A 1:4 Adduct of 1,7,10,16-Tetraoxa-4,13-diazacyclooctadecane* and Thiourea

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Abstract. $C_{12}H_{26}N_2O_4.4CH_4N_2S$, $M_r = 566.83$, triclinic, $P\bar{1}$, $a = 9.121$ (3), $b = 9.849$ (3), $c = 9.883$ (3) Å, $\alpha = 117.07$ (2), $\beta = 109.12$ (2), $\gamma = 97.09$ (2)°, $U = 706.7$ Å^3, $Z = 1$, $D_c = 1.332$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0.71069$ Å) = 0.361 mm^{-1}; $R = 0.036$, $R_w = 0.043$ for 2314 independent diffractometer data. Two N–H⋯O and two N–H⋯N hydrogen bonds between the host and two guest molecules and two additional intra-annular N–H⋯O contacts give rise to the 'biangular' conformation of the macrocycle. The remaining thiourea molecules are involved in N–H⋯S bridges linking these units.

Introduction. Complexes of the monocyclic secondary aminopolyether 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (tdco) with metal cations are well known (Herceg & Weiss, 1973; Moras, Metz, Herceg & Weiss, 1972; Metz & Weiss, 1973). With neutral molecules, adduct formation *via* H bridges was considered difficult unless intramolecular N–H⋯O bonds (Herceg & Weiss, 1972) were avoided by N,N'-substitution of the diamine (von Deuten, Knöchel, Kopf, Oehler & Rudolph, 1979). The title compound (Vögtle, Sieger & Müller, 1981), however, contains the unsubstituted ligand. Moreover, few X-ray studies of molecular complexes with urea or thiourea have been reported (Harkema, van Hummel, Daasvatn & Reinhoudt, 1981; Suh & Saenger, 1978; Weber & Saenger, 1980). Hence a structural analysis, to investigate the conformation of the macrocycle and the pattern of H bridges, seemed worthwhile.

Colourless crystals were grown from methanol. Preliminary Weissenberg photographs showed triclinic symmetry. Cell dimensions were determined on an automated four-circle diffractometer by least squares from 26 strong reflexions between $2\theta = 20$ and $25°$. 2476 unique intensities up to $2\theta = 50°$ were measured from a plate *ca* $0.7 \times 0.5 \times 0.1$ mm in a profile-fitting mode (Clegg, 1981) with monochromated Mo $K\alpha$ radiation. Lp corrections were applied.

The structure was solved by direct methods and refined anisotropically using 2314 observed data with $F \geq 3\sigma(F)$. Methylene H atoms were positioned geometrically (C–H = 0.96 Å); other H atoms were located from a difference Fourier map and refined, with N–H bond lengths constrained to 1.02 ± 0.1 Å (Elcombe & Taylor, 1968). All H atoms were assigned fixed isotropic thermal parameters 1.2 times the U values of attached atoms.

Application of an empirical extinction correction $[F^* = F/(1.0 + 0.002xF^2/\sin 2\theta)^{1/4}$, where x refined to 3.4 (9) × $10^{-3}]$ resulted in final discrepancy factors $R = 0.036$ and $R_w = 0.043$ with $w^{-1} = \sigma^2(F) +$

Table 1. *Atom coordinates* (×10^4) *and isotropic temperature factors* (Å^2 ×10^4)

	x	y	z	U^*
O(1)	1943 (1)	−375 (1)	17 (1)	404 (6)
C(2)	2777 (2)	504 (2)	1802 (2)	442 (9)
C(3)	3680 (2)	2225 (2)	2506 (2)	421 (8)
N(4)	5056 (2)	2422 (2)	2084 (2)	387 (7)
C(5)	6250 (2)	4055 (2)	3284 (2)	451 (9)
C(6)	7713 (2)	4233 (2)	2932 (2)	441 (9)
O(7)	8475 (1)	3104 (1)	3105 (1)	421 (6)
C(8)	9702 (2)	2945 (2)	2511 (2)	442 (9)
C(9)	9024 (2)	1970 (2)	628 (2)	433 (9)
S(1)	2393 (1)	1452 (1)	−4327 (1)	444 (2)
C(11)	2786 (2)	1399 (2)	−2542 (2)	352 (8)
N(11)	4210 (2)	2250 (2)	−1199 (2)	525 (9)
N(12)	1654 (2)	486 (2)	−2477 (2)	564 (9)
S(2)	7387 (1)	4685 (1)	−1162 (1)	480 (2)
C(21)	7652 (2)	3115 (2)	−2655 (2)	430 (9)
N(21)	6358 (2)	1920 (2)	−4039 (2)	568 (9)
N(22)	9127 (2)	3027 (2)	−2505 (2)	583 (10)
H(4)	5613 (21)	1605 (17)	2139 (23)	462
H(11a)	4403 (26)	2234 (25)	−136 (16)	625
H(11b)	5066 (19)	2993 (20)	−1219 (26)	625
H(12a)	1990 (27)	336 (26)	−1479 (18)	665
H(12b)	612 (16)	−222 (21)	−3569 (15)	665
H(21a)	6520 (28)	880 (15)	−4766 (24)	673
H(21b)	5215 (12)	1977 (26)	−4213 (28)	673
H(22a)	9185 (28)	2014 (16)	−3406 (21)	701
H(22b)	10109 (18)	3877 (20)	−1413 (16)	701

