

(KBr) 1752 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.12 [s, 9, C(CH<sub>3</sub>)<sub>3</sub>], 1.30 (s, 3, angular CH<sub>3</sub>), 2.27 (s, 3, SCH<sub>3</sub>), 3.59–3.67 [m, 1, CHOC(CH<sub>3</sub>)<sub>3</sub>], 4.75 (d, J = 4.6 Hz, 1, CHCl); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 15.3, 17.6, 21.8, 23.6, 28.7, 29.9, 30.0, 47.3, 52.0, 56.3, 56.8, 60.5, 72.8, 94.1, 209.0. Elemental analysis for C<sub>17</sub>H<sub>27</sub>ClO<sub>2</sub>S: calculated C 61.70, H 8.22%; found C 61.62, H 8.35%.

Most of the reflections from TRICYC correspond to the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub> but a small number appear to define a monoclinic supercell. The two cells are related by the matrix equation  $a_{\text{monoclinic}} = (1\ 0\ 1 / 0\ 1\ 0 / -1\ 0\ 2) a_{\text{orthorhombic}}$ ; the constants of the larger ( $V_{\text{monoclinic}} = 3V_{\text{orthorhombic}}$ ) monoclinic cell are  $a = 14.694$  (2),  $b = 17.837$  (2),  $c = 20.278$  (1) Å and  $\beta = 93.96$  (1)°. Data corresponding to the smaller cell were measured at Enraf-Nonius in New York. Data for the apparent supercell were also collected for a quadrant of reciprocal space having  $2\theta < 50^\circ$ , but, of the 3924 reflections having  $h + l \neq 3n$ , only 30 had  $l > 3\sigma(l)$ . Since there are no indications in the anisotropic displacement parameters of the fully refined structure (see Figs. 1 and 2) of disorder or of any unusual patterns, it is possible that the extra reflections correspond to a second (and much smaller) individual of a twin. The diffraction patterns of three other crystals from the same batch could not be indexed automatically, presumably because they were twins.

All calculations were performed at the University of Kentucky. As part of the data processing, intensities of reflections having  $l < 3\sigma(l)$  were set equal to zero if the only counts available were for the fast (10.2° min<sup>-1</sup> in  $\omega$ ) prescan. The Cl and S atoms were located using the *MULTAN77* direct-methods package (Main, Lessinger, Woolfson, Germain & Declercq, 1977); the remainder of the molecule was then revealed by the *DIRDIF* program (Beurskens *et al.*, 1983). Methyl H atoms could be located in difference Fourier maps. The H atoms were idealized at a late point in the refinement and added as fixed contributions (C–H = 1.00 Å; B values 1 Å<sup>2</sup> greater than  $B_{\text{eq}}$  of the attached C atom). Inclusion of an isotropic extinction coefficient improved the agreement factor  $R$  from 0.047 to 0.042 {extinction correction:  $k|F_c| = F_o[x^* + (1 + x^{*2})^{1/2}]^{1/2}$ , where  $x^* = (EC)\beta I_{\text{int}}$ ; the value of  $EC$  is refined,  $\beta = [1 + \cos^2(2\theta_{\text{monoclinic}})] \times [1 + \cos^2(2\theta_{\text{monoclinic}})\cos^4(2\theta)] / [1 + \cos^2(2\theta_{\text{monoclinic}})\cos^2(2\theta)]^2$ , and  $I_{\text{int}}$  is the integrated intensity before correction for Lorentz and polarization effects; see equations (3) and (4) of Zachariasen (1968)}. The absolute chirality was assigned on the basis of refinements of the two enantiomers and was consistent with the synthetic pathway; the ratio of the  $wR$  factors for the two enantiomers is 1.32 ( $R = 0.054$ ,  $wR = 0.075$ ,  $S = 4.37$  for the other enantiomer), which means that the enantiomer choice is essentially certain [ $N = 1266$  and  $\alpha < 1 \times 10^{-4}$  (Rogers, 1981)]. The largest peaks and deepest troughs in the final difference map are associated with the S and Cl atoms and with the centers of the C–C bonds.

