

O43	0.1423 (2)	0.1025 (2)	-0.08178 (12)	0.0516 (4)
C41	0.0532 (2)	0.1785 (2)	-0.1751 (2)	0.0403 (5)
C42	-0.0647 (2)	0.3016 (2)	-0.1618 (2)	0.0396 (5)
C43	-0.1683 (3)	0.3938 (2)	-0.2643 (2)	0.0533 (6)

Table 2. Selected bond lengths (Å) and angles (°)

N11—C12	1.278 (3)	N31—C32	1.275 (2)
N11—O11	1.378 (2)	N31—O31	1.381 (2)
O12—C11	1.212 (2)	O32—C31	1.211 (2)
O13—C11	1.313 (2)	O33—C31	1.316 (2)
C11—C12	1.489 (3)	C31—C32	1.487 (3)
C12—C13	1.484 (3)	C32—C33	1.485 (3)
N21—C22	1.273 (2)	N41—C42	1.269 (2)
N21—O21	1.380 (2)	N41—O41	1.383 (2)
O22—C21	1.210 (2)	O42—C41	1.212 (2)
O23—C21	1.314 (2)	O43—C41	1.313 (2)
C21—C22	1.493 (3)	C41—C42	1.488 (3)
C22—C23	1.482 (3)	C42—C43	1.485 (3)
C12—N11—O11	113.0 (2)	C32—N31—O31	113.0 (2)
O12—C11—O13	125.0 (2)	O32—C31—O33	124.7 (2)
O12—C11—C12	120.5 (2)	O32—C31—C32	121.0 (2)
O13—C11—C12	114.5 (2)	O33—C31—C32	114.3 (2)
N11—C12—C13	126.2 (2)	N31—C32—C33	125.7 (2)
N11—C12—C11	115.2 (2)	N31—C32—C31	115.0 (2)
C13—C12—C11	118.6 (2)	C33—C32—C31	119.4 (2)
C22—N21—O21	112.7 (2)	C42—N41—O41	112.4 (2)
O22—C21—O23	124.8 (2)	O42—C41—O43	124.8 (2)
O22—C21—C22	120.0 (2)	O42—C41—C42	120.2 (2)
O23—C21—C22	115.2 (2)	O43—C41—C42	115.0 (2)
N21—C22—C23	125.8 (2)	N41—C42—C43	125.6 (2)
N21—C22—C21	115.7 (2)	N41—C42—C41	116.3 (2)
C23—C22—C21	118.5 (2)	C43—C42—C41	118.1 (2)

Table 3. Selected dihedral angles (°)

Plane *A* is defined by atoms Ox2, Ox3, Cx1 and Cx2, and plane *B* is defined by atoms Cx1, Cx2, Nx1 and Ox1, where *x* is 1, 2, 3 and 4 for molecules (I), (II), (III) and (IV), respectively.

A(I) ^ B(I)	8.4 (3)	A(III) ^ B(III)	0.6 (3)
B(I) ^ A(II)	9.4 (3)	B(III) ^ A(IV)	0.1 (3)
A(II) ^ B(II)	1.6 (2)	A(IV) ^ B(IV)	0.8 (2)
B(II) ^ A(III)	3.2 (2)	B(IV) ^ A(I)	6.9 (2)

All non-H atoms were found from an *E* map. Most of the H atoms were localized from the  $\Delta\rho$  map including those of the disordered methyl groups. All non-H atoms were refined with anisotropic displacement parameters. The oxime and carboxyl H atoms were refined with isotropic displacement parameters, whereas the disordered methyl H atoms were placed in calculated positions and their site occupation and isotropic displacement parameters refined.

Data collection: Kuma KM-4 system (Kuma, 1991). Cell refinement: Kuma KM-4 system. Data reduction: Kuma KM-4 system. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1262). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Fuson, R. C. (1962). *Reactions of Organic Compounds*, p. 406. New York: John Wiley.

