The deviation of the ring conformation from the ideal boat form (torsion angles 0, 60, −60, 0, 60, −60° in cyclic order; Bucourt & Hainaut, 1965) is greater than that observed in previously determined structures of cyclotrisilazanes (Adamson & Daly, 1970; Clegg, Noltemeyer, Sheldrick & Vater, 1981), to the extent of approximating more closely to the twist conformation (33·1, 33·1, −70·6, 33·1, 33·1, −70·6°). Other cyclotrisilazanes have been reported with almost planar rings (Rozsondai, Hargittai, Golubinskii, Vilkov & Mastyukov, 1975; Clegg, Noltemeyer, Sheldrick & Vater, 1980).

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2,5,8-Trithia[9](2,6)-pyridinophane,* $C_{11}H_{15}NS_3$

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Abstract. $M_r = 257{\cdot}44$, monoclinic, $P2_1/c$, $a = 9{\cdot}049\,(3)$, $b = 15{\cdot}875\,(5)$, $c = 9{\cdot}523\,(4)$ Å, $\beta = 114{\cdot}09\,(2)°$, $U = 1248{\cdot}9\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}369$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}539$ mm^{-1}, $F(000) = 544$, $T = 291$ K. Final $R = 0{\cdot}0426$ for 1871 observed $[I > 2\sigma(I)]$ diffractometer data. The macrocycle is disordered, the major component (84%) adopting a 'chair-like' conformation. However, the minor component of the thioether chain possesses an alternative conformation which may be suitable for forming transition-metal complexes, the four heteroatoms being coplanar to within ± 0·09 Å.

Introduction. The title compound may be considered as a hetero analogue of '12-crown-4' and was reported to form crystalline complexes with $AgNO_3$, $HgCl_2$, $HAuCl_4$, $PdCl_2$, H_2PtCl_6 and $Co(SCN)_2$ (Weber & Vögtle, 1976). The present X-ray investigation was undertaken to study possible structural changes on complex formation.

Experimental. Colourless rod *ca* 0·5 × 0·15 × 0·1 mm (kindly provided by Dr E. Weber and Professor F. Vögtle, Bonn, Federal Republic of Germany) chosen for crystallographic measurements on an automated Stoe X-ray four-circle diffractometer, cell dimensions determined by least squares from settings of 38 strong reflexions in range $20 < 2\theta < 25°$; out of 3642 data collected between $2\theta = 7$ and 50° in a profile fitting mode (Clegg, 1981), 109 systematically absent ($h0l$, $l = 2n+1$; $0k0$, $k = 2n+1$) and 2190 unique ($R_{\text{int}} = 0{\cdot}0194$); structure solved by multisolution direct methods and refined anisotropically minimizing $\sum w(|F_o| - |F_c|)^2$, with scattering factors as incorporated in *SHELXTL*.

A difference map then revealed all H-atom positions, but also a minor disorder component $[f = 0{\cdot}163\,(2)]$ of atoms S(4)′ to S(10)′. Except C(3)—S(4) and C(3)—S(4)′, corresponding distances in both conformations were restrained to be equal by the method of additional observational equations with weights derived from $\sigma = 0{\cdot}005$ Å. Restraining C(3)—S(4)′ resulted in a dominant peak of 0·6 e Å^{-3} [close to S(4) and S(4)′] in the difference map, at distances of 1·48 and 1·75 Å to C(3) and C(5)′, respectively, possibly indicating some additional non-resolvable disorder. Isotropic temperature factors of primed S atoms were allowed to vary freely whilst those of C(5)′, C(6)′, C(8)′ and C(9)′ were kept fixed at U_{eq} of corresponding C atoms of the major component. Only for that part of the chain were H atoms included [in calculated positions, C—H = 0·96 Å, $U_{\text{iso}}(\text{H}_i) = 1{\cdot}2\,U_{\text{eq}}(\text{C}_i)$].

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* Nomenclature according to Vögtle & Neumann (1970).

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Application of an empirical extinction correction $[F_c^* = F_c/(1\cdot0 + 0\cdot002xF_c^2/\sin2\theta)^{1/4}$, where x refined to $5\cdot4\,(9) \times 10^{-4}]$ resulted in $R_w = 0\cdot0538$ $[w^{-1} = \sigma^2(F_o) + 11 \times 10^{-4}F_o^2$, which gave a flat variance analysis] and a goodness-of-fit of 1·637, with a maximum shift of 0·12 and a mean shift of 0·02 e.s.d.'s in the last cycle of refinement; final difference map showed a maximum of 0·27 e $Å^{-3}$ [close to C(6)′] and a minimum of 0·28 e $Å^{-3}$; diffractometer program written by Dr W. Clegg, Göttingen, program for structure solution, refinement and graphical display (*SHELX TL*) by GMS.

