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Structure of 6,14,17,22,25-Pentaoxa-1,3,9,11-tetraazabicyclo[9.8.8]heptacosane-2,10-dithione

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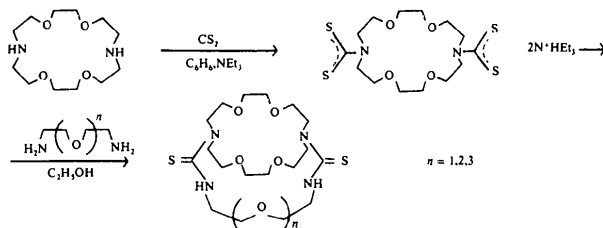
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Abstract. $C_{18}H_{34}N_4O_5S_2$, $M_r = 450.61$, orthorhombic, *Pbca*, $a = 16.714(4)$, $b = 17.254(4)$, $c = 15.526(3) \text{ \AA}$, $V = 4477.4(4) \text{ \AA}^3$, $Z = 8$, $D_x = 1.337 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 2.28 \text{ cm}^{-1}$, $F(000) = 1936$, $T = 293 \text{ K}$. Final $R = 0.058$ for 1947 observed reflections. In the cryptand $[3_{\text{NON}}, 2_{\text{O}}, 2_{\text{O}}]$ the conformation of the diaza-18-crown-6 fragment is described by the sequence of $g^-, g^+, g^-, t, g^+, t, g^+, g^-, g^-, g^+, g^+, g^-, g^-, t, g^+, g^-$ rotamers. Both thiourea fragments have a *cis* configuration, which is stabilized by N—H...O intramolecular hydrogen bonds of 2.830 and 2.825 Å. Distances between neighbouring molecules are equal to or exceed van der Waals radii.

Introduction. The reaction of 1,10-diaza-18-crown-6 with carbon disulfide in benzene gives dithiocarbamate salts in the presence of triethylamine. Boiling the salt with 1,5-diamino-3-oxapentane in ethanol gave 6,14,17,22,25-pentaoxa-1,3,9,11-tetraazabicyclo[9.8.8]-heptacosane-2,10-dithione (cryptand $[3_{\text{NON}}, 2_{\text{O}}, 2_{\text{O}}]$) (Lukyanenko, Bogatsky, Kiritchenko, Scherbakov & Nazarova, 1984).



Cationic selectivity of this cryptand in relation to alkaline metal ions is unusual, if it is compared with the traditional cryptands. It can be explained by the effect of the thiourea fragments (Lukyanenko *et al.*, 1984). The study of cryptand $[3_{\text{NON}}, 2_{\text{O}}, 2_{\text{O}}]$, investigated by X-ray methods, is presented in this paper. Colourless crystals of this compound were obtained by slow crystallization of a diluted acetone solution.

Experimental. Full set of integral intensity data obtained within angle range $2 < 2\theta < 50^\circ$ from a single crystal of prismatic habit with dimensions $0.4 \times 0.5 \times 0.5 \text{ mm}$. Equi-inclined DAR-UMB automatic diffractometer operated by M-6000 computer, graphite-monochromated Mo *K* α radiation, used to obtain experimental data by combined ω - $\theta/2\theta$ scanning with constant rate 8° min^{-1} . 2346 reflections recorded, 1947 independent with $I(hkl) > 3\sigma(I)$ used for calculations (h 0–20, k 0–20, l 0–16, 17 standard reflections, 5% intensity variation, three reflections used for measuring lattice parameters). Corrections made for Lorentz and polarization effects. Absorption and extinction corrections neglected. Structure solved by direct methods with *YANX* (Gerr, Yanovsky & Struchkov, 1983). On first *E* map all non-H atoms located. Refinement of atomic coordinates by full-matrix LS carried out taking into account both anisotropy for non-H atoms and isotropic vibrations for H atoms, located on difference Fourier map. Final R index of 0.058 obtained with unit weights. Remaining peaks within 0.45 and -0.28 e \AA^{-3} , $(\Delta/\sigma)_{\text{max}} = 0.01$;

