientations in order to avoid unfavourable O...S interactions within the macrocyclic cavity.

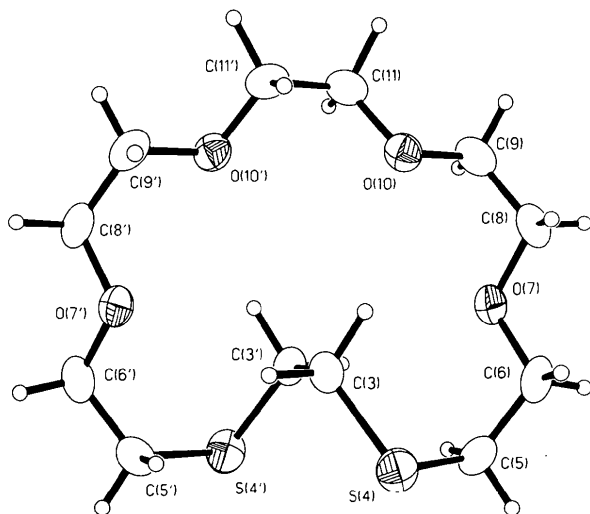


Fig. 2. The structure of the [18]aneS₂O₄ ionophore. Primed atoms are related to unprimed atoms by the operation of a twofold rotation axis ($-x, y, \frac{1}{2} - z$). Displacement ellipsoids enclose 30% probability surfaces.

Experimental

[15]aneS₂O₃ was prepared using a literature method (Bradshaw, Hui, Haymore, Christensen & Izatt, 1973) involving co-condensation of 1,2-ethanedithiol with 1,11-dichloro-3,6,9-trioxaundecane under basic high-dilution conditions. [18]aneS₂O₄ was prepared in an analogous fashion (Bradshaw, Hui, Chan, Haymore, Izatt & Christensen, 1974) by co-condensation of 1,2-ethanedithiol with 1,14-dichloro-3,6,9,12-tetraoxatetradecane, also under basic high-dilution conditions. Single crystals suitable for X-ray diffraction studies were obtained by employing a low-temperature two-phase diffusion technique in which *n*-hexane was allowed to diffuse into a solution of the relevant ionophore in EtOAc at 248 K, affording colourless crystals of high purity for both compounds.

[15]aneS₂O₃

Crystal data

C₁₀H₂₀O₃S₂

$M_r = 252.38$

Triclinic

$P\bar{1}$

$a = 7.213(2) \text{ \AA}$

$b = 9.102(3) \text{ \AA}$

$c = 10.080(4) \text{ \AA}$

$\alpha = 80.49(3)^\circ$

$\beta = 86.85(3)^\circ$

$\gamma = 74.32(2)^\circ$

$V = 628.4(4) \text{ \AA}^3$

$Z = 2$

$D_x = 1.334 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 30 reflections

$\theta = 14\text{--}17^\circ$

$\mu = 0.410 \text{ mm}^{-1}$

$T = 150.0(2) \text{ K}$

Block

$0.540 \times 0.424 \times 0.386 \text{ mm}$

Colourless

Data collection

Stoe Stadi-4 four circle diffractometer

ω - 2θ scans with on-line profile fitting (Clegg, 1981)

Absorption correction:

ψ scans

$T_{\min} = 0.776, T_{\max} =$

0.796

3173 measured reflections

2173 independent reflections

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0248$

$wR(F^2) = 0.0666$

$S = 1.037$

2161 reflections

217 parameters

All H-atom parameters

refined

$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 0.242P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.06$

1998 observed reflections

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

$R_{\text{int}} = 0.0127$

$\theta_{\max} = 25.05^\circ$

$h = -8 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -1 \rightarrow 11$

3 standard reflections

frequency: 60 min

intensity decay: <0.5%

$\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.008 (2)

Atomic scattering factors

from *International Tables for Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for [15]aneS₂O₃

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S1	0.18663 (5)	0.29927 (4)	0.42663 (4)	0.02580 (12)
C2	-0.0442 (2)	0.3556 (2)	0.34327 (15)	0.0250 (3)
C3	-0.0299 (2)	0.3419 (2)	0.19462 (15)	0.0247 (3)
S4	-0.25167 (5)	0.44147 (4)	0.10653 (4)	0.02969 (13)
C5	-0.4101 (2)	0.3192 (2)	0.1650 (2)	0.0282 (3)
C6	-0.3844 (2)	0.1795 (2)	0.0978 (2)	0.0279 (3)
O7	-0.23096 (15)	0.05757 (12)	0.15869 (10)	0.0273 (2)
C8	-0.1928 (2)	-0.0734 (2)	0.0916 (2)	0.0279 (3)
C9	-0.0694 (2)	-0.2113 (2)	0.1773 (2)	0.0282 (3)
O10	0.10615 (14)	-0.18137 (11)	0.20627 (10)	0.0260 (2)
C11	0.2260 (2)	-0.3097 (2)	0.2888 (2)	0.0294 (3)
C12	0.3903 (2)	-0.2640 (2)	0.3404 (2)	0.0318 (4)
O13	0.33130 (15)	-0.15984 (11)	0.43535 (10)	0.0281 (2)
C14	0.2766 (2)	-0.0015 (2)	0.3743 (2)	0.0264 (3)
C15	0.2199 (2)	0.0954 (2)	0.48507 (15)	0.0247 (3)

