

Fig. 1. View of the title compound showing the atom numbering.

Discussion. Table 1 lists the atomic coordinates for the non-hydrogen atoms, and Table 2 the bond lengths and bond angles.* A perspective view of the structure is presented in Fig. 1, which also shows the crystallographic numbering. The stereochemistry of the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51140 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cycloadduct, hereby established as (IV), is analogous to that reported for the adduct (V) from bicyclo[2.2.1]-hepta-2,5-diene (II) and the quinone anhydride (VI) (Kanematsu, Morita, Fukushima & Osawa, 1981). The exclusive formation of (V), in which the cyclohexenedione ring takes up the *endo* configuration in preference to the anhydride ring, was explained on the basis of secondary orbital interactions, which in (VI) could involve either of the pairs of carbonyl C atoms, but would be expected to be greater at C(1) and C(4) where the LUMO coefficients are larger.

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Structure of 1,4-Dioxo-10,13-dithia-7,16-diazacyclooctadecane-6,17-dione

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Abstract. C₁₂H₂₂N₂O₄S₂, *M_r* = 322.44, monoclinic, *P*2₁/*c*, *a* = 7.760 (2), *b* = 21.425 (5), *c* = 9.658 (2) Å, β = 91.17 (2)°, *V* = 1605.3 (6) Å³, *Z* = 4, *D_x* = 1.334 g cm⁻³, λ(Mo Kα) = 0.71069 Å, μ = 2.96 cm⁻¹, *F*(000) = 688.0, *T* = 296 K, final *R* = 0.035 for 2152 observed reflections. The conformation of the 18-membered ring is characterized by the exodentate orientation of sulfur atoms and the *gauche* torsion angles for all C–S–C–C units and *anti* torsion angles for the S–C–C–S and S–C–C–N fragments. The planar amide groups are *trans* with *exo*- and *endo*-dentate carbonyl oxygens involved in inter- and intramolecular C=O⋯H–N interactions, respectively.

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Introduction. The structural chemistry of unsubstituted and substituted crown-ether-type ligands has received considerable attention (Dale, 1980; Dobler, 1981; Hilgenfeld & Saenger, 1982; Truter, 1973). However, very little work has been reported on the structures of *oxa*- and *thia*-substituted macrocyclic amides (Samuel & Weiss, 1970; Ganin, Lukyanenko, Dvorkin, Popkov, Simonov, Bogatskii & Malinovskii, 1981; Simonov, Malinovskii, Ganin, Dvorkin, Bogatskii, Lukyanenko & Popkov, 1981; Ganin, Sobolev, Bel-skii, Simonov, Lukyanenko, Popkov & Malinovskii, 1984). Compounds of this type are of interest owing to their metal ion complexation properties and their ability to transport cations across membranes (Tümmeler, Maass, Weber, Wehner & Vögtle, 1977). The replacement of

ether oxygen donor atoms by sulfur atoms has pronounced effects on the solid-state structures of the ligands (Wolf, Hartman, Storey, Foxman & Cooper, 1987; Dalley, Larson, Smith, Matheson, Izatt & Christensen, 1981; Ammon, Chandrasekhar, Bhattacharjee, Shinkai & Honda, 1984). As part of our continuing studies on the effects of donor atom substitution of the properties of macrocyclic ligands we have determined the crystal structure of the title compound, abbreviated $2_{S,2O,da}$.