Gielen, A., Hübner, T. & Ruiz-Perez, C. (1986a). *Chem. Ztg.* **110**, 73–76.

Gielen, A., Hübner, T. & Ruiz-Perez, C. (1986b). *Chem. Ztg.* **110**, 76–78.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kuma (1991). *KM-4 Diffractometer Operating System and Data Reduction Software*. Kuma Diffraction, Wrocław, Poland.

Maurin, J. K., Leś, A. & Winnicka-Maurin, M. (1995). *Acta Cryst.* **B51**, 232–240.

Maurin, J. K., Paul, I. C. & Curtin, D. Y. (1992a). *Acta Cryst.* **C48**, 2163–2165.

Maurin, J. K., Paul, I. C. & Curtin, D. Y. (1992b). *Acta Cryst.* **C48**, 2165–2167.

Maurin, J. K., Paul, I. C. & Curtin, D. Y. (1994). *Acta Cryst.* **C50**, 78–81.

Padmanabhan, K., Paul, I. C. & Curtin, D. Y. (1989). *Acta Cryst.* **B45**, 411–416.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

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## Five-, Six- and Seven-Membered-Ring Substituted Thiazolidine-2-thione

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## Abstract

The X-ray structures of 3,3a,4,5,6,6a-hexahydro-2H-cyclopenta[d]thiazole-2-thione, (1), 3-methyl-2,3,3a,4,5,6,7,7a-octahydrobenzo[d]thiazole-2-thione, (2), and 3,3a,4,5,6,7,8,8a-octahydro-2H-cyclohepta[d]thiazole-2-thione, (3), are presented. The condensation of a five-, six- or seven-membered ring onto the C4—C5 bond of a thiazolidine-2-thione ring does not affect the flexibility of the heteroatomic ring, which adopts different

conformations in each case. In both compounds (2) and (3), C<sub>8</sub>H<sub>13</sub>NS<sub>2</sub> (six- and seven-membered condensed rings, respectively), the observed conformation is half chair, with torsion angles  $\tau$  (S1—C5—C4—N3) of 36.6 (2) and 21.3 (7)°, respectively, whereas in compound (1), C<sub>6</sub>H<sub>9</sub>NS<sub>2</sub> (five-membered condensed ring), the thiazolidine-2-thione ring is almost planar [ $\tau = 3.4$  (3)°].

### Comment

It has been shown previously, by spectroscopic (Chanon, Rajzmann, Chanon, Metzger, Pouzard & Drakenberg, 1980) and crystallographic (Kubiak & Glowing, 1982; Raper & Oughtred, 1983; Nuzzo, Pierrot, Baldy, Chanon & Chanon, 1984) studies, that the thiazolidine-2-thione ring can exhibit conformational changes according to the nature and position of the substituents of the heteroatomic ring. The aim of the study reported here was to observe whether the condensation of a five-, six- or seven-membered ring onto the C4—C5 bond of the thiazolidine-2-thione ring [giving compounds (1), (2) and (3), respectively] affects the flexibility of the heteroatomic five-membered ring.

