

- Sheldrick, G. M. (1990). *SHELXTL-Plus*. Release 4.21/V. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1989). *P3/V*. Release 4.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). *XPW. Molecular Graphics Program. SHELXTL*. Release 5.0.5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Simonsen, O. (1992). *Acta Cryst.* **C48**, 1900–1902.
- Sood, C. K., Sood, A., Spielvogel, B. F., Yousef, J. A., Burnham, B. & Hall, J. H. (1991). *J. Pharm. Sci.* **80**, 1133–1140.
- Vigorita, M. G., Ottaná, R., Rotondo, E. & Maccari, R. (1998). In preparation.

*Acta Cryst.* (1998). **C54**, 1040–1042

### A New Bis(dithioester): Methanediyl Bis(*N,N*-diethyldithiocarbamate), Derived from *cis*-Dichlorobis(*N,N*-diethyldithiocarbamato-*S,S'*)tin(IV)

ARMANDO MARZOTTO,<sup>a</sup> DORE AUGUSTO CLEMENTE<sup>b</sup> AND GIOVANNI VALLE<sup>c</sup>

<sup>a</sup>*Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università degli Studi di Padova, Via Loredan n. 4, I-35131 Padova, Italy.* <sup>b</sup>*Dipartimento di Ingegneria dei Materiali e Chimica Applicata, Università degli Studi di Trieste, Via Valerio n. 2, I-34127 Trieste, Italy.* and <sup>c</sup>*Centro di Studio sui Biopolimeri, CNR, Università degli Studi di Padova, Via Marzolo n. 2, I-35131 Padova, Italy.* E-mail: marzotto@chim02.chin.unipd.it

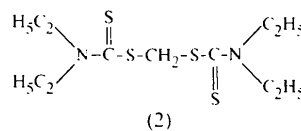
(Received 30 January 1997; accepted 13 January 1998)

#### Abstract

The title compound, C<sub>11</sub>H<sub>22</sub>N<sub>2</sub>S<sub>4</sub> [or CH<sub>2</sub>(Et<sub>2</sub>DTC)<sub>2</sub>, where DTC is dithiocarbamate], was unexpectedly obtained during studies on the reactivity of *cis*-dichlorobis(*N,N*-diethyldithiocarbamato-*S,S'*)tin(IV) {*cis*-[Cl<sub>2</sub>Sn(Et<sub>2</sub>DTC)<sub>2</sub>]} with 2-thiouracil in dimethyl sulfoxide. The X-ray structural analysis of the title compound shows that two *N,N*-diethyldithiocarbamate units are linked together through a methylene C atom, so that the compound can be described as a dithioester, where the –CH<sub>2</sub>(*N,N*-diethyldithiocarbamate) group itself constitutes the esteric organic radical. Structural parameters and IR spectra are in agreement with the crystal chemistry of this class of compounds. Of major interest is the methylene C atom, which presents an S—CH<sub>2</sub>—S angle of 116.9(2)°, larger than the ideal tetrahedral value of 109.47°.

#### Comment

In the course of our work, which was undertaken to obtain a strong metal–nitrogen bond between metal complexes and DNA bases, particularly adenine (Marzotto *et al.*, 1993, 1995), we prepared *cis*-dichlorobis(*N,N*-diethyldithiocarbamato-*S,S'*)tin(IV) {*cis*-[Cl<sub>2</sub>Sn(Et<sub>2</sub>DTC)<sub>2</sub>]} (1), in order to study its reactivity towards DNA bases. The interest in (1), whose molecular structure is already known (Bohra *et al.*, 1994; Selvaraju *et al.*, 1994), is due to its antitumor activity (Smith, 1978; Crowe & Smith, 1980; Crowe *et al.*, 1980; Oskarsson, 1983; Cardarelli & Libby, 1984). Then, during reactivity studies of (1) with 2-thiouracil [which exhibits a marked affinity for melanin-producing tissue (Wätjen *et al.*, 1982)], we unexpectedly obtained white crystals of the title compound, (2), identified as methanediyl bis(*N,N'*-diethyldithiocarbamate) by X-ray structure and IR spectroscopic analysis. It consists of two dithiocarbamate units, bridged by a methylene group, *i.e.* (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N—CS—S—CH<sub>2</sub>—S—CS—N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>.