Discussion. Atomic parameters are given in Table 1.†

Bond lengths and angles (Table 2) are comparable to those found in other cyclic thioethers (*e.g.* Glick, Gavel, Diaddario & Rorabacher, 1976; Campbell, Larson & Dalley, 1981*a*,*b*; Weber, 1982). The non-restrained C(3)—S(4)′ distance of 1·64 Å is unreliable since it probably indicates an insufficient resolution of the disorder of atoms in this section of the ligand (see *Experimental*). Similarly shortened distances in 1,4,7,10,13-pentaoxa-16-thiacyclooctadecane (Huffman, Campbell, Dalley & Larson, 1981) were explained as mean values of C—O and C—S lengths resulting from a 0·5:0·5 occupancy by O or S; this hypothesis could not be proved for the present structure.

Table 1. *Atomic coordinates* (×10⁴) *and isotropic thermal parameters* ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*
N(1)	6348 (2)	920 (1)	946 (2)	40 (1)*
C(2)	7572 (3)	390 (1)	1693 (3)	42 (1)*
C(3)	8920 (3)	381 (2)	1153 (3)	56 (1)*
S(4)	10783 (1)	864 (1)	2556 (1)	64 (1)*
S(4)′	10639 (8)	883 (4)	2018 (7)	49 (2)
C(5)	10060 (4)	1862 (2)	2927 (3)	57 (1)*
C(5)′	9895 (20)	1945 (7)	1554 (16)	57
C(6)	9502 (4)	2454 (2)	1599 (4)	61 (1)*
C(6)′	9712 (22)	2305 (6)	2909 (11)	61
S(7)	8630 (1)	3444 (1)	1855 (2)	71 (1)*
S(7)′	8861 (6)	3350 (4)	2526 (6)	55 (2)
C(8)	6520 (3)	3161 (2)	1157 (4)	58 (1)*
C(8)′	7004 (10)	3021 (10)	2618 (13)	58
C(9)	5997 (3)	2850 (2)	2390 (3)	47 (1)*
C(9)′	5648 (10)	2939 (9)	1044 (12)	47
S(10)	3894 (1)	2526 (1)	1681 (1)	49 (1)*
S(10)′	3857 (5)	2627 (3)	1294 (6)	59 (1)
C(11)	3816 (3)	1583 (2)	548 (3)	50 (1)*
C(12)	5125 (2)	963 (1)	1394 (2)	41 (1)*
C(13)	5089 (3)	475 (2)	2591 (3)	52 (1)*
C(14)	6363 (3)	−55 (2)	3362 (3)	59 (1)*
C(15)	7632 (3)	−99 (2)	2916 (3)	55 (1)*

Occupancy factor for S(4), C(5), C(6), S(7), C(8), C(9) and S(10): $f = 0\cdot837\,(2)$; occupancy factor for corresponding primed atoms: $f' = 1 - f$.