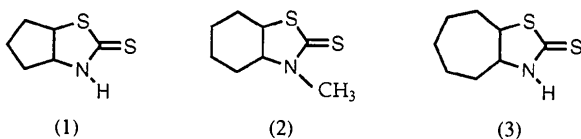


Table 2 shows that most of the bond distances and angles are remarkably conserved in the three title structures. The S1—C2 [1.751 (3) in (2), 1.732 (4) and 1.737 (8) Å in (1) and (3), respectively] and C4—C5 [1.525 (4) in (2), 1.554 (5) and 1.53 (1) Å in (2) and (3), respectively] bonds are slightly different in compounds (1), (2) and (3). Three bond-angle values are smaller in (2) than in both (1) and (3): C2—S1—C5 [91.9 (1), 94.5 (1) and 93.8 (4)° in compounds (2), (1) and (3), respectively], C2—N3—C4 [116.0 (2), 120.2 (3) and 120.2 (6)°] and C4—C5—S1 [102.7 (2), 106.2 (2) and 105.0 (5)°]. The S1—C2—S2—N3 fragment is almost perfectly planar in the three structures. The most remarkable feature is the variation of the torsion angle  $\tau$  (S1—C5—C4—N3). For compound (1),  $\tau$  is 3.4 (3)° and the thiazolidine-2-thione ring is almost planar. However, in compounds (2) and (3),  $\tau$  is 36.6 (2) and 21.3 (7)°, respectively, and each thiazolidine-2-thione ring adopts a half-chair conformation, with atom C4 on one side and atom C5 on the other side of the S1—C2—S2—N3 fragment (Table 3).

Analysis of the packing of the molecules does not indicate any particularly short intermolecular contacts, except in compound (1), where a short distance of 3.396 (3) Å is found between atom N3 and atom S2 of the related molecule along the [111] direction. This

distance is shorter than the van der Waals contact distance (3.50 Å; Allinger, 1976) and may correspond to a hydrogen bond between these atoms.

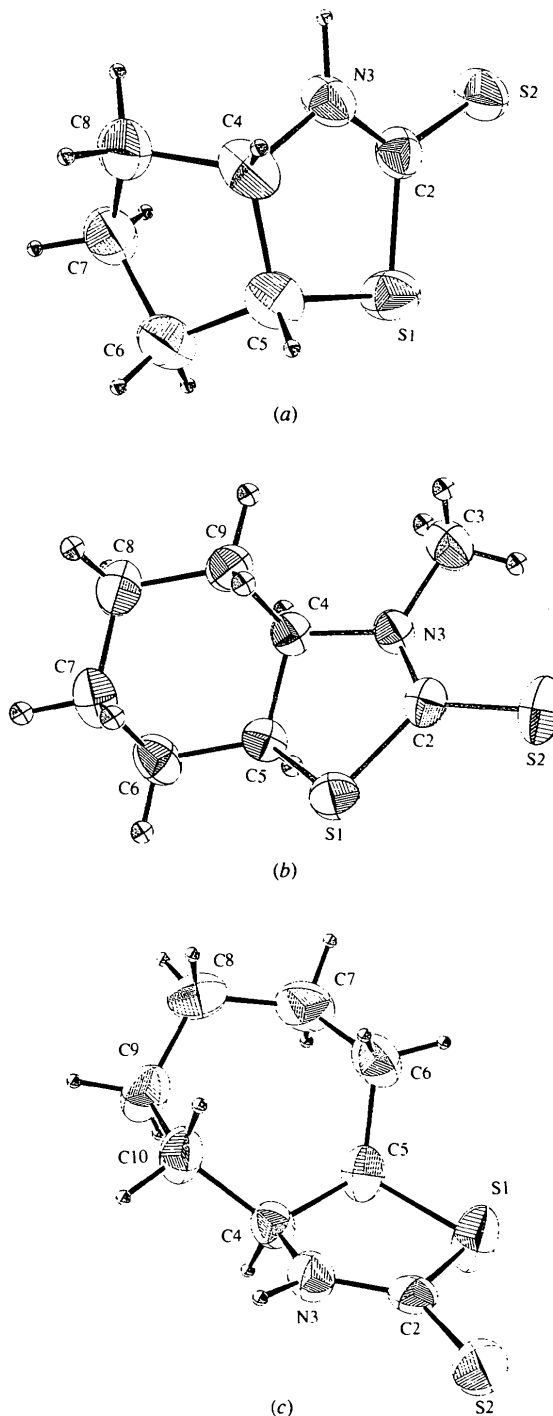


Fig. 1 ORTEP drawings (Johnson, 1976) of molecules of (a) compound (1), (b) compound (2) and (c) compound (3), with heavy atoms represented as 50% probability ellipsoids and H atoms as spheres of arbitrary radii.