Table 2. Selected geometric parameters ($\text{\AA}, ^\circ$) for [15]aneS₂O₃

S1—C15	1.806 (2)	C8—C9	1.496 (2)
S1—C2	1.814 (2)	C9—O10	1.420 (2)
C2—C3	1.520 (2)	O10—C11	1.420 (2)
C3—S4	1.810 (2)	C11—C12	1.501 (2)
S4—C5	1.813 (2)	C12—O13	1.426 (2)
C5—C6	1.502 (2)	O13—C14	1.428 (2)
C6—O7	1.421 (2)	C14—C15	1.507 (2)
O7—C8	1.422 (2)		
C15—S1—C2	102.97 (7)	O10—C9—C8	110.00 (12)
C3—C2—S1	113.88 (11)	C9—O10—C11	111.40 (11)
C2—C3—S4	112.49 (11)	O10—C11—C12	110.00 (13)
C3—S4—C5	103.27 (8)	O13—C12—C11	113.14 (13)
C6—C5—S4	115.90 (11)	C12—O13—C14	113.24 (12)
O7—C6—C5	109.86 (12)	O13—C14—C15	107.77 (12)
C6—O7—C8	111.61 (11)	C14—C15—S1	113.12 (10)
O7—C8—C9	109.95 (12)		

C15—S1—C2—C3	-90.14 (12)	C8—C9—O10—C11	179.41 (12)
S1—C2—C3—S4	-165.93 (8)	C9—O10—C11—C12	-168.57 (12)
C2—C3—S4—C5	-72.70 (12)	O10—C11—C12—O13	69.1 (2)
C3—S4—C5—C6	-80.60 (13)	C11—C12—O13—C14	-87.7 (2)
S4—C5—C6—O7	83.07 (14)	C12—O13—C14—C15	-179.44 (12)
C5—C6—O7—C8	-175.80 (12)	O13—C14—C15—S1	169.94 (10)
C6—O7—C8—C9	-165.27 (12)	C2—S1—C15—C14	75.58 (12)
O7—C8—C9—O10	-58.7 (2)		

[18]janeS₂O₄*Crystal data*C₁₂H₂₄O₄S₂M_r = 296.43

Monoclinic

C2/c

a = 15.9074 (12) Å

b = 9.5181 (8) Å

c = 12.5255 (10) Å

β = 124.351 (4)°

V = 1565.7 (2) Å³

Z = 4

D_x = 1.258 Mg m⁻³*Data collection*

Stoe Stadi-4 four circle diffractometer

ω-2θ scans [width (0.90 + 0.35tanθ)° in ω]

Absorption correction: none

1268 measured reflections

1268 independent reflections

*Refinement*Refinement on F²R[F² > 2σ(F²)] = 0.0386wR(F²) = 0.1194

S = 1.030

1266 reflections

84 parameters

H atoms in fixed, calculated positions

w = 1/[σ²(F_o²) + (0.072P)² + 0.636P]where P = (F_o² + 2F_c²)/3(Δ/σ)_{max} = -0.003

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 70 reflections

θ = 15–16°

μ = 0.344 mm⁻¹

T = 295 (2) K

Column

0.66 × 0.47 × 0.39 mm

Colourless

998 observed reflections

[I > 2σ(I)]

θ_{max} = 24.99°

h = -18 → 15

k = 0 → 11

l = 0 → 13

3 standard reflections

frequency: 60 min
intensity decay: <0.5%Δρ_{max} = 0.22 e Å⁻³Δρ_{min} = -0.30 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.029 (3)

Atomic scattering factors

from *International Tables for Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 4. Selected geometric parameters (Å, °) for [18]janeS₂O₄

C3—C3'	1.511 (4)	O7—C8	1.412 (3)
C3—S4	1.802 (2)	C8—C9	1.486 (4)
S4—C5	1.807 (3)	C9—O10	1.416 (3)
C5—C6	1.492 (3)	O10—C11	1.422 (3)
C6—O7	1.413 (3)	C11—C11'	1.484 (5)
C3'—C3—S4	115.97 (11)	O7—C8—C9	108.7 (2)
C3—S4—C5	104.02 (9)	O10—C9—C8	109.6 (2)
C6—C5—S4	115.4 (2)	C9—O10—C11	112.0 (2)
O7—C6—C5	108.7 (2)	O10—C11—C11'	110.0 (2)
C8—O7—C6	113.8 (2)		
S4'—C3'—C3—S4	60.0 (2)	C6—O7—C8—C9	-173.7 (2)
C3'—C3—S4—C5	58.8 (2)	O7—C8—C9—O10	65.5 (3)
C3—S4—C5—C6	66.8 (2)	C8—C9—O10—C11	-179.2 (2)
S4—C5—C6—O7	-76.8 (2)	C9—O10—C11—C11'	-178.7 (2)
C5—C6—O7—C8	166.8 (2)	O10—C11—C11'—O10'	-77.8 (3)

Symmetry code: (i) -x, y, ½ - z.