Experimental. Prepared according to the literature method (Dietrich, Lehn & Sauvage, 1970) and recrystallized from a benzene–heptane mixture. Colorless crystalline parallelepipeds, $0.20 \times 0.25 \times 0.35$ mm, D_m not determined. Nonius CAD-4 diffractometer, monochromated $Mo K\alpha$, data collected in ω - 2θ scan mode, variable scan speed with maximum recording time 90 s, ω scan width $(0.75 + 0.35 \tan\theta)^\circ$, extended 25% on each side for background measurement; three standard reflections measured every 7200 s showed no significant decay; three orientation reflections measured after every 200 measurements showed no significant crystal movement; $\sigma^2(I) = [N + 4(B_1 + B_2) + (0.04N)^2]$, N = net count, B_1 and B_2 = background counts, equation for L_p factor assumes graphite monochromator crystal 50% mosaic and 50% perfect. Cell constants from 24 high-angle reflections ($2\theta = 30$ – 40°). 3016 reflections measured ($\pm h, k, l$, max. $h = 9$, $k = 24$, $l = 11$; $2\theta_{max} = 50^\circ$), 2152 unique reflections [$I > 2\sigma(I)$]. Lorentz and polarization corrections applied. Solved by direct methods and full-matrix least-squares refinement using program *SHELX* (Sheldrick, 1978). Function minimized, $\sum w(|F_o| - |F_c|)^2$. Hydrogen atoms located from difference Fourier map. Refinement anisotropic for the non-H atoms and isotropic for the H atoms. Final $R = 0.035$, $wR = 0.041$ for 2152 unique observed reflections (number of variables = 270), $w = [\sigma^2(F)]^{-1}$, $S = 1.35$. Largest shift/e.s.d. in final cycle

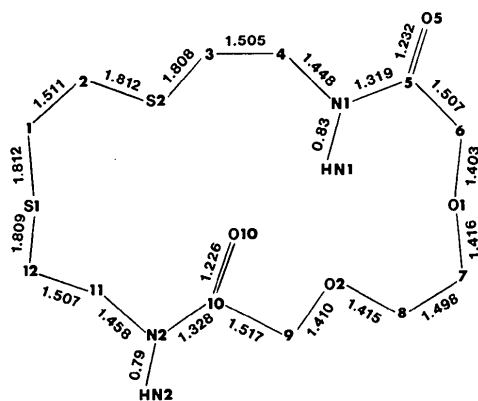


Fig. 1. Atom numbering and bond distances (Å) in macrocycle $2_{S,2O,da}$. The standard deviations for the bond lengths involving C, N, S and O atoms range from 0.002 to 0.003 Å.

Table 1. Atomic coordinates and U_{eq} values ($\text{Å}^2 \times 10^3$) with e.s.d.'s for the last digit in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}
S(1)	0.21424 (9)	-0.00157 (3)	0.34899 (7)	58.4 (2)
S(2)	0.65306 (8)	0.08736 (3)	0.13640 (7)	54.5 (2)
O(1)	0.3097 (2)	0.3489 (1)	0.2717 (2)	48.6 (5)
O(2)	0.1625 (2)	0.3206 (1)	0.5333 (2)	48.5 (5)
O(5)	0.7324 (2)	0.3166 (1)	0.1708 (2)	65.8 (7)
O(10)	0.2448 (2)	0.2089 (1)	0.4059 (2)	57.6 (6)
N(1)	0.5404 (2)	0.2600 (1)	0.2890 (2)	42.2 (6)
N(2)	0.0090 (2)	0.1627 (1)	0.4867 (2)	44.8 (6)
C(1)	0.3417 (3)	0.0358 (1)	0.2175 (3)	51.0 (8)
C(2)	0.5254 (3)	0.0479 (1)	0.2648 (3)	52.4 (9)
C(3)	0.5714 (4)	0.1661 (1)	0.1492 (3)	49.6 (8)
C(4)	0.6287 (3)	0.2007 (1)	0.2777 (2)	44.8 (7)
C(5)	0.5939 (3)	0.3118 (1)	0.2301 (2)	42.4 (8)
C(6)	0.4784 (3)	0.3679 (1)	0.2435 (3)	47.4 (8)
C(7)	0.2075 (3)	0.3905 (1)	0.3488 (3)	49.1 (8)
C(8)	0.0770 (3)	0.3523 (1)	0.4233 (2)	48.9 (8)
C(9)	0.0824 (4)	0.2648 (1)	0.5753 (3)	50.5 (9)
C(10)	0.1192 (3)	0.2100 (1)	0.4810 (2)	42.2 (7)
C(11)	0.0305 (3)	0.1068 (1)	0.4028 (3)	49.7 (8)
C(12)	0.1685 (3)	0.0640 (1)	0.4603 (3)	51.1 (8)