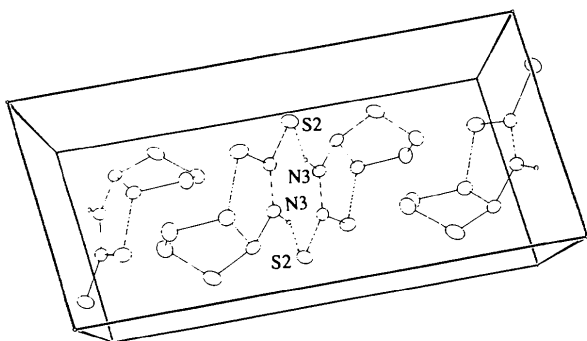


Fig. 2. The molecular packing in compound (1). The short contact between atoms N3 and S2 is indicated by a broken line.

## Experimental

The three title compounds were prepared according to the procedure described by Bafford, Chanon & Metzger (1973). They were recrystallized by evaporation at room temperature of a 50/50 *v/v* benzene/cyclohexane solution.

### Compound (1)

#### Crystal data

$C_6H_9NS_2$   
 $M_r = 159.27$   
 Monoclinic  
 $P2_1/n$   
 $a = 6.139 (3) \text{ \AA}$   
 $b = 9.231 (5) \text{ \AA}$   
 $c = 13.273 (4) \text{ \AA}$   
 $\beta = 97.26 (5)^\circ$   
 $V = 746.2 (8) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.418 \text{ Mg m}^{-3}$

#### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 none  
 1464 measured reflections  
 1404 independent reflections  
 868 observed reflections  
 $[I > 3\sigma(I)]$

#### Refinement

Refinement on  $F$   
 $R = 0.036$   
 $wR = 0.044$   
 $S = 1.356$   
 868 reflections  
 82 parameters  
 H-atom parameters not  
 refined

### Compound (2)

#### Crystal data

$C_8H_{13}NS_2$   
 $M_r = 187.33$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 25  
 reflections  
 $\theta = 12\text{--}14^\circ$   
 $\mu = 0.597 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Rectangular prism  
 $0.6 \times 0.4 \times 0.2 \text{ mm}$   
 Colourless

$R_{\text{int}} = 0.027$   
 $\theta_{\text{max}} = 25^\circ$   
 $h = -6 \rightarrow 6$   
 $k = 0 \rightarrow 11$   
 $l = 0 \rightarrow 19$   
 2 standard reflections  
 frequency: 60 min  
 intensity decay: 1%

$w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\text{max}} = 0.01$   
 $\Delta\rho_{\text{max}} = 0.546 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.513 \text{ e \AA}^{-3}$   
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$

Monoclinic  
 $P2_1/n$   
 $a = 5.359 (2) \text{ \AA}$   
 $b = 10.433 (5) \text{ \AA}$   
 $c = 16.812 (6) \text{ \AA}$   
 $\beta = 91.49 (4)^\circ$   
 $V = 939.7 (9) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.324 \text{ Mg m}^{-3}$

#### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 none  
 1622 measured reflections  
 1567 independent reflections  
 1331 observed reflections  
 $[I > 3\sigma(I)]$

#### Refinement

Refinement on  $F$   
 $R = 0.0360$   
 $wR = 0.0431$   
 $S = 0.793$   
 1331 reflections  
 100 parameters  
 H-atom parameters not  
 refined

### Compound (3)

#### Crystal data

$C_8H_{13}NS_2$   
 $M_r = 187.33$   
 Monoclinic  
 $P2_1/n$   
 $a = 8.629 (3) \text{ \AA}$   
 $b = 12.282 (6) \text{ \AA}$   
 $c = 8.844 (3) \text{ \AA}$   
 $\beta = 98.02 (4)^\circ$   
 $V = 928 (1) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.341 \text{ Mg m}^{-3}$

#### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 none  
 1830 measured reflections  
 729 independent reflections  
 582 observed reflections  
 $[I > 3\sigma(I)]$