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

N(1)—C(2)	1·341 (3)	C(2)—N(1)—C(12)	118·3 (2)
N(1)—C(12)	1·339 (3)	N(1)—C(2)—C(3)	115·7 (2)
C(2)—C(3)	1·505 (4)	N(1)—C(2)—C(15)	122·6 (3)
C(2)—C(15)	1·383 (4)	C(3)—C(2)—C(15)	121·6 (2)
C(3)—S(4)	1·837 (2)	C(2)—C(3)—S(4)	112·3 (2)
S(4)—C(5)	1·803 (3)	C(3)—S(4)—C(5)	102·1 (1)
C(5)—C(6)	1·488 (4)	S(4)—C(5)—C(6)	114·4 (3)
C(6)—S(7)	1·820 (4)	C(5)—C(6)—S(7)	116·6 (3)
S(7)—C(8)	1·804 (3)	C(6)—S(7)—C(8)	100·8 (2)
C(8)—C(9)	1·516 (5)	S(7)—C(8)—C(9)	114·5 (2)
C(9)—S(10)	1·815 (3)	C(8)—C(9)—S(10)	114·6 (2)
S(10)—C(11)	1·830 (3)	C(9)—S(10)—C(11)	103·5 (1)
C(11)—C(12)	1·497 (3)	S(10)—C(11)—C(12)	112·9 (1)
C(12)—C(13)	1·391 (4)	C(11)—C(12)—C(13)	122·0 (2)
C(13)—C(14)	1·373 (3)	N(1)—C(12)—C(11)	115·9 (2)
C(14)—C(15)	1·379 (5)	N(1)—C(12)—C(13)	122·1 (2)
		C(12)—C(13)—C(14)	119·0 (3)
		C(13)—C(14)—C(15)	119·3 (3)
		C(2)—C(15)—C(14)	118·7 (2)
C(3)—S(4)′	1·639 (7)	C(2)—C(3)—S(4)′	124·0 (3)
S(4)′—C(5)′	1·802 (13)	C(3)—S(4)′—C(5)′	98·5 (6)
C(5)′—C(6)′	1·481 (22)	S(4)′—C(5)′—C(6)′	108·1 (9)
C(6)′—S(7)′	1·802 (13)	C(5)′—C(6)′—S(7)′	111·7 (8)
S(7)′—C(8)′	1·795 (13)	C(6)′—S(7)′—C(8)′	93·1 (8)
C(8)′—C(9)′	1·506 (13)	S(7)′—C(8)′—C(9)′	112·0 (9)
C(9)′—S(10)′	1·801 (12)	C(8)′—C(9)′—S(10)′	107·7 (9)
S(10)′—C(11)	1·798 (5)	C(9)′—S(10)′—C(11)	94·4 (5)
		S(10)′—C(11)—C(12)	120·6 (2)

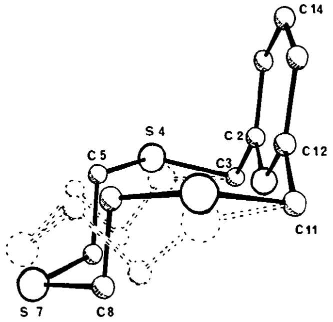

Fig. 1. The chair conformation of the heterocycle and the minor-component conformation (broken lines). Radii are arbitrary.

The predominantly occupied chair form of the heterocycle as displayed in Fig. 1, is probably best described by the following planes: (*A*) = N(1), C(2), C(12), C(13), C(14) and C(15), coplanar to within ±0·009 Å; (*B*) = N(1), C(3), S(4), C(5), C(9), S(10) and C(11), coplanar to within ±0·16 Å; (*C*) = C(5), C(6), C(8) and C(9), coplanar to within ±0·014 Å; (*D*) = C(6), S(7) and C(8); (*E*) = N(1), C(3), C(6), C(8) and C(11), coplanar to within ±0·05 Å; dihedral angles: (*A*)/(*B*) = 84·0, (*A*)/(*C*) = 3·2, (*A*)/(*D*) = 71·0, (*A*)/(*E*) = 57·3°; (*B*)/(*C*) = 87·1, (*B*)/(*D*) = 13·0, (*B*)/(*E*) = 26·7°; (*C*)/(*D*) = 74·2, (*C*)/(*E*) = 60·5, (*D*)/(*E*) = 13·8° (mean e.s.d. = 1°). The sequence of endocyclic torsion angles (see Table 3) reflects the (non-crystallographic) mirror running through S(7), N(1) and C(14). It seems remarkable that no torsion about a C—C bond is *gauche* as is normally observed, even with uncomplexed '12-crown-4' (Groth, 1978) or

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† Lists of H-atom parameters, anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38258 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

with 1,4,8,11-tetrathiacyclotetradecane [in its $Cu(ClO_4)_2$ complex] (Glick *et al.*, 1976). Strained torsion angles of 90 to 110° may be attributed to the small ring size [*cf.* '12-crown-4' (Groth, 1978)] as compared to the large diameter of the S atoms, whilst the pyridine moiety does not necessarily induce conformational irregularities (Maverick, Grossenbacher & Trueblood, 1979; Weber, 1982).

Ca 16% occupied and hence less precisely determined minor-component positions may indicate a relatively small energy difference between the major and minor conformation. In the latter, the coplanarity of the four heteroatoms (within ± 0·09 Å) and the angle $N(1)\cdots S(7)'/S(4)'\cdots S(10)' = 89{\cdot}8\ (7)°$ meet two conditions required for transition-metal complexes with regular coordination polyhedra. From the $N(1)\cdots S(7)'$ distance of 4·42 (1) Å as compared to the sum of the van der Waals radii of N and S = 3·35 Å (*Handbook of Chemistry and Physics*, 1970), cations with $r = 0{\cdot}5$ to *ca* 0·7 Å should be suitable guest species. The same procedure, applied to $S(4)'\cdots S(10)' = 6{\cdot}51\ (2)$ Å, however, results in $r = 1{\cdot}4$ to *ca* 1·6 Å. Therefore it might be assumed that (*a*) the ligand has to adopt a third conformation on coordinating (which seems rather doubtful in view of the restricted flexibility of the small macrocycle) or (*b*) that not all heteroatoms will serve as electron donors; the latter might explain some unusual stoicheiometric ligand:cation ratios (Weber & Vögtle, 1976).