Table 2. Selected bond angles ($^\circ$) and torsion angles ($^\circ$) with e.s.d.'s for the last digit in parentheses

C(1)–S(1)–C(12)	100.9 (1)	O(5)–C(5)–N(1)	123.8 (2)
C(2)–S(2)–C(3)	101.0 (1)	O(5)–C(5)–C(6)	120.0 (2)
C(6)–O(1)–C(7)	116.9 (2)	N(1)–C(5)–C(6)	116.2 (2)
C(8)–O(2)–C(9)	114.8 (2)	O(1)–C(6)–C(5)	110.1 (2)
C(4)–N(1)–C(5)	123.6 (2)	O(1)–C(7)–C(8)	107.4 (2)
C(10)–N(2)–C(11)	121.5 (2)	O(2)–C(8)–C(7)	108.2 (2)
S(1)–C(1)–C(2)	112.9 (2)	O(2)–C(9)–C(10)	113.2 (2)
S(1)–C(12)–C(11)	113.6 (2)	O(10)–C(10)–N(2)	121.9 (2)
S(2)–C(2)–C(1)	113.5 (2)	O(10)–C(10)–C(9)	122.1 (2)
S(2)–C(3)–C(4)	114.7 (2)	N(2)–C(10)–C(9)	115.9 (2)
N(1)–C(4)–C(3)	111.2 (2)	N(2)–C(11)–C(12)	112.5 (2)
N(1)–C(4)–C(3)–S(2)	-172.5 (2)	O(10)–C(10)–C(9)–O(2)	21.8 (3)
C(4)–C(3)–S(2)–C(2)	73.2 (2)	C(10)–C(9)–O(2)–C(8)	79.3 (3)
C(3)–S(2)–C(2)–C(1)	75.3 (2)	C(9)–O(2)–C(8)–C(7)	-154.3 (2)
S(2)–C(2)–C(1)–S(1)	-178.3 (1)	O(2)–C(8)–C(7)–O(1)	73.3 (2)
C(2)–C(1)–S(1)–C(12)	77.8 (2)	C(8)–C(7)–O(1)–C(6)	-153.2 (2)
C(1)–S(1)–C(12)–C(11)	76.6 (2)	C(7)–O(1)–C(6)–C(5)	151.2 (2)
S(1)–C(12)–C(11)–N(2)	-173.8 (2)	O(1)–C(6)–C(5)–O(5)	160.9 (2)
C(12)–C(11)–N(2)–C(10)	77.2 (3)	O(1)–C(6)–C(5)–N(1)	-21.6 (3)
C(11)–N(2)–C(10)–O(10)	-0.5 (3)	C(6)–C(5)–N(1)–C(4)	175.4 (2)
C(11)–N(2)–C(10)–C(9)	-179.2 (2)	O(5)–C(5)–N(1)–C(4)	-7.2 (3)
N(2)–C(10)–C(9)–O(2)	-159.5 (2)	C(5)–N(1)–C(4)–C(3)	-86.3 (3)

= 0.03. No features of chemical significance in final difference map; largest peak $0.2 e \text{ Å}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atom-labeling scheme and bond distances are shown in Fig. 1. The atomic coordinates are listed in Table 1* and selected bond angles and torsion angles are listed in Table 2. A stereoview of the molecule is shown in Fig. 2.