Compound (1), *cis*-[Cl<sub>2</sub>Sn(Et<sub>2</sub>DTC)<sub>2</sub>], has been identified as hexacoordinate on the basis of the cell parameters, which are in agreement with those found by both Bohra *et al.* (1994) and Selvaraju *et al.* (1994). The subsequent interaction of (1) with 2-thiouracil in dimethyl sulfoxide yielded (together with other products which are under investigation) the title compound, methanediyl bis(*N,N*-diethyldithiocarbamate) [CH<sub>2</sub>(Et<sub>2</sub>DTC)<sub>2</sub>, (2)], which has been characterized using X-ray diffraction and IR spectroscopy. The monoclinic cell contains two discrete molecules of methanediyl bis(*N,N*-diethyldithiocarbamate). In each molecule, the methylene carbon, C11, bridges two *N,N*-diethyldithiocarbamate moieties, which are closely related by a twofold molecular axis passing through C11 and the midpoint of the S1, S2, S3 and S4 atoms. This axis is nearly perpendicular [98.9(2)°] to the unique *b* axis, and also to the 2<sub>1</sub> screw axis, so that centrosymmetric (*P*2<sub>1</sub>/*m*) or other space groups must be ruled out.

The atom joining the two dithiocarbamate units was identified as carbon by Fourier synthesis, which shows four positive maxima around it; the two highest peaks (0.43 and 0.41 e Å<sup>-3</sup>) occupy the positions expected for methylene H atoms, and the other two peaks (0.19 and 0.24 e Å<sup>-3</sup>) may be interpreted as bonding electrons. Three additional reasons support this choice: (i) the C11—S1 and C11—S2 distances of 1.792(3) and 1.789(3) Å, respectively, correspond exactly to a C<sub>sp<sup>3</sup></sub>—S single bond; (ii) the S1—C11—S2 angle of

116.9(2)° is larger than the ideal tetrahedral value (109.47°), probably due to repulsion of the C11—S1 and C11—S2 bonding electron pairs; (iii) a structure-factor calculation including the two H atoms gives  $R = 0.0293$ , whereas, excluding the two H atoms, it gives a higher value of 0.0341, for 1636 reflections with  $I > 2\sigma(I)$ . The C1—S3 and C6—S4 bond lengths of 1.668 (3) and 1.661 (3) Å, respectively, are slightly longer than a normal C=S double bond (*ca* 1.61 Å; Pauling, 1960), while the C1—S2 and C6—S1 distances of 1.775 (3) and 1.789 (3) Å, respectively, are clearly single bonds. The C1—N1 and C6—N2 bond lengths of 1.334 (3) and 1.333 (3) Å, respectively, are in good agreement with the values reported in the literature (Allen *et al.*, 1979) and indicate a marked double-bond character. In fact, the shortening of the C—N single bond and the lengthening of the C=S double bond indicate that the N-atom lone pair participates strongly in the  $\pi$  system of the thiocarbonyl group (Heinemann *et al.*, 1992), a fact originally discovered through IR spectroscopy (Chatt *et al.*, 1956). The two dithiocarbamate planes are slightly bent; C1, S2, S3 and N1 are perfectly coplanar and the two methylene C atoms, C2 and C4, are on opposite sides of this plane, with deviations of 0.094 (4) and 0.092 (5) Å, respectively. Similarly, atoms C6, S1, S4 and N2 are coplanar, with C7 and C9 on opposite sides of the plane, with deviations of 0.142 (5) and 0.074 (4) Å, respectively. This situation is common for the dithiocarbamate moiety in all its forms, whether as a neutral molecule, an anion or a dithioester (Clemente *et al.*, 1987; Oskarsson & Ymén, 1983).

The most closely related compound is bis(*N,N*-diethyldithiocarbamate), (Et<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>, in which two *N,N*-diethyldithiocarbamate units are directly linked through an S—S disulfide bridge with a bond length of 2.001 (3) Å (Shi & Wang, 1992), but a detailed comparison is not possible given the spread of the reported equivalent distances. Crystal packing shows normal van der Waals contacts, the most stabilizing interaction being between C4 and S3<sup>1</sup> [symmetry code: (i)  $x, y - 1, z$ ].

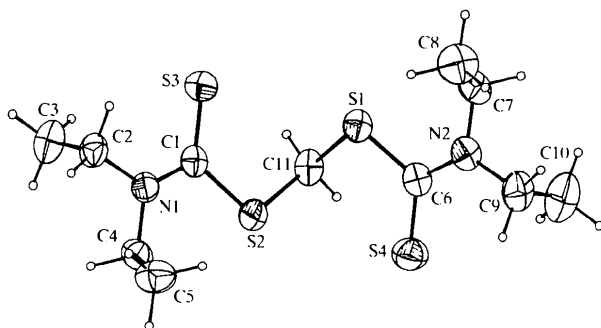


Fig. 1. ORTEP (Johnson, 1976) plot showing the molecular structure and atomic numbering scheme of (2). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