Data collection: *CAD-4VAX* (Enraf-Nonius, 1988). Cell refinement: *CAD-4VAX*. Data reduction: local program (Brock). Program(s) used to refine structure: local program based on Ibers's version of *ORFLS* (Busing, Martin & Levy, 1962). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *ORFFE* (Busing, Martin & Levy, 1964) and a local program (Brock).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71444 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1062]

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. J. (1987). *Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, Th. E. M., Prick, P. A., Noordik, J. H., Beurskens, G., Parthasarathi, V., Bruins Slot, H. J. & Haliwanger, R. C. (1983). *DIRDIF*. Technical Report 1983/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
- Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.
- Enraf-Nonius (1988). *CAD-4 Manual*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Hajos, Z. G. & Parrish, D. R. (1974). *J. Org. Chem.* **39**, 1615–1621.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Richardson, S. K., Sabol, M. R. & Watt, D. S. (1989). *Synth. Commun.* **19**, 359–367.
- Rogers, D. (1981). *Acta Cryst.* **A37**, 734–741.
- Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

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## Structure of a Cyclophane Containing a 1,5,2,4,6,8-Dithiatetrazocine Ring

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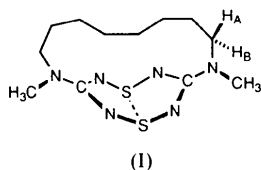
### Abstract

(*N,N'*-Dimethyl-*N,N'*-octamethylene-3,7-diamino)-1,5,2,4,6,8-dithiatetrazocine, C<sub>12</sub>H<sub>22</sub>N<sub>6</sub>S<sub>2</sub>, is the first cyclophane to contain the dithiatetrazocine ring system. The heterocycle is sharply folded, with a dihedral angle of 101.8°, along an axis drawn through the two S atoms. The bridging octamethylene chain passes over one side, rather than over the center, of the heterocyclic ring.

### Comment

The 1,5,2,4,6,8-dithiatetrazocines, first reported by the Woodward group (Ernest *et al.*, 1981), exhibit a remarkable structural dichotomy. In derivatives where the 3,7-substituent groups are aryl (Ernest *et al.*, 1981), *tert*-butyl (Gleiter, Bartetzko & Cremer, 1984), furyl or thienyl (Amin & Rees, 1989), the heterocycle is planar and easily understood as a ten  $\pi$ -electron aromatic system. However, where both (Ernest *et al.*, 1981) or one (Amin & Rees, 1989) of the substituents is a dimethylamino group, the heterocycle is sharply folded, with a dihedral angle of  $101^\circ$  in the one crystallographically characterized example (Ernest *et al.*, 1981).

The synthesis of compound (I) has been outlined previously (Pascal, 1993). This compound is the first cyclophane to contain a 1,5,2,4,6,8-dithiatetrazocine ring, which, because of the diamine substitution, is expected to be folded. In addition, the 500 MHz  $^1\text{H}$  NMR spectrum of this material shows a single methyl resonance ( $\delta$  2.98) but two  $\alpha$ -methylene resonances ( $\delta$  2.86 and 4.38,  $\text{H}_A$  and  $\text{H}_B$ ), clearly indicating that only one isomer of the bridging chain, with either *cis* or *trans* methyl groups, is present in solution. In order to confirm the folded structure and to establish the stereochemistry of the bridging chain, a single-crystal analysis of compound (I) was performed.



The crystal structure establishes the stereochemistry of the methyl groups to be *cis*, and that the bridging octamethylene chain passes over one side rather than over the center of the dithiatetrazocine ring. As expected, the dithiatetrazocine ring itself is folded along an axis drawn through the two S atoms. The least-squares plane containing S(1), S(2), N(1), N(2), N(5), C(1), C(3) and C(4), and the plane containing S(1), S(2), N(3), N(4), N(6), C(2), C(11), and C(12) intersect at an angle of  $101.8^\circ$ , which is nearly identical to the dihedral angle of  $101^\circ$  reported for the corresponding planes in the structure of 3,7-bis(dimethylamino)-1,5,2,4,6,8-dithiatetrazocine (Ernest *et al.*, 1981). Furthermore, the bond distances and angles for the dithiatetrazocine ring of (I), and in particular the short S...S distance of  $2.408(2) \text{ \AA}$ , are all quite similar to the corresponding data reported for the compound of Ernest *et al.* Thus, the octamethylene chain in (I) appears to be too long to have much effect on the conformation of the bent heterocycle.