* Lists of complete bond lengths and angles, anisotropic thermal parameters, structure factors and least-squares planes and deviations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51128 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal structure consists of polymeric chains formed by the inter- and intramolecular hydrogen bonds (O...H-N), approximately parallel to the [101] axis (Fig. 3). The macrocycle exists in a relatively flat conformation. The donor atoms S(1), S(2), N(2), O(2) and O(5) adopt an exodentate orientation with respect to the central cavity. The other carbonyl oxygen atom, O(10), points into the center of the cavity and is involved in an intramolecular hydrogen bond with the amido hydrogen atom, H(N1) attached to N(1). One electron lone pair from O(1) is oriented toward the center of the ring cavity. The major structural elements of the macrocycle consist of the 'square' N-C-C-S-C-C-S-C-N segment, with the sulfur atoms at the corners, and the planar six-atom extended amide segments, C-N(H)-C(=O)-C. The torsion-angle sequence for the N-C-C-S-C-C-S-C-C-N subunit is (*gag*), where *g* and *a* indicate *gauche* ($\pm 120^\circ$) and antiperiplanar ($\pm 120-180^\circ$) torsion angles, respectively (Dale, 1980). The strong preference for the *gauche* conformation of the C-S-C-C segments and for the *anti* conformation of the S-C-C-S (and N-C-C-S) segments has been noted

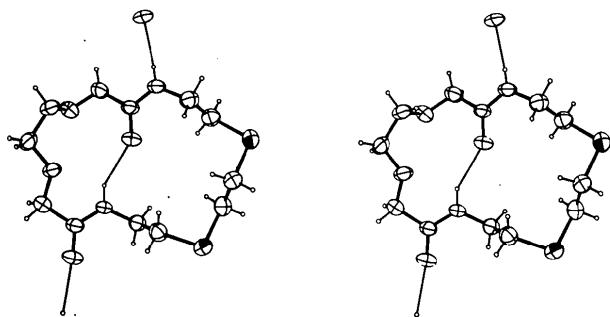


Fig. 2. Stereoview (ORTEP, Johnson, 1965) of macrocycle 2_s,2_o,da. Thermal ellipsoids are drawn at the 50% probability level for the nonhydrogen atoms and the hydrogen atoms are drawn as spheres of 0.05 Å radius.

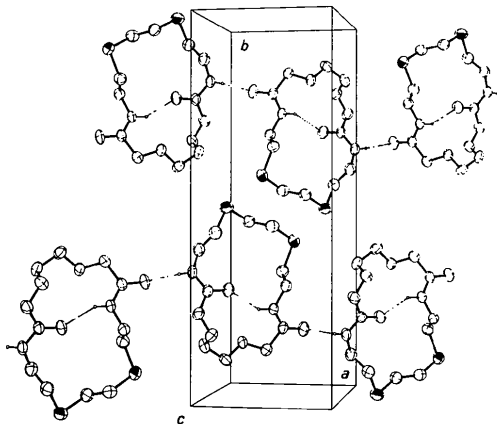


Fig. 3. Packing diagram of macrocycle 2_s,2_o,da; hydrogen atoms omitted for clarity.

for a variety of thiaether macrocyclic ligands (Wolf, Hartman, Storey, Foxman & Cooper, 1987; Ammon, Chandrasekhar, Bhattacharjee, Shinkai & Honda, 1984). This behavior has been attributed to 1-4 interactions which disfavor the *gauche* conformation at S-C-C-S bonds but not at C-S-C-C bonds while the opposite trends are expected for O-C-C-O and C-O-C-C subunits (Wolf, Hartman, Storey, Foxman & Cooper, 1987). The *g*, *aga*, *a* torsion-angle sequence found for the C-O-C-C-O-C segment of the title compound follows the expected pattern except for one C-O bond. The C(*sp*³)-C(*sp*³) bond lengths (1.498-1.512 Å) are in the range found for a wide variety of substituted crown-ether-type ligands (1.46-1.52 Å) (Maverick, Seiler, Schweizer & Dunitz, 1980; Goldberg, 1975, 1978; Ott, Barnes, Taylor & van der Helm, 1982; Wolf *et al.*, 1987).