Pyridine nuclei related by inversion at $\frac{1}{2}$,0,0, are 3·59 (2) Å apart; this distance and an overlap of *ca* 15% will probably not allow appreciable $\pi\cdots\pi$ interactions.

Table 3. *Torsion angles* (°)

C(12)–N(1)–C(2)–C(3)	−179·0 (2)		
C(12)–N(1)–C(2)–C(15)	−1·2 (3)		
C(2)–N(1)–C(12)–C(11)	178·4 (2)		
C(2)–N(1)–C(12)–C(13)	−0·4 (3)		
N(1)–C(2)–C(3)–S(4)	109·2 (2)	N(1)–C(2)–C(3)–S(4)′	99·9 (3)
C(15)–C(2)–C(3)–S(4)	−68·7 (3)	C(15)–C(2)–C(3)–S(4)′	−78·0 (4)
N(1)–C(2)–C(15)–C(14)	1·6 (3)		
C(3)–C(2)–C(15)–C(14)	179·4 (2)		
C(2)–C(3)–S(4)–C(5)	−51·4 (2)	C(2)–C(3)–S(4)′–C(5)′	−69·9 (7)
C(3)–S(4)–C(5)–C(6)	−68·0 (3)	C(3)–S(4)′–C(5)′–C(6)′	99·7 (11)
S(4)–C(5)–C(6)–S(7)	176·0 (2)	S(4)′–C(5)′–C(6)′–S(7)′	−176·7 (9)
C(5)–C(6)–S(7)–C(8)	−90·8 (3)	C(5)′–C(6)′–S(7)′–C(8)′	112·2 (12)
C(6)–S(7)–C(8)–C(9)	92·2 (3)	C(6)′–S(7)′–C(8)′–C(9)′	−103·1 (11)
S(7)–C(8)–C(9)–S(10)	−177·7 (2)	S(7)′–C(8)′–C(9)′–S(10)′	178·9 (8)
C(8)–C(9)–S(10)–C(11)	67·5 (2)	C(8)′–C(9)′–S(10)′–C(11)′	−110·1 (10)
C(9)–S(10)–C(11)–C(12)	49·3 (2)	C(9)′–S(10)′–C(11)–C(12)	66·4 (5)
S(10)–C(11)–C(12)–C(13)	73·3 (3)	S(10)′–C(11)–C(12)–C(13)	84·0 (3)
S(10)–C(11)–C(12)–N(1)	−105·5 (2)	S(10)′–C(11)–C(12)–N(1)	−94·7 (3)
N(1)–C(12)–C(13)–C(14)	1·5 (3)		
C(11)–C(12)–C(13)–C(14)	−177·2 (2)		
C(12)–C(13)–C(14)–C(15)	−1·0 (4)		
C(13)–C(14)–C(15)–C(2)	−0·5 (4)		

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Ethyl [1,2,4]Triazolo[1,5-*a*]pyridine-2-carboxylate, $C_9H_9N_3O_2$

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Abstract. $M_r = 191{\cdot}189$, monoclinic, $P2_1/c$, $a = 9{\cdot}853\ (3)$, $b = 6{\cdot}232\ (3)$, $c = 16{\cdot}020\ (3)$ Å, $\beta = 106{\cdot}45\ (2)°$, $V = 943{\cdot}4\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}316$, $D_m = 1{\cdot}34$ Mg m^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}7833$ mm^{-1}, $\lambda = 1{\cdot}5418$ Å, $F(000) = 400$. Final $R = 0{\cdot}056$ for 1350 observed reflections. The molecules, which are practically planar, are held together only by van der Waals interactions.

Introduction. The structure of the title compound has been determined and refined to characterize unambiguously the conformation of the molecule and the positions of the N atoms.

Experimental. Samples provided by Drs C. Avendaño and E. Gomez-Molinero from the Departamento de Química Orgánica de la Facultad de Farmacia de la

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