The crystal of [15]janeS₂O₃ was cooled in the nitrogen gas stream of an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986).

For both compounds, data collection: *DIF4* (Stoe & Cie, 1990a); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1990b); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1992); software used to prepare material for publication: *SHELXL93*.

We thank the SERC for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms, and torsion angles have been deposited with the IUCr (Reference: NA1189). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for [18]janeS₂O₄

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
C3	0.05320 (14)	-0.0089 (2)	0.2652 (2)	0.0553 (6)
S4	0.13222 (4)	0.13847 (7)	0.35757 (6)	0.0736 (3)
C5	0.1373 (2)	0.1318 (2)	0.5053 (2)	0.0658 (7)
C6	0.1919 (2)	0.0083 (3)	0.5902 (2)	0.0657 (6)
O7	0.12773 (10)	-0.11056 (15)	0.53706 (13)	0.0588 (4)
C8	0.1783 (2)	-0.2391 (3)	0.5921 (2)	0.0673 (7)
C9	0.1064 (2)	-0.3562 (2)	0.5191 (2)	0.0672 (6)
O10	0.08108 (12)	-0.35828 (14)	0.39102 (14)	0.0586 (4)
C11	0.0111 (2)	-0.4675 (2)	0.3161 (2)	0.0700 (7)

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Acta Cryst. (1995). **C51**, 2671–2672

Diflufenican, *N*-(2,4-Difluorophenyl)-2-[3-(trifluoromethyl)phenoxy]-3-pyridine-carboxamide

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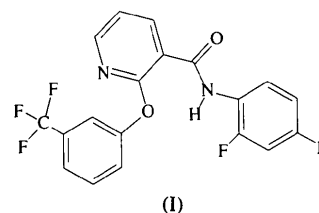
Abstract

Diflufenican, $C_{19}H_{11}F_5N_2O_2$, has an approximately planar molecular skeleton, except for the 3-trifluoromethylphenyl group which lies almost perpendicular to the rest of the molecule. The amide N—H group and ether O atom are linked by an intramolecular hydrogen bond.

Comment

Diflufenican, (I), is an active material used as a weed killer. More precisely, it acts as a carotenoid synthesis and photosynthetic electron-flow inhibitor. Its identification code is CAS RN [83164-33-4]. This product is conditioned, in association with another weed killer (isoproturon), as a flowable and concentrated suspension (under the trademarks Quartz GT, Javelin or Fenican). It is applied on autumn-sown wheat and barley (before emergence or in early emergence) in order to control grass and broad-leaved weeds. In order to obtain good quality crystals for X-ray analysis, (I) was recrystallized from *p*-xylene and acetone solutions, using non-industrial solvents. The solubilities at 293 K in these solvents were 3.36 and 8.25 g per 100 g of solvent,

respectively. Supersaturation was achieved by dissolving an excess of 10 to 20% of material, with respect to solubility, in hot solutions, which were then allowed to cool to 293 K without stirring. In both solvents, thick plate-like crystals appeared within one or two days. The crystal structure of diflufenican was determined as part of an investigation of the effect of different media on the crystal morphology. The ultimate objective was to obtain crystals shaped as isometrically as possible in order to facilitate the conditioning.



A strong intramolecular N9...O18 hydrogen bond [2.65 (1) Å] is observed. The π -system deformation can be characterized by the torsion angles C12—C17—C10—O11 3.8 (3), C24—C19—O18—C16 -77.4 (5), C5—C4—N9—C10 -6.3 (5) and C17—C10—N9—C4 -174.8 (5)°. The large values of the displacement parameters of the F atoms of the CF₃ group indicate slight disorder of these atom positions. The crystal is stabilized by π - π and van der Waals interactions.

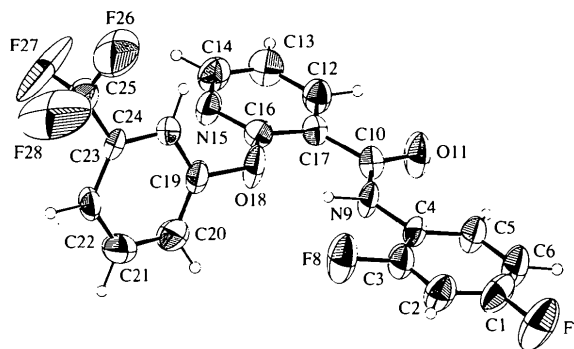


Fig. 1. ORTEP drawing (Johnson, 1976) of the molecule of diflufenican with displacement ellipsoids of 50% probability.

Experimental

The title compound was recrystallized from *p*-xylene and acetone solutions (see *Comment*). The crystal density D_m was measured by flotation.

Crystal data

$C_{19}H_{11}F_5N_2O_2$
 $M_r = 394.3$

Cu $K\alpha$ radiation
 $\lambda = 1.5418$ Å