## Experimental

Compound (1), *cis*-[Cl<sub>2</sub>Sn(Et<sub>2</sub>DTC)<sub>2</sub>], was prepared essentially according to the method of Srivastava & Bhargava (1978) by reacting 2 mmol of SnCl<sub>4</sub>·5H<sub>2</sub>O, dissolved in 10 ml of methanol, with 4 mmol of NaDTC·Et<sub>2</sub>·3H<sub>2</sub>O, dissolved in 10 ml of the same solvent. The resulting yellow solution was heated to 328 K and stirred for 3 h, and the yellow precipitate obtained was filtered off and washed, both with methanol and with water, to remove excess reagents and the NaCl which is formed. The compound was then dried under vacuum at 333 K. Pale-yellow crystals were obtained by slow evaporation from an acetone solution. Yield 85%, m.p. 488 K. Found: C 24.64, H 4.07, N 5.67, S 26.54, Cl 14.50%; calculated for C<sub>10</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>2</sub>S<sub>4</sub>Sn: C 24.71, H 4.14, N 5.76, S 26.38, Cl 14.58%. White crystals of the title compound, (2), were obtained after two weeks by reaction of *cis*-[Cl<sub>2</sub>Sn(Et<sub>2</sub>DTC)<sub>2</sub>] with 2-thiouracil in dimethyl sulfoxide at 328 K. Found: C 42.48, H 7.19, N 9.00, S 41.02%; calculated for C<sub>11</sub>H<sub>22</sub>N<sub>2</sub>S<sub>4</sub>: C 42.54, H 7.14, N 9.02, S 41.29%.

## Crystal data

C<sub>11</sub>H<sub>22</sub>N<sub>2</sub>S<sub>4</sub>  
 $M_r = 310.55$   
 Monoclinic  
 $P2_1$   
 $a = 9.755(2)$  Å  
 $b = 7.430(2)$  Å  
 $c = 11.255(2)$  Å  
 $\beta = 99.80(10)^\circ$   
 $V = 803.9(3)$  Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.283$  Mg m<sup>-3</sup>  
 $D_m$  not measured

Mo K $\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 25 reflections  
 $\theta = 12-16^\circ$   
 $\mu = 0.574$  mm<sup>-1</sup>  
 $T = 293(2)$  K  
 Irregular  
 0.80 × 0.30 × 0.20 mm  
 White

## Data collection

Philips PW1100/20 diffractometer  
 $\omega-2\theta$  scans  
 Absorption correction:  
 $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.758$ ,  $T_{\max} = 0.892$   
 2264 measured reflections  
 2090 independent reflections

1636 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.019$   
 $\theta_{\text{max}} = 28.01^\circ$   
 $h = -12 \rightarrow 12$   
 $k = 0 \rightarrow 9$   
 $l = 0 \rightarrow 14$   
 3 standard reflections every 52 reflections  
 intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.076$   
 $S = 0.975$   
 2090 reflections  
 153 parameters  
 Only coordinates of H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0461P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = -0.001$   
 $\Delta\rho_{\text{max}} = 0.206$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.197$  e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.01 (10)

Table 1. Selected geometric parameters (Å, °)

C11—S2	1.789 (3)	N1—C1	1.334 (3)
C11—S1	1.792 (3)	N1—C2	1.468 (3)
S1—C6	1.789 (3)	N1—C4	1.472 (4)

S2—C1	1.775 (3)	N2—C6	1.333 (3)
S3—C1	1.668 (3)	N2—C7	1.468 (4)
S4—C6	1.661 (3)	N2—C9	1.474 (4)
S2—C11—S1	116.9 (2)	S3—C1—S2	122.5 (2)
C6—S1—C11	102.12 (14)	N2—C6—S4	125.0 (2)
C1—S2—C11	102.65 (14)	N2—C6—S1	112.9 (2)
N1—C1—S3	124.1 (2)	S4—C6—S1	122.1 (2)
N1—C1—S2	113.4 (2)		

The systematic extinctions ( $0k0$ :  $k = 2n + 1$ ) indicate two possible space groups,  $P2_1$  (No. 7) and  $P2_1/m$  (No. 11). The non-centrosymmetric space group was chosen since the cell contains two molecules, each formed by two *N,N*-diethylthiocarbamate moieties, closely related by a twofold symmetry axis and not by a mirror plane (see *Comment*). The structure was solved by standard Fourier and Patterson methods. The refinement was carried out with anisotropic displacement parameters for all non-H atoms, while H atoms were refined isotropically. The *U* displacement parameters of the methylene and methyl H atoms were fixed at, respectively, 1.2 and 1.5 times the  $U_{eq}$  of the atom to which they are bonded. In addition, the C—H distances were constrained to be 0.97 Å for methylene and 0.96 Å for methyl groups.

Data collection: Philips PW1100/20 software. Cell refinement: locally modified Philips PW1100/20 software. Data reduction: *RIFLUP80* (Biagini *et al.*, 1980). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

MURST (40%) and Programma Finalizzato CNR—Rome are gratefully acknowledged for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1097). Services for accessing these data are described at the back of the journal.