* Equivalent isotropic U except for H; $U_{eq} = \frac{1}{3}$(trace of orthogonalized U_{ij} matrix).

0·00025F^2. Atom parameters are listed in Table 1,* bond lengths and angles in Tables 2 and 3; a view of the adduct and the numbering scheme adopted is presented in Fig. 1.

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*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 36937 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å)

C(2)—O(1)	1·418 (6)	C(2)—C(3)	1·497 (6)
C(3)—N(4)	1·465 (6)	C(5)—N(4)	1·472 (6)
C(5)—C(6)	1·495 (7)	C(6)—O(7)	1·426 (6)
C(8)—O(7)	1·419 (6)	C(8)—C(9)	1·497 (6)
C(9)—O(1)'	1·424 (6)	C(11)—S(1)	1·709 (7)
C(11)—N(11)	1·319 (5)	C(11)—N(12)	1·321 (6)
C(21)—S(2)	1·696 (6)	C(21)—N(21)	1·335 (5)
C(21)—N(22)	1·323 (6)	N(4)—H(4)	1·02 (2)
N(11)—H(11a)	1·01 (2)	N(11)—H(11b)	1·01 (2)
N(12)—H(12a)	1·02 (2)	N(12)—H(12b)	1·02 (1)
N(21)—H(21a)	1·01 (2)	N(21)—H(21b)	1·01 (1)
N(22)—H(22a)	1·01 (2)	N(22)—H(22b)	1·01 (1)

Table 3. Bond angles (°)

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C(2)—O(1)—C(9)'	111·3 (3)	O(1)—C(2)—C(3)	111·9 (4)
C(2)—C(3)—N(4)	113·6 (3)	C(3)—N(4)—C(5)	110·9 (3)
N(4)—C(5)—C(6)	111·3 (3)	C(5)—C(6)—O(7)	107·9 (4)
C(6)—O(7)—C(8)	113·4 (4)	O(7)—C(8)—C(9)	113·5 (3)
C(8)—C(9)—O(1)'	110·3 (4)	S(1)—C(11)—N(11)	121·8 (3)
S(1)—C(11)—N(12)	120·2 (3)	N(11)—C(11)—N(12)	118·0 (4)
S(2)—C(21)—N(21)	120·5 (3)	S(2)—C(21)—N(22)	121·9 (3)
N(21)—C(21)—N(22)	117·7 (3)	C(3)—N(4)—H(4)	108 (1)
C(5)—N(4)—H(4)	109 (1)	C(11)—N(11)—H(11a)	121 (1)
C(11)—N(11)—H(11b)	119 (1)	H(11a)—N(11)—H(11b)	121 (2)
C(11)—N(12)—H(12a)	118 (1)	C(11)—N(12)—H(12b)	116 (1)
H(12a)—N(12)—H(12b)	125 (2)	C(21)—N(21)—H(21a)	119 (1)
C(21)—N(21)—H(21b)	120 (1)	H(21a)—N(21)—H(21b)	120 (2)
C(21)—N(22)—H(22a)	117 (1)	C(21)—N(22)—H(22b)	118 (1)
H(22a)—N(22)—H(22b)	124 (2)		
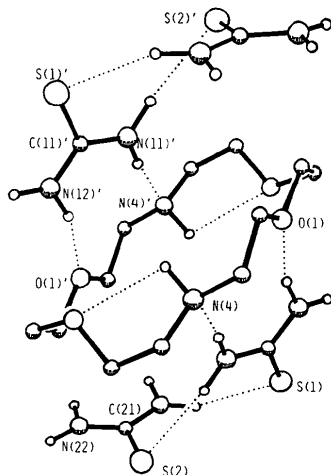
Fig. 1. The tdco.4tu adduct viewed approximately along **c**. Primed atoms are generated by inversion at the centre of tdco (½,0,0). Radii are arbitrary.