As noted by other workers, these values are less than the expected paraffinic value of 1.537 (5) Å (Sutton, 1965). The C(*sp*³)-S and C(*sp*³)-O bond lengths, 1.808-1.812 and 1.403-1.416 Å, respectively, are in the ranges found for similar compounds, 1.785-1.822 and 1.408-1.433 Å (Wolf *et al.*, 1987; Dalley, Larson, Smith, Matheson, Izatt & Christensen, 1981; Glass, Wilson & Setzer, 1980; Ammon, Chandrasekhar, Bhattacharjee, Shinkai & Honda, 1984). The average C(*sp*³)-S [1.810 (2) Å] and C(*sp*³)-O [1.411 (6) Å] bond lengths are close to the expected values of 1.815 (10) and 1.426 (5) Å, respectively (Sutton, 1965).

Least-squares calculations indicate that the four-atom amide group, N(2)-C(10)[O(10)]-C(9), is essentially planar with an average deviation of ≤ 0.004 Å. Furthermore, atoms C(11) (0.013 Å) and H(N2) (0.001 Å) also lie in the calculated plane. Similar treatment of the N(1)-C(5)[O(5)]-C(6) amide moiety gives an average deviation of ≤ 0.007 Å with atoms C(4) (0.105 Å) and H(N1) (0.050 Å) close to the calculated plane. The amide bond lengths and bond angles are in the respective ranges: C(*sp*³)-C(*sp*²), 1.505-1.532; C=O, 1.218-1.237; C(*sp*²)-N, 1.320-1.379 Å; C-C=O, 117.9-122.3; N-C=O, 122.1-124.9; C-C-N, 115.0-119.1°, found for a variety of other macrocyclic amides (Samuel & Weiss, 1970; Northolt & Alexander, 1968; Simonov *et al.*, 1981; Ganin *et al.*, 1981, 1984). The least-squares planes of the two amide segments have a dihedral angle of 40.5 (2)°.

Both amide groups adopt a *trans* (H-N-C=O) conformation and lie in the general plane defined by the entire molecule. An intramolecular hydrogen bond is formed involving O(10)...H(N1)-N(1) with the distances: O(10)...N(1), 2.801 (2); H(N1)-N(1), 0.83 (2), O(10)...H(N1), 2.05 (2) Å and the O(10)...H(N1)-N(1) angle 149 (2)°. A similar C=O...H-N bond is found in the macrocycle, 1,7,13-trioxa-4,10-diazacyclopentadecane-3,11,15-trione where the

O...N, O...H and H—N interatomic distances are 3.087, 2.30, and 0.86 Å, respectively, and the O...H—N angle is 152° (Simonov, Malinovskii, Ganin, Dvorkin, Bogatskii, Lukyanenko & Popkov, 1981). The individual molecules are linked together by means of C=O...H—N hydrogen bonds. The O(5)...N(2'), O(5)...H(N2'), and H(N2)—N(2) bond distances are 2.850 (3), 2.06 (2), and 0.79 (2) Å, respectively. The O(5)...H(N2')—N(2') angle is almost linear with a value of 176 (2)°. These values fall in the ranges (N...O, 2.859–3.094; O...H, 1.92–2.36 Å; O...H—N, 161–177°) found for other macrocyclic amides (Northolt & Alexander, 1968; Simonov, Malinovskii, Ganin, Dvorkin, Bogatskii, Lukyanenko & Popkov, 1981).

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***trans*-3-(3,4-Dimethoxyphenyl)-6,7,8-trimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline—Methanol (1/1)**

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Abstract. C₂₁H₂₇NO₅.CH₄O, *M_r* = 405.49, triclinic, *P* $\bar{1}$, *a* = 8.918 (2), *b* = 11.259 (1), *c* = 11.561 (3) Å, α = 101.37 (1), β = 94.37 (2), γ = 103.30 (1)°, *V* =

1098.5 (4) Å³, *Z* = 2, *D_x* = 1.226 Mg m⁻³, m.p. = 359 K, λ (Mo *K* α) = 0.7107 Å, μ = 0.095 mm⁻¹, *T* = 295 K, *F*(000) = 436, final *R* = 0.068 for 2047 observed reflections. The heterocyclic fragment of the molecule exhibits a half-chair conformation. The

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