scattering factors from *International Tables for X-ray Crystallography* (1974). The coordinates of the non-H atoms and effective isotropic temperature parameters are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42625 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for non-H atoms with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
S(1)	487 (2)	3867 (1)	1433 (1)	65 (1)
S(2)	1898 (1)	155 (1)	273 (1)	54 (1)
N(1)	850 (4)	3398 (3)	3036 (4)	43 (2)
C(2)	1484 (5)	3989 (4)	3057 (6)	57 (3)
C(3)	2320 (5)	3627 (5)	3167 (6)	61 (3)
O(4)	2483 (3)	3094 (3)	2482 (4)	56 (2)
C(5)	2785 (6)	3473 (5)	1714 (6)	78 (4)
C(6)	2765 (6)	2863 (6)	1012 (6)	73 (4)
O(7)	3360 (3)	2295 (3)	1217 (4)	57 (2)
C(8)	3312 (5)	1597 (5)	718 (5)	59 (3)
C(9)	3235 (4)	903 (4)	1301 (5)	47 (3)
N(10)	2432 (4)	840 (4)	1704 (3)	39 (2)
C(11)	2288 (4)	1308 (4)	2485 (4)	38 (2)
C(12)	2391 (5)	861 (4)	3319 (4)	43 (3)
O(13)	1713 (3)	367 (3)	3486 (3)	46 (2)
C(14)	1242 (5)	546 (5)	4230 (4)	48 (3)
C(15)	477 (5)	973 (5)	3980 (5)	51 (3)
O(16)	602 (3)	1709 (3)	3576 (3)	48 (2)
C(17)	934 (5)	2291 (4)	4104 (5)	52 (3)
C(18)	594 (5)	3068 (4)	3868 (4)	53 (3)
C(19)	405 (5)	3294 (4)	2312 (4)	43 (2)
N(20)	-122 (4)	2696 (4)	2351 (4)	51 (2)
C(21)	-740 (5)	2534 (6)	1709 (6)	69 (3)
C(22)	-484 (7)	1946 (6)	1111 (6)	77 (4)
C(23)	-344 (3)	1230 (3)	1562 (4)	62 (2)
C(24)	-75 (5)	641 (5)	970 (5)	59 (3)
C(25)	410 (5)	43 (5)	1435 (5)	56 (3)
N(26)	1158 (4)	367 (4)	1764 (4)	44 (2)
C(27)	1820 (4)	469 (4)	1302 (4)	40 (2)

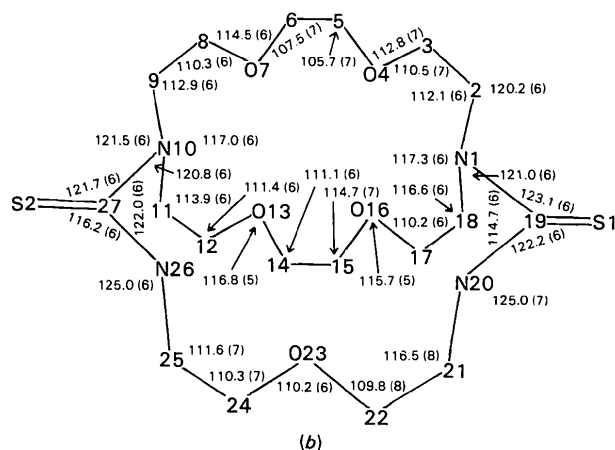
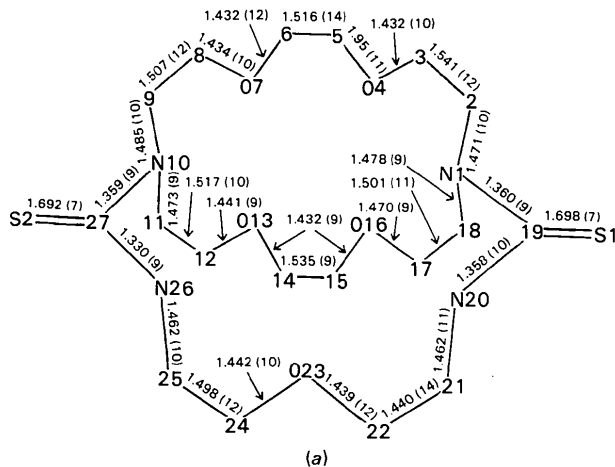


Fig. 1. (a) Bond distances (\AA) and (b) angles ($^\circ$) with numbering scheme. E.s.d.'s are in parentheses.

Table 2. Some important torsion angles ($^\circ$)

	E.s.d.'s ca 0.7° .		
N(1)-C(2)-C(3)-O(4)	58.3	C(2)-C(3)-O(4)-C(5)	83.8
C(3)-O(4)-C(5)-C(6)	-169.0	O(4)-C(5)-C(6)-O(7)	-68.9
C(5)-C(6)-O(7)-C(8)	167.8	C(6)-O(7)-C(8)-C(9)	-123.8
O(7)-C(8)-C(9)-N(10)	73.2	C(8)-C(9)-N(10)-C(11)	-82.7
C(9)-N(10)-C(11)-C(12)	-97.9	N(10)-C(11)-C(12)-O(13)	-76.7
C(11)-C(12)-O(13)-C(14)	-115.1	C(12)-O(13)-C(14)-C(15)	101.5
O(13)-C(14)-C(15)-O(16)	-62.4	C(14)-C(15)-O(16)-C(17)	-67.3
C(15)-O(16)-C(17)-C(18)	-145.2	O(16)-C(17)-C(18)-N(1)	-70.9
C(17)-C(18)-N(1)-C(2)	-99.8	C(18)-N(1)-C(2)-C(3)	78.6
S(2)-C(27)-N(10)-C(9)	-7.6	S(1)-C(19)-N(1)-C(2)	-5.3
S(2)-C(27)-N(10)-C(11)	161.7	S(1)-C(19)-N(1)-C(18)	159.9
S(2)-C(27)-N(26)-C(25)	-5.6	S(1)-C(19)-N(20)-C(21)	-8.0
C(9)-N(10)-C(27)-N(26)	172.2	C(2)-N(1)-C(19)-N(20)	175.6
N(10)-C(27)-N(26)-C(25)	174.5	N(1)-C(19)-N(20)-C(21)	171.1
C(27)-N(26)-C(25)-C(24)	-81.4	C(19)-N(20)-C(21)-C(22)	97.8
N(26)-C(25)-C(24)-O(23)	-66.2	N(20)-C(21)-C(22)-O(23)	62.4
C(25)-C(24)-O(23)-C(22)	154.5	C(21)-C(22)-O(23)-C(24)	-179.0