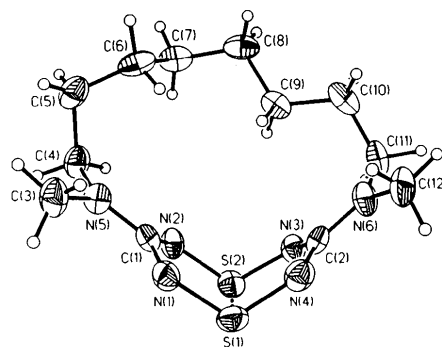


Fig. 1. A view of compound (I) showing the labeling of the non-H atoms. Thermal ellipsoids are drawn at the 50% probability level and H atoms appear as small circles of arbitrary size.

### Experimental

#### Crystal data

$\text{C}_{12}\text{H}_{22}\text{N}_6\text{S}_2$   
 $M_r = 314.5$   
 Monoclinic  
*Cc*  
 $a = 8.497(1) \text{ \AA}$   
 $b = 20.881(4) \text{ \AA}$   
 $c = 9.541(2) \text{ \AA}$   
 $\beta = 115.72(1)^\circ$   
 $V = 1524.9(4) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.370 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 9\text{--}16.5^\circ$   
 $\mu = 0.350 \text{ mm}^{-1}$   
 $T = 240 \text{ K}$   
 Prism  
 $0.20 \times 0.12 \times 0.12 \text{ mm}$   
 Yellow  
 Crystal source: from  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$

#### Data collection

Siemens P4 diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 2504 measured reflections  
 2389 independent reflections  
 1650 observed reflections  
 $[F > 3.0\sigma(F)]$

$R_{\text{int}} = 0.0149$   
 $\theta_{\text{max}} = 30^\circ$   
 $h = -1 \rightarrow 11$   
 $k = -2 \rightarrow 29$   
 $l = -13 \rightarrow 12$   
 3 standard reflections monitored every 97 reflections  
 intensity variation:  $<2.0\%$

#### Refinement

Refinement on  $F$   
 $R = 0.0576$   
 $wR = 0.0507$   
 $S = 1.17$   
 1650 reflections  
 179 parameters  
 H atoms: riding model  
 $[\text{C}—\text{H} = 0.96 \text{ \AA},$   
 $U(\text{H}) = 1.2U(\text{C})]$

$w = [\sigma^2(F) + 0.0004F^2]^{-1}$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	<i>U</i> <sub>eq</sub>
S(1)	0.1563	0.1611 (1)	0.0696	0.039 (1)
S(2)	0.0103 (3)	0.2326 (1)	-0.1464 (2)	0.036 (1)
N(1)	0.1492 (6)	0.1057 (2)	-0.0498 (5)	0.036 (2)
N(2)	-0.0007 (6)	0.1757 (2)	-0.2632 (5)	0.035 (2)
N(3)	-0.1527 (6)	0.2357 (2)	-0.1057 (6)	0.036 (2)
N(4)	-0.0149 (7)	0.1620 (2)	0.1014 (6)	0.041 (2)
N(5)	0.0368 (7)	0.0692 (2)	-0.3013 (5)	0.036 (2)
N(6)	-0.3056 (7)	0.1882 (2)	0.0136 (6)	0.037 (2)
C(1)	0.0569 (7)	0.1174 (3)	-0.2033 (7)	0.031 (2)
C(2)	-0.1569 (8)	0.1940 (3)	0.0012 (6)	0.031 (2)
C(3)	0.1265 (9)	0.0079 (3)	-0.2451 (8)	0.049 (3)
C(4)	-0.0584 (8)	0.0766 (3)	-0.4700 (6)	0.040 (2)
C(5)	-0.2034 (9)	0.0275 (3)	-0.5392 (7)	0.047 (3)
C(6)	-0.3446 (9)	0.0329 (3)	-0.4813 (7)	0.046 (3)
C(7)	-0.4694 (8)	0.0884 (3)	-0.5533 (7)	0.042 (2)
C(8)	-0.5770 (8)	0.1060 (3)	-0.4665 (7)	0.044 (2)
C(9)	-0.4698 (8)	0.1458 (3)	-0.3202 (7)	0.040 (2)
C(10)	-0.5695 (8)	0.1685 (3)	-0.2322 (8)	0.049 (3)
C(11)	-0.4698 (8)	0.2147 (3)	-0.1037 (7)	0.044 (3)
C(12)	-0.3163 (9)	0.1473 (3)	0.1334 (7)	0.048 (3)

Table 2. Geometric parameters (Å, °)

