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3,3,10,10-Tetramethyl-1,2-dithia-5,8-diazacyclodeca-4,8-diene

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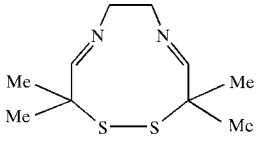
The title compound, $C_{10}H_{18}N_2S_2$, acts as an important precursor for the synthesis of the pharmaceutically important diaminedithiol ligand system. The molecule has a local twofold axis and the arrangement of the S_2N_2 donor atoms in the macrocycle is anticlinal.

Comment

The diaminedithiol ligand system had been employed for complexation with ^{99m}Tc to produce significant radiopharmaceuticals (Lever *et al.*, 1985; Cheesman *et al.*, 1988; Kung *et al.*, 1989; Scheffel *et al.*, 1998). Diaminedithiol ligands have also been synthetically modified into bifunctional chelating agents for carrying ^{99m}Tc, as well as for coupling to bioactive molecules, such as proteins, antibodies and peptides (Baidoo & Lever, 1990; Baidoo *et al.*, 1998). ^{99m}Tc-labelled biomolecules exhibit the potential for use in non-invasive *in vivo* imaging of cancers (Baidoo *et al.*, 1998). In the synthesis of diaminedithiol ligands, or of derivatives that are bifunctional chelating agents, the title compound, (I), is an important precursor. We describe here the preparation of (I) and its X-ray crystal structure, which may further support its identification by NMR and elemental analysis. The cyclic structure of (I) is in contrast with the linear structure of the diaminedithiol compound obtained from a reduction reaction of (I) (Baidoo & Lever, 1990; Baidoo *et al.*, 1998).



(I)

In (I), two symmetrical aliphatic units ($Me_2C-C{=}N-C$) of nearly identical geometry are connected by an S1—S2 bond [2.0201 (10) Å], thus forming a four-atom-donor macrocycle (Fig. 1). The S1—S2 bond length is slightly shorter than that in 6-ethoxycarbonyl-3,3,10,10-tetramethyl-1,2-dithia-5,8-diazadeca-4,8-diene [2.025 (1) Å; Wrench *et al.*, 1993]. This shorter length may be mainly due to the intermolecular interaction of the outward-branched 6-ethoxycarbonyl group from the ring in the latter compound. The molecule contains two double bonds (C4═N5 and C9═N8), with essentially planar atomic arrangements [C3—C4═N5—C6 = −171.6 (2)° and C7—N8═C9—C10 = −173.3 (2)°]. The torsion angles associated with the donor atoms [N5═C4—C3—S2 = 123.8 (2)° and N8═C9—C10—S1 = 123.4 (2)°] show that the donor-atom arrangement is anticlinal. The bond distances (Table 1) are in good agreement with standard values. The crystal structure is mainly stabilized by van der Waals forces, and no hydrogen bonds or π–π interactions are observed.

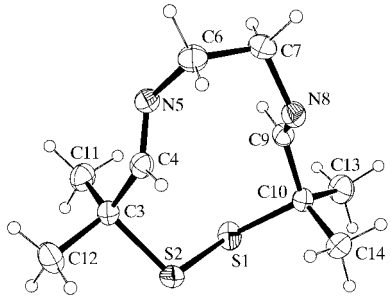


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids.

Experimental

The title compound was synthesized following a procedure similar to that reported by Merz & Specker (1963), by condensation of 2,2-dithiobis(2-methylpropanal) with ethylenediamine in a 1:5 molar ratio. The former compound was synthesized from the reaction of isobutylaldehyde with sulfur monochloride according to the procedure reported by Baidoo (1988). The reaction was exothermic, so external cooling to keep the temperature below 298 K was needed. The resulting yellow solid was separated and washed successively with cold methanol and ether until the product became white. The white solid was then dissolved in ethyl acetate and the solution filtered, yielding a clear solution. This solution was allowed to stand at room temperature for a few days, whereupon crystals of (I) suitable for X-ray structure analysis were formed (m.p. 437–438 K). ^{1}H NMR ($CDCl_3$): δ $C(CH_3)_2$ 1.34, 1.42, 2*s*, 12H; ═NCH_2-CH_2N═ 3.20, 3.23, 4.11, 4.14, 2*d*, 4H; N═CH 6.84, *s*, 2H. ^{13}C NMR ($CDCl_3$): δ 21.49, 24.67, 53.09, 61.53, 78.04. Analysis calculated for $C_{10}H_{18}N_2S_2$: C 52.11, H 7.87, N 12.20, S 27.82%; found: C 51.95, H 8.31, N 12.18, S 28.81%.

Crystal data

$C_{10}H_{18}N_2S_2$
M_r = 230.38
Orthorhombic, $P2_12_12_1$
a = 8.7393 (9) Å
b = 8.9284 (9) Å
c = 15.9117 (17) Å
V = 1241.6 (2) Å^3
Z = 4
D_x = 1.233 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8043 reflections
θ = 2.6–28.2°
μ = 0.40 mm^{-1}
T = 294 (2) K
Parallelepiped, colourless
0.28 × 0.20 × 0.15 mm

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Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.807, T_{max} = 0.891
8043 measured reflections
2963 independent reflections
2057 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 28.2°
$h = -11 \rightarrow 10$
$k = -11 \rightarrow 7$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.084
S = 1.03
2963 reflections
127 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 0.0808P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Flack (1983), 1172 Friedel pairs
Flack parameter = 0.01 (10)

Table 1
Selected geometric parameters (Å, °).

S1—C10	1.865 (2)	N5—C6	1.457 (3)
S1—S2	2.0201 (10)	C6—C7	1.525 (3)
S2—C3	1.865 (2)	C7—N8	1.460 (3)
C3—C4	1.498 (3)	N8—C9	1.255 (3)
C4—N5	1.252 (3)	C9—C10	1.501 (3)
C10—S1—S2	109.32 (8)	C11—C3—C12	112.0 (2)
C3—S2—S1	109.26 (8)	C4—C3—S2	106.40 (15)
C4—C3—C11	113.6 (2)	C11—C3—S2	112.61 (19)
C4—C3—C12	109.6 (2)	C12—C3—S2	101.91 (17)

H atoms bonded to C atoms were positioned geometrically and treated as riding [U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for other H atoms].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1167). Services for accessing these data are described at the back of the journal.

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