Discussion. By analogy with the recently reported 1:5 complex between 18-crown-6 and urea (Harkema *et al.*, 1981), the present compound may be considered a 1:2 adduct: two thiourea molecules tu(1), related by inversion at the centre of tdco, are inclined with dihedral angles 67 (1)° 'above' and 'below' the plane of the hexagon of heteroatoms which is coplanar to within ±0·24 Å, with O(1)···N(4) = 2·995 (6), N(4)···O(7) = 2·827 (6) and O(7)···O(1)' = 2·884 (6) Å. Short H···O and H···N contacts of ≤2 Å between the chelating tu(1) and two neighbouring heteroatoms of the crown, N—H···X (X = N,O) angles of 162 and 173° and the almost ideal hybridization of the H-bond acceptors N(4) (sp^3) and O(1) (sp^2) (see Table 4) all indicate strong linkages between host and guests.

In uncomplexed tdco, both N—H groups form two H bonds of equal length to the neighbouring O atoms; this probably assists in stabilizing the 'round', *i.e.* approximate D_{3d}, conformation of the macrocycle (Herceg & Weiss, 1972). Interactions with the thiourea molecules in the present structure force the aminoether into the more elongated 'biangular [99]' (Dale, 1973) conformation (Fig. 2). This is reflected in (*a*) the widely varying distances of heteroatoms opposite each other [N(4)···N(4)' = 4·631 (6), O(1)···O(1)' = 5·547 (6), O(7)···O(7)' = 6·784 (6) Å], (*b*) the increased H(4)···O(1) distance of 3·08 (2) Å as compared to H(4)···O(7) = 2·46 (2) Å (*cf.* 2·51 and 2·52 Å in the free ligand), and, particularly, (*c*) the sequence of torsion angles (Table 5). A biangular conformation appears quite common with the analogous 18-crown-6 when H bonding to guest species such as amines,

Table 4. H-*bond geometry* (Å *and* deg)

For superscripts see Fig. 3.

N(4)···O(7)	2·827 (6)	N(12)···S(1)^{iii}	3·518 (6)
N(4)···N(11)	2·996 (5)	N(21)···S(1)^{ii}	3·492 (6)
N(11)···S(2)	3·505 (6)	N(21)···S(1)	3·488 (5)
N(12)···O(1)	2·898 (6)	N(22)···S(1)^{ii}	3·776 (6)
		N(22)···S(2)^{iv}	3·402 (6)
H(4)···O(7)	2·46 (2)	N(4)—H(4)···O(7)	101 (1)
H(11a)···N(4)	1·99 (2)	N(11)—H(11a)···N(4)	173 (1)
H(11b)···S(2)	2·50 (2)	N(11)—H(11b)···S(2)	174 (1)
H(12a)···O(1)	1·91 (2)	N(12)—H(12a)···O(1)	162 (1)
H(12b)···S(1)^{iii}	2·54 (1)	N(12)—H(12b)···S(1)^{iii}	161 (1)
H(21a)···S(1)^{ii}	2·52 (2)	N(21)—H(21a)···S(1)^{ii}	162 (1)
H(21b)···S(1)	2·52 (1)	N(21)—H(21b)···S(1)	161 (1)
H(22a)···S(1)^{ii}	2·91 (2)	N(22)—H(22a)···S(1)^{ii}	144 (1)
H(22b)···S(2)^{iv}	2·41 (1)	N(22)—H(22b)···S(2)^{iv}	166 (1)
H(12a)···O(1)—C(2)	128 (1)	H(12b)^{iii}···S(1)—C(11)	115 (1)
H(12a)···O(1)—C(9)^i	121 (1)	H(21a)^{ii}···S(1)—C(11)	85 (1)
C(2)—O(1)—C(9)^i	111·3 (3)	H(21b)···S(1)—C(11)	101 (1)
		H(22a)^{ii}···S(1)—C(11)	94 (1)
H(4)—N(4)—C(3)	108 (1)	H(12b)^{iii}···S(1)···H(21a)^{ii}	104 (2)
H(4)—N(4)—C(5)	109 (1)	H(12b)^{iii}···S(1)···H(22a)^{ii}	58 (2)
H(4)—N(4)···H(11a)	112 (1)	H(12b)^{iii}···S(1)···H(21b)	141 (2)
H(11a)···N(4)—C(3)	113 (1)	H(21a)^{ii}···S(1)···H(21b)	62 (2)
H(11a)···N(4)—C(5)	104 (1)	H(21a)^{ii}···S(1)···H(22a)^{ii}	47 (2)
C(3)—N(4)—C(5)	110·9 (3)	H(22a)^{ii}···S(1)···H(21b)	105 (2)
H(4)···O(7)—C(6)	81 (1)	H(11b)···S(2)—C(21)	95 (1)
H(4)···O(7)—C(8)	138 (1)	H(22b)^{iv}···S(2)—C(21)	109 (1)
C(6)—O(7)—C(8)	113·4 (4)	H(11b)···S(2)···H(22b)^{iv}	117 (2)

