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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

Disorder in main residue

R factor = 0.035

wR factor = 0.089

Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

1,5-[5,5'-(3-Oxa-1,5-pentylenedithio)bis(2,3-dihydro-2-oxo-1,3,4-thiadiazol-3-yl)]-3-oxapentane

The title compound, 4,14-dioxa-9,11,17,19-tetrathia-1,7,21,22-tetraazatricyclo[16.2.1.1^{7,10}]docosa-18(21),10(22)-diene-8,20-dione, C₁₂H₁₆N₄O₄S₄, has crystallographic twofold symmetry, with a half molecule in the asymmetric unit and a dihedral angle of 52.59 (6)° between the two planar five-membered rings of the macrocycle, giving the molecule a twisted conformation.

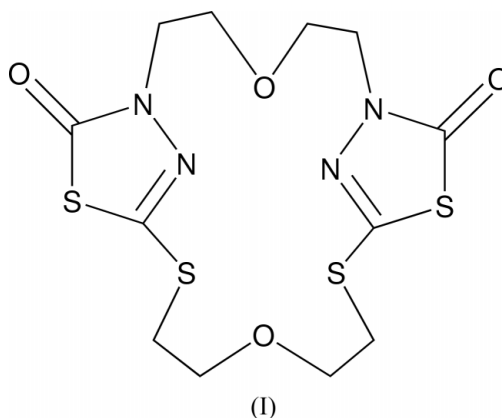
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Comment

As a continuation of our studies of macrocyclic compounds containing 1,3,4-thiadiazole subunits (Cho, Park & Hwang, 1999; Cho, Park, Kim *et al.*, 1999; Cho, Park, Hwang *et al.*, 1999; Cho *et al.*, 2000), we have turned our attention to macrocycles composed of two 5-mercapto-2,3-dihydro-1,3,4-thiadiazole-2-one units. For the formation of macrocycle (I), these two heterocyclic rings are linked by ether chains. These compounds have been shown to be artificial receptors of transition metals (Cho, Park, Kim *et al.*, 1999) and furthermore are potential hosts of small organic molecules. The determination of the structure of title compound, (I), is part of a study of these macrocycles.



The title compound, (I), with the atom-labelling scheme is shown in Fig. 1. A half molecule belongs to an asymmetric unit and the other half molecule is generated by applying a twofold rotation [symmetry code: (i) $-x, y, -z + \frac{3}{2}$] passing through O1 and O3. The S—C distances range from 1.674 (5) to 1.970 (9) Å, with a mean value of 1.782 (2) Å, and the N2—C4 and O2—C3 distances of 1.279 (3) and 1.215 (3) clearly show double-bond character. The remainder of the bonds are single bonds; in the five-membered ring, C3—S1—C4 = 88.89 (11)°. These values are comparable with those found in 4,17,25,26-tetraaza-6,9,12,15-tetraoxa-2,19,21,24-tetrathiatricyclo[18.4.1^{1,4}.1^{17,20}]hexacos-1(25),20(26)-diene-3,5,16,18-

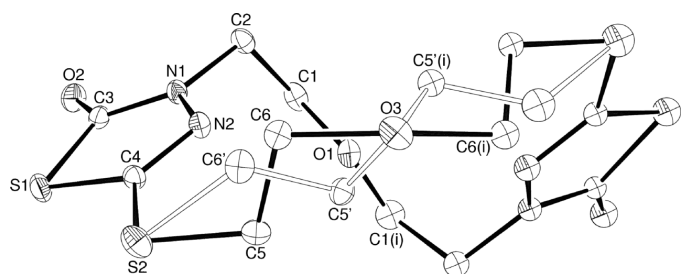


Figure 1
ORTEP-3 (Farrugia, 1997) diagram of (I) showing 25% probability displacement ellipsoids. C atoms are shown with ellipsoids with only enveloping ellipsoids and the remaining atoms are shown with ellipsoids with octant shading. Only the asymmetric unit is labelled and H atoms have been omitted for clarity [symmetry code: (i) $-x, y, -z + \frac{3}{2}$].

tetraone (Cho *et al.*, 2000) and 1,5-[5,5'-(1,3-phenylene-dimethylenedithio)bis(2,3-dihydro-2-oxo-1,3,4-thiadiazol-3-yl)]-3-oxapentane (Cho *et al.*, 2001).

The five-membered ring, 5-mercapto-2,3-dihydro-1,3,4-thiadiazole-2-one, is planar within 0.016 (1) Å and the ethyl ether linkage (atoms C2, C1, O1, C1ⁱ and C2ⁱ) is planar within 0.085 (2) Å. The dihedral angle between the five-membered ring and that related by twofold symmetry is 52.59 (6)°; the dihedral angle between the five-membered ring and the ethyl ether linkage is 79.02 (6)°. Therefore, the molecule has a twisted conformation with a C2–C1–O1–C1ⁱ torsion angle of 171.4 (2)°. The interatomic distances N1···N1ⁱ = 5.609 (4) Å, N2···N2ⁱ = 4.842 (4) Å, N2···O3 = 4.223 (3) Å, N2···S2ⁱ = 6.158 (2) Å, O1···O3 = 5.431 (3) Å and S2···S2ⁱ = 7.322 (2) Å appear to be sufficient to introduce a guest ion inside the molecule. The closest intermolecular distance is O2···H5A = 2.572 (5) Å.

Experimental

The preparation of (I) followed the general procedure previously reported by Cho, Park, Kim *et al.* (1999). Details will be reported elsewhere.

Crystal data

C₁₂H₁₆N₄O₄S₄
M_r = 408.53
Monoclinic, C2/c
a = 8.7369 (8) Å
b = 15.741 (3) Å
c = 13.3967 (12) Å
β = 103.833 (8)°
V = 1788.9 (4) Å³
Z = 4

D_x = 1.517 Mg m⁻³
Mo Kα radiation
Cell parameters from 25 reflections
θ = 11.4–13.7°
μ = 0.56 mm⁻¹
T = 293 (2) K
Block, colorless
0.53 × 0.43 × 0.26 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω/2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.745, T_{max} = 0.861
3139 measured reflections
1573 independent reflections
1201 reflections with I > 2σ(I)

R_{int} = 0.026
θ_{max} = 25.0°
h = -10 → 10
k = -18 → 18
l = -15 → 0
3 standard reflections
frequency: 300 min
intensity decay: none

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.035
wR(F²) = 0.089
S = 1.02
1573 reflections
130 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.7080P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.16 e Å⁻³
Δρ_{min} = -0.20 e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.0028 (6)

Table 1

Selected geometric parameters (Å, °).

S1–C4	1.737 (2)	S2–C6'	1.970 (9)
S1–C3	1.784 (3)	N2–C4	1.279 (3)
S2–C5	1.674 (5)	O2–C3	1.215 (3)
S2–C4	1.747 (3)		
C4–S1–C3	88.89 (11)		

Atoms C5 and C6 were disordered over two positions and their coordinates together with site-occupation factors were refined anisotropically using the PART command of SHELXL97 (Sheldrick, 1997). All H atoms were located geometrically with U_{iso} constrained to be 1.2 times the equivalent isotropic displacement of the parent atoms. The highest peak and deepest holes in the final difference density map are at 0.85 Å from H6A and 0.91 Å from S1, respectively.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD4 (Harms & Wocadlo, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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