#### Refinement

Refinement on  $F$   
 $R = 0.047$   
 $wR = 0.052$   
 $S = 1.406$

Cell parameters from 25  
 reflections  
 $\theta = 12\text{--}14^\circ$   
 $\mu = 0.484 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Rectangular prism  
 $0.8 \times 0.5 \times 0.3 \text{ mm}$   
 Colourless

$R_{\text{int}} = 0.017$   
 $\theta_{\text{max}} = 24^\circ$   
 $h = -6 \rightarrow 6$   
 $k = 0 \rightarrow 11$   
 $l = 0 \rightarrow 19$   
 2 standard reflections  
 frequency: 60 min  
 intensity decay: 0.92%

$w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\text{max}} = 0.04$   
 $\Delta\rho_{\text{max}} = 0.637 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.627 \text{ e \AA}^{-3}$   
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 25  
 reflections  
 $\theta = 14\text{--}16^\circ$   
 $\mu = 0.490 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Rectangular prism  
 $0.5 \times 0.3 \times 0.2 \text{ mm}$   
 Colourless

$R_{\text{int}} = 0.029$   
 $\theta_{\text{max}} = 25^\circ$   
 $h = -10 \rightarrow 10$   
 $k = 0 \rightarrow 10$   
 $l = 0 \rightarrow 14$   
 2 standard reflections  
 frequency: 60 min  
 intensity decay: 0.1%

$w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\text{max}} = 0.01$   
 $\Delta\rho_{\text{max}} = 0.477 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.427 \text{ e \AA}^{-3}$

582 reflections  
100 parameters  
H-atom parameters not refined

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Program used for data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Program used throughout the analysis: *SDP-Plus* (Frenz, 1985). Program used to solve the structures: *MULTAN11/82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson (1982) (completed by Fourier synthesis). Molecular graphics: *ORTEPII* (Johnson, 1976).

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Compound (1)	x	y	z	B <sub>eq</sub>
S1	0.6401 (1)	0.0984 (1)	0.40165 (7)	3.93 (2)
S2	0.7957 (1)	0.3555 (1)	0.52468 (7)	4.13 (2)
N3	0.3891 (4)	0.3054 (3)	0.4347 (2)	3.35 (6)
C5	0.3599 (5)	0.0801 (4)	0.3394 (3)	3.41 (7)
C4	0.2326 (5)	0.2139 (4)	0.3724 (2)	3.58 (7)
C2	0.5947 (5)	0.2645 (4)	0.4559 (2)	3.00 (7)
C6	0.3441 (6)	0.0887 (4)	0.2240 (3)	3.92 (8)
C7	0.2981 (6)	0.2466 (4)	0.2001 (3)	3.96 (8)
C8	0.1431 (6)	0.2886 (4)	0.2738 (3)	4.51 (8)
Compound (2)				
C2	0.4821 (6)	0.0849 (3)	0.2986 (2)	2.97 (6)
C4	0.1835 (5)	0.2366 (3)	0.3401 (2)	2.77 (6)
C5	0.1584 (6)	0.1352 (2)	0.4048 (2)	3.00 (6)
C3	0.3069 (7)	0.2271 (4)	0.1965 (2)	4.35 (8)
C6	0.3253 (6)	0.3562 (3)	0.3665 (2)	3.34 (7)
C8	0.2567 (7)	0.3065 (4)	0.5091 (2)	4.22 (8)
N3	0.3166 (5)	0.1723 (3)	0.2759 (1)	2.87 (5)
C7	0.2277 (7)	0.4076 (4)	0.4446 (2)	4.09 (8)
S1	0.4534 (2)	0.04754 (8)	0.39948 (5)	3.51 (2)
S2	0.7001 (2)	0.0169 (1)	0.24372 (6)	4.27 (2)
C9	0.1039 (6)	0.1885 (4)	0.4869 (2)	3.92 (7)
Compound (3)				
S2	0.7680 (3)	0.0806 (2)	0.3857 (3)	4.21 (5)
S1	0.8758 (3)	0.3110 (2)	0.4174 (3)	4.83 (6)
N3	1.0598 (7)	0.1529 (5)	0.4653 (7)	3.3 (2)
C2	0.9108 (8)	0.1717 (7)	0.4249 (8)	2.9 (2)
C7	1.283 (1)	0.4596 (7)	0.330 (1)	4.8 (2)
C4	1.1669 (8)	0.2427 (7)	0.5091 (8)	3.0 (2)
C10	1.3230 (9)	0.2181 (6)	0.455 (1)	3.8 (2)
C9	1.4431 (9)	0.3109 (7)	0.480 (1)	4.3 (2)
C8	1.430 (1)	0.3907 (7)	0.350 (1)	4.3 (2)
C6	1.127 (1)	0.3973 (7)	0.302 (1)	4.3 (2)
C5	1.0833 (9)	0.3462 (6)	0.4460 (9)	3.4 (2)