Table 5. *Torsion angles* (°)

The sign convention is as defined by Klyne & Prelog (1960).

C(9)′–O(1)–C(2)–C(3)	−174·9 (3)	O(1)–C(2)–C(3)–N(4)	−67·1 (4)
C(2)–C(3)–N(4)–C(5)	−158·1 (3)	C(3)–N(4)–C(5)–C(6)	176·2 (4)
N(4)–C(5)–C(6)–O(7)	−60·8 (4)	C(5)–C(6)–O(7)–C(8)	169·3 (3)
C(6)–O(7)–C(8)–C(9)	−76·2 (4)	O(7)–C(8)–C(9)–O(1)′	−60·8 (4)
C(8)–C(9)–O(1)′–C(2)′	172·1 (4)		

amides and water (*e.g.* Knöchel, Kopf, Oehler & Rudolph, 1978; Bombieri, de Paoli & Immirzi, 1978; Harkema *et al.*, 1981; Weber & Sheldrick, 1981; Weber, 1982); and it can also be deduced from the coordinates of *N,N'*-bis(2-cyanoethyl)tdco in its adduct with malonodinitrile (von Deuten *et al.*, 1979), with 'genuine corners' (Dale, 1980) $g^{\pm}g^{\pm}a$ between N and O, due to the hindering *N*-substituents. In the title compound, however, 'corners' between O atoms allow both the free electron pair and H(4) to point towards the centre of the macrocycle and thus to form a (weaker) intra-annular H(4)···O(7) bridge of 2·46 (2) Å, accompanied by an N–H···O angle of *ca* 100° and an irregular geometry at O(7) (Table 4).

In complexes of open-chained oligoethers with thiourea (Suh & Saenger, 1978; Weber & Saenger, 1980), the latter is 'wrapped' by the ligand in such a way that strong interactions between the complex units are precluded. As in the 1:5 adduct of 18-crown-6 and urea (Harkema *et al.*, 1981), the 'sandwich' configuration of the present adduct allows additional contacts between tu molecules (Table 4), resulting in a three-dimensional network of H bridges as shown in Fig. 3. Characteristic features are zigzag strips of eight-membered rings each sharing two atoms. They are built up from alternating tu(1)···tu(1) and tu(2)··· tu(2) entities *via* ···S–C–N–H···S–C–N–H··· bonds and thus link the tdco.2tu(1) units. The dihedral angle of 71 (1)° between tu(1) and tu(2) and separations of 0·64 (2) and 0·54 (2) Å between the symmetry-related planes of tu(1) and tu(1)^{iii} and of
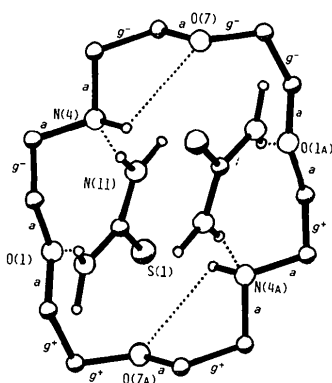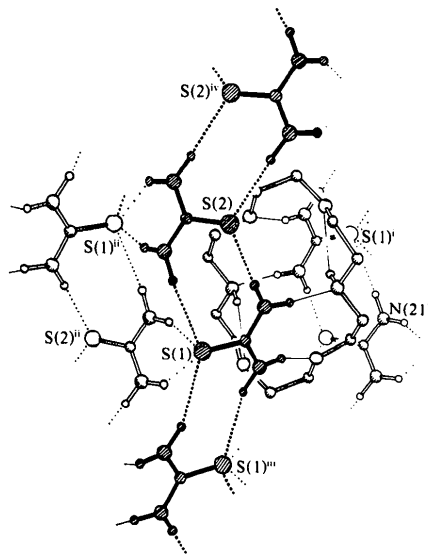

Fig. 3. A section of the network of H bonds viewed along **b**. Interactions between tu molecules are indicated by dotted lines, those between tu(1) and tdco by narrow unbroken lines. Symmetry code: (i) $1 - x$, $-y$, $-z$; (ii) $1 - x$, $-y$, $-z - 1$; (iii) $-x, -y, -z - 1$; (iv) $2 - x, 1 - y, -z$.

tu(2) and tu(2)^{iv}, respectively, reflect the step-like arrangement of these strips.