## References

- Allen, F., Bellard, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink, T., Motherwell, W. D. S., Rodgers, J. R. & Watson, D. G. (1979). *Acta Cryst.* **B35**, 2331–2339.
- Biagini, C. M., Bandoli, G., Clemente, D. A. & Tiripicchio, A. (1980). *J. Appl. Cryst.* **13**, 197–198.
- Bohra, R., Sharma, S. & Dhammani, A. (1994). *Acta Cryst.* **C50**, 1447–1449.
- Cardarelli, N. F. & Libby, E. P. (1984). *Aust. J. Exp. Biol. Med. Sci.* **62**, 199–208.
- Chat, J., Duncanson, L. A. & Venanzi, L. M. (1956). *Nature (London)*, **177**, 1042–1043.
- Clemente, D. A., Faraglia, G., Sindellari, L. & Trincia, L. (1987). *J. Chem. Soc. Dalton Trans.* pp. 1823–1826.
- Crowe, A. J., Atassi, G. & Smith, P. J. (1980). *Chem. Biol. Interact.* **32**, 171–178; *Inorg. Chim. Acta*, **93**, 179–184.
- Crowe, A. J. & Smith, P. J. (1980). *Chem. Ind.* **5**, 200–201.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Heinemann, F., Dölling, W. & Hartung, H. (1992). *Acta Cryst.* **C48**, 2266–2268.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Marzotto, A., Ciccacese, A., Clemente, D. A. & Valle, G. (1995). *J. Chem. Soc. Dalton Trans.* pp. 1461–1468.
- Marzotto, A., Clemente, D. A., Ciccacese, A. & Valle, G. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 119–131.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Oskarsson, Å. (1983). *Arch. Toxicol. Suppl.* **6**, 279–281.
- Oskarsson, Å. & Ymén, I. (1983). *Acta Cryst.* **C39**, 66–68.
- Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, New York: Cornell University Press.
- Selvaraju, R., Panchanatheswaran, K. & Venkatasbramanian, K. (1994). *Polyhedron*, **13**, 903–908.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Shi, B. & Wang, J. (1992). *Xiamen Daxue Xuebao Ziran Kexueban (J. Xiamen Univ. Nat. Sci.)*, **31**, 176–181.
- Smith, P. J. (1978). In *Toxicological Data on Organotin Compounds*. IRTI Publication No. 538.
- Srivastava, T. N. & Bhargava, A. (1978). *Indian J. Chem.* **16A**, 148–151.
- Wätjen, F., Buchardt, O. & Langvad, E. (1982). *J. Med. Chem.* **25**, 956–960.

*Acta Cryst.* (1998). **C54**, 1042–1047

## Five 3,4-Dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]-benzopyran-5-one Derivatives

GIANLUIGI CASALONE,<sup>a</sup> TULLIO PILATI<sup>a</sup> AND ARIANNA BINELLO<sup>b</sup>

<sup>a</sup>*CNR—Centro per lo Studio delle Relazioni fra Struttura e Reattività Chimica, Via Golgi 19, I-20133 Milano, Italy; and*  
<sup>b</sup>*Dipartimento di Scienza e Tecnologia del Farmaco, Via Giura 9, I-10125 Torino, Italy. E-mail: pila@sg1.csrsrc.mi.cnr.it*

(Received 5 December 1997; accepted 6 January 1998)

## Abstract

The molecular structures of five 3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one derivatives, namely, *cis,anti*-7,7*a*,8,9-tetrahydro-7-phenyl-6*H*,10*aH*-furo[2',3':2,3]pyrano[5,6-*c*][1]benzopyran-6-one [C<sub>20</sub>H<sub>16</sub>O<sub>4</sub>, (I)], *cis*-2-ethoxy-3,4-dihydro-4-furyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one [C<sub>18</sub>H<sub>16</sub>O<sub>5</sub>, (II)], *cis*-2-ethoxy-3,4-dihydro-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one [C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>, (III)], *cis*-2-ethoxy-3,4-dihydro-4-(2-nitrophenyl)-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one [C<sub>20</sub>H<sub>17</sub>NO<sub>6</sub>, (IV)] and methyl *cis*-2-ethoxy-3,4-dihydro-5-oxo-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-4-carboxylate [C<sub>22</sub>H<sub>20</sub>O<sub>6</sub>, (V)] have been studied by single-crystal diffractometry. The conformation of the dihydropyran ring is compared with that found in 36 entries in the Cambridge Structural Database [version of 28 February 1997; Allen & Kennard (1993). *Chem. Des. Autom. News*, **8**, 31–37]. A scatterplot of the conformation of 46 independent molecules is shown. These molecules present a more or less distorted half-chair conformation, with few exceptions; in particular,