Table 2. Selected geometric parameters (Å, °)

	(1)	(2)	(3)
S1—C2	1.732 (4)	1.751 (3)	1.737 (8)
S1—C5	1.819 (3)	1.830 (3)	1.825 (8)
S2—C2	1.666 (3)	1.665 (3)	1.664 (8)
N3—C2	1.313 (3)	1.321 (4)	1.306 (9)
N3—C4	1.456 (4)	1.471 (4)	1.46 (1)
C4—C5	1.554 (5)	1.525 (4)	1.53 (1)
C2—S1—C5	94.5 (1)	91.9 (1)	93.8 (4)
S1—C2—S2	121.8 (2)	121.5 (2)	122.3 (4)
S2—C2—N3	126.7 (3)	127.6 (2)	127.6 (6)
C2—N3—C4	120.2 (3)	116.0 (2)	120.2 (6)
N3—C4—C5	107.6 (2)	105.1 (2)	106.5 (6)
C4—C5—S1	106.2 (2)	102.7 (2)	105.0 (5)

Table 3. Distances (Å) to the S1—C2—S2—N3 fragment and values of the torsion angle τ (°)

	(1)	(2)	(3)
C4	0.010 (3)	-0.290 (3)	-0.121 (7)
C5	0.077 (3)	0.315 (3)	0.243 (8)
τ	3.4 (3)	36.6 (2)	21.3 (7)

H atoms were introduced at idealized positions in the calculations before the last refinement cycle, but were not refined.

For all three structures, lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: NA1157). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Allinger, N. L. (1976). *Adv. Phys. Org. Chem.* **13**, 1–76.  
 Bafford, K. A., Chanon, F. & Metzger, J. (1973). *Bull. Soc. Chim. Fr.* pp. 973–977.  
 Chanon, F., Rajzmann, M., Chanon, M., Metzger, J., Pouzard, G. & Drakenberg, T. (1980). *Can. J. Chem.* **58**, 599–603.  
 Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.  
 Frenz, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Kubiak, M. & Glowing, T. (1982). *Acta Cryst.* **B38**, 2031–2034.  
 Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 Nuzzo, O., Pierrot, M., Baldy, A., Chanon, F. & Chanon, M. (1984). *Can. J. Chem.* **62**, 1410–1413.  
 Raper, E. S. & Oughtred, R. E. (1983). *Inorg. Chim. Acta Lett.* **77**, L89.  
 Acta Cryst. (1995). **C51**, 2116–2118

## 3,7-Di-tert-butyl-1,5,2,4,6,8-dithiatetrazocine

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## Abstract

The eight-membered ring in the title compound, C<sub>10</sub>H<sub>18</sub>N<sub>4</sub>S<sub>2</sub>, lies about an inversion centre and is essentially planar with normal bond lengths and angles [mean C—S 1.569 (2) and mean C—N 1.326 (3) Å].