The polymeric structure is further extended by linkages between the tu(1)/tu(2) rings of different layers, resulting in another eight-membered ring [···H–N(21)–H···S(1)···H–N(21)^{ii}–H··· S(1)^{ii}···], and also by a six-membered ring completed by the twofold H bonding of H–N(21)–C(20)– N(22)–H of tu(2)^{ii} to S(1) [though H(22a)^{ii}···S(1) = 2·91 (2) Å must be considered a weak interaction].

Fig. 2. The conformation of the macrocycle (a = *anti*, $g^{\pm}$ = $\pm gauche$) and the system of H bridges involving the ligand, as viewed in a direction normal to the best plane of its heteroatoms. Atoms indicated by A correspond to primed atoms in Fig. 1.

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Structure of (9S,P)-(+)-7,9-Di-*tert*-butyl-9H-naphtho[1',2':3,4]cyclopenta[1,2-c]phenanthrene

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Abstract. $C_{33}H_{32}$, orthorhombic, $P2_12_12_1$, $a = 11 \cdot 148$ (1), $b = 22 \cdot 163$ (2), $c = 9 \cdot 998$ (1) Å, $Z = 4$, $D_x = 1 \cdot 152$ Mg m^{-3}. The structure was solved by *MULTAN* 78 and refined by the block-diagonal least-squares method to $R = 0 \cdot 056$ for 2161 observed reflexions. The molecule has a spiral structure, *i.e.* a rel-(9S,P) configuration. Distortion from planarity is significant for all the benzene rings. The cyclopentadiene ring is deformed into an envelope form. The consecutive ring planes are considerably bent. The molecule is more stable in the (9S,P) than in the (9S,M) configuration.

Introduction. Recently, the photolysis of (1S)-(−)-3,3'-di-*tert*-butyl-1,1'-spirobi[benz[g]indene] (1) at 238 K has been reported to yield the (9S,M)-(−) configuration (2) of the title compound stereospecifically as the initial product which can be completely converted at room temperature into the title compound (9S,P)-(+)-7,9-di-*tert*-butyl-9H-naphtho[1',2':3,4]cyclopenta[1,2-c]phenanthrene (3) by epimerization at the helix structure (from left- to right-handed) (Imajo, Shingu, Kuritani & Kato, 1981).

(1) (2) (3)
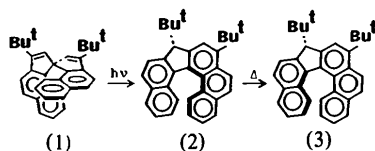
In order to establish the mechanism of this reaction, crystal-structure analysis of (3) was undertaken. The relative configuration of the two chiral centers in (2) was deduced from that of (3). Furthermore, the differences between (2) and (3) in the conformation and strain energy were estimated using the program *MMPI* (Allinger & Yuh, 1977) to seek the factor affecting the stability of (2) and (3).

Yellow needle-like crystals of (3) were obtained from a methyl acetate–ethanol solution. Three-dimensional intensity data were collected on a Rigaku diffractometer with graphite-monochromatized Cu $K\alpha$ radiation using a crystal of dimensions $0 \cdot 1 \times 0 \cdot 2 \times 0 \cdot 3$ mm. Integrated intensities were measured in the range $\theta \leq 70°$ with an ω–2θ scan. The intensities of 2601 independent reflexions were corrected for Lorentz and polarization factors, but not for absorption effects.

The structure was solved using the program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declerq & Woolfson, 1978). In a difference electron-density map calculated after block-diagonal least-squares refinement, all the H atoms were located. Successive refinement of the positional and anisotropic thermal parameters of the non-H atoms gave an R value ($\sum |\Delta F| / \sum |F_o|$) of $0 \cdot 056$ for 2161 reflexions. The atomic scattering factors were calculated using the analytical expression

$$f = \sum [a_i \exp(-b_i \lambda^{-2} \sin^2 \theta)] + c \quad (i = 1–4)$$