S(1)—S(2)	2.408 (2)	S(1)—N(1)	1.606 (5)
S(1)—N(4)	1.610 (7)	S(2)—N(2)	1.604 (5)
S(2)—N(3)	1.593 (7)	N(1)—C(1)	1.350 (7)
N(2)—C(1)	1.343 (7)	N(3)—C(2)	1.353 (8)
N(4)—C(2)	1.348 (7)	N(5)—C(1)	1.334 (8)
N(5)—C(3)	1.466 (7)	N(5)—C(4)	1.463 (7)
N(6)—C(2)	1.324 (10)	N(6)—C(11)	1.467 (7)
N(6)—C(12)	1.460 (9)	C(4)—C(5)	1.516 (9)
C(5)—C(6)	1.528 (12)	C(6)—C(7)	1.518 (8)
C(7)—C(8)	1.521 (11)	C(8)—C(9)	1.537 (8)
C(9)—C(10)	1.505 (11)	C(10)—C(11)	1.500 (8)
S(2)—S(1)—N(1)	89.6 (2)	S(2)—S(1)—N(4)	89.0 (2)
N(1)—S(1)—N(4)	112.5 (3)	S(1)—S(2)—N(2)	89.3 (2)
S(1)—S(2)—N(3)	89.8 (2)	N(2)—S(2)—N(3)	113.8 (3)
S(1)—N(1)—C(1)	117.7 (4)	S(2)—N(2)—C(1)	118.4 (4)
S(2)—N(3)—C(2)	117.9 (4)	S(1)—N(4)—C(2)	118.4 (5)
C(1)—N(5)—C(3)	121.0 (4)	C(1)—N(5)—C(4)	122.2 (5)
C(3)—N(5)—C(4)	116.5 (5)	C(2)—N(6)—C(11)	121.7 (6)
C(2)—N(6)—C(12)	120.6 (5)	C(11)—N(6)—C(12)	117.1 (6)
N(1)—C(1)—N(2)	123.9 (5)	N(1)—C(1)—N(5)	117.5 (5)
N(2)—C(1)—N(5)	118.3 (5)	N(3)—C(2)—N(4)	123.1 (6)
N(3)—C(2)—N(6)	117.7 (5)	N(4)—C(2)—N(6)	119.1 (6)
N(5)—C(4)—C(5)	111.4 (5)	C(4)—C(5)—C(6)	114.1 (6)
C(5)—C(6)—C(7)	113.4 (6)	C(6)—C(7)—C(8)	113.9 (6)
C(7)—C(8)—C(9)	111.4 (5)	C(8)—C(9)—C(10)	114.9 (5)
C(9)—C(10)—C(11)	113.8 (6)	N(6)—C(11)—C(10)	113.2 (5)

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71432 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1065]

## References

Amin, M. & Rees, C. W. (1989). *J. Chem. Soc. Perkin Trans. 1*, pp. 2495–2501.

Ernest, I., Holick, W., Rihs, G., Schomburg, D., Shoham, G., Wenkert, D. & Woodward, R. B. (1981). *J. Am. Chem. Soc.* **103**, 1540–1544.  
Gleiter, R., Bartetzko, R. & Cremer, D. (1984). *J. Am. Chem. Soc.* **106**, 3437–3442.  
Pascal, R. A. Jr (1993). *Pure Appl. Chem.* **65**, 105–110.  
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Release 4.21. Siemens Analytical Instruments Inc., Madison, Wisconsin, USA.

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## Structure du L-2-(1,2:5,6-Di-*O*-isopropylidène- $\alpha$ -D-allofuranos-3-yl)-dibenzylglycinate de *tert*-Butyle, C<sub>32</sub>H<sub>43</sub>NO<sub>8</sub>

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## Abstract

The condensation reaction of the enolate of *tert*-butyl dibenzylaminoacetate with the carbonyl of 1,2:5,6-di-*O*-isopropylidène- $\alpha$ -D-ribo-hexofuranos-3-ulose is diastereoselective and leads to the title compound with absolute stereochemistry 2*S*,3'*R*. The furanose ring has a half-chair conformation. An intramolecular hydrogen bond links the hydroxyl group at C3' to the carboxyl O atom of the glycinate group.

## Commentaire

La condensation de l'énolate issu du dibenzylaminoacétate de *tert*-butyle sur le carbonyle du 1,2:5,6-di-*O*-isopropylidène- $\alpha$ -D-ribo-hexofuranos-3-ulose est doublement diastéréosélective. Elle conduit exclusivement au stéréoisomère 2*S*,3'*R* du glycosyl- $\alpha$ -amino ester (1) dont la stéréochimie a été précisée par la détermination de