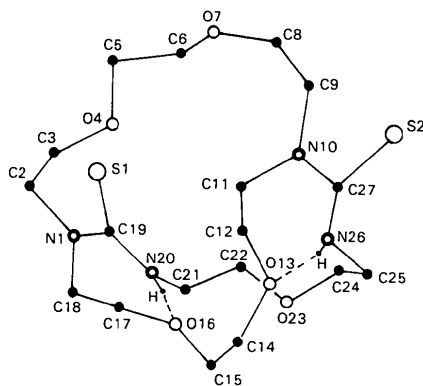


Fig. 2. General view of the molecule. The hydrogen bonds are shown by a broken line.

Discussion. The structure of the molecule, the bond lengths and valence angles are shown in Figs. 1(a) and 1(b). The mean bond lengths in the diaza-18-crown-6 fragment are characteristic of the macrocyclic polyethers: C—C 1.517, C—N 1.476 and C—O 1.433 Å. The mean lengths of C—C and C—O bonds in the polyoxyethylene bridge are 1.468 and 1.441 Å, respectively. The C—C bonds in the cryptand [3_{NON},2_O,2_O], like in other macrocyclic polyethers (Goldberg, 1980), are shorter than the standard value 1.54 Å. The C—S bond lengths 1.691 and 1.692 (7) Å in the almost planar thiourea groups are close in value to those found in other cyclic thioureas (Malinowsky, Kiritchenko, Simonov, Lukyanenko & Bogatsky, 1981; Ganin, Simonov, Lukyanenko, Bogatsky, Kiritchenko & Botoshansky, 1981), which is characteristic of the thione form of thiourea. The lengths of the C—N bonds are within the range 1.329–1.360 Å. The configurations of the C—N—C(=S)—N—C fragment in cyclic thiourea, *cis-cis*, *cis-trans* and *trans-trans*, may depend on the size of the ring. The torsion angles at the C(19)—N(20) and C(27)—N(26) bonds in cryptand [3_{NON},2_O,2_O] are 8.2 and 5.5°, respectively. This testifies to the *cis* configuration of the fragments. Such a configuration is stabilized additionally by the intramolecular hydrogen bonds N(26)H...O(13) 2.830 Å [N—H 0.85, O...H 2.06 Å, angle N—H—O 150°] and N(20)H...O(16) 2.825 Å [N—H 1.12, O...H 1.85 Å, angle N—H—O 143°] (Fig. 2). The torsion angles are presented in Table 2. The most convenient *gauche*, *trans* and *trans* conformations are in the bridge N(20)C(21)...C(25)—N(26) *via* C—C, C—O and C—N bonds. Considerable conformational strains are observed in the diaza-18-crown-6 fragment. The conformation of this cycle is

described by the sequence of $g^-, g^+, g^-, t, g^+, t, g^+, g^-, g^+, g^+, g^-, g^-, g^+, t, g^+, g^-$ rotamers. Convenient *trans* rotamers are realized only in three out of 12 C—O and C—N bonds. In contrast to the above, the convenient *trans-gauche-trans* conformations are realized *via* X—CH₂—CH₂—X bonds (X=O,N) (Dale, 1973; Herceg & Weiss, 1972; Moras, Metz, Herceg & Weiss, 1972; Weber, 1982) in a monocyclic diaza-18-crown-6 molecule.

The structure of the cryptand is molecular. The distances between the neighbouring molecules are equal to or exceed van der Waals radii.

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Sarcophinone at 115 K: a Cembranolide Diterpenoid from the South China Sea

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Abstract. C₂₀H₂₈O₃, *M_r* = 316.44, orthorhombic, *P*2₁2₁2₁, *a* = 11.197 (6), *b* = 12.582 (6), *c* =

12.569 (6) Å, *V* = 1771 Å³, *Z* = 4, *D_x* = 1.19 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 0.44 cm⁻¹, *F*(000) = 688, *T* = 115 K, *R* = 0.062 for 1235 unique observed reflections. This cembranolide diterpenoid, isolated

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