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# Bis(*N*,*N*-dimethylthiocarbamoylthio)-acetic acid

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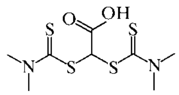
Bis(*N*,*N*-dimethylthiocarbamoylthio)acetic acid, $[(CH_3)_2N\text{-}C({=}S)S]_2CHC({=}O)OH$ or $C_8H_{14}N_2O_2S_4$, exists as a centrosymmetric hydrogen-bonded dimer [O···O 2.661 (3) Å].

## Comment

The thiocarbamoylthioacetic acids, $R_2NC(S)SCH_2C(O)OH$, are plant growth-regulating compounds (Fawcett *et al.*, 1956; van der Kerk *et al.*, 1995) that are readily synthesized by displacing the chloride of chloroacetic acid by the dithiocarbamate nucleophile (Nachmias, 1952). Their acid dissociation constants (Janssen, 1963) have been explained in terms of extensive mesomeric electron displacements of the thiocarbonyl group; the $R_2NC(S)S$ portion also exerts an appreciable electron-withdrawing effect (Janssen, 1962). The analogous $[R_2NC(S)S]_2CHC(O)OH$ acid is known only for the $R = CH_3$ homolog as other homologs cannot be synthesized by the reaction of the dithiocarbamate ion with dichloroacetic acid (Pluijgers, 1959). The title compound, (I), crystallizes as a centrosymmetric dimer that is held together by a short hydrogen bond [O···O 2.664 (3) Å]. Bond dimensions in the acid are similar to those found in the dicyclohexylammonium (Ng, 1996) and tetramethylammonium (Ng, 1997) salts. The tetramethylammonium salt crystallizes with a molecule of the acid, and the carboxylate and acid moieties are linked across a center of inversion by the acid H atom [O···O 2.486 (3) Å].



(I)

An examination of the bond dimensions found in $[(CH_3)_2NC(S)S]_2CHC(O)OH$ acid does not suggest any particularly abnormal values. The bond dimensions that are calculated by the *GAUSSIAN* suite (Frisch *et al.*, 1995) compare well with those found experimentally. Similar calculations were also performed on $[(C_2H_5)_2N\text{-}C(S)S]_2CHC(O)OH$ to ascertain why this and other homologs could not be isolated. The calculations, which used the same model chemistry (HF/3-21G), gave insignificant differences, other than for somewhat longer carbon–sulfur double-bonds, *i.e.* this acid should be thermodynamically stable (Table 2).

## Experimental

The title acid was synthesized from dimethylamine, carbon disulfide and dichloroacetic acid (Nachmias, 1952; Pluijgers & van der Kerk, 1961), and crystals were obtained upon recrystallization of the compound from ethanol.

*Crystal data*

$C_8H_{14}N_2O_2S_4$
$M_r = 298.45$
Triclinic, $P\bar{1}$
$a = 7.3275$ (1) Å
$b = 7.6321$ (2) Å
$c = 12.6379$ (4) Å
$\alpha = 95.809$ (2)°
$\beta = 96.991$ (1)°
$\gamma = 92.244$ (2)°
$V = 696.96$ (3) Å$^3$
$Z = 2$
$D_x = 1.422$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3176 reflections
$\theta = 2.80$–28.28°
$\mu = 0.669$ mm$^{-1}$
$T = 293$ (2) K
Block, faint tan
0.38 × 0.30 × 0.16 mm

*Data collection*

Siemens CCD area-detector diffractometer
*w* scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.785$, $T_{max} = 0.900$
5032 measured reflections
3349 independent reflections
2292 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 28.28°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 9$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.139$
$S = 0.946$
3349 reflections
151 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.38$ e Å$^{-3}$
$\Delta\rho_{min} = -0.39$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.030 (5)

**Table 1**
Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···O2$^{i}$ | 0.82 | 1.84 | 2.661 (3) | 178 |

Symmetry code: (i) $-x, -y, -z$.

**Table 2**
Bond distances (Å) and angles (°) derived from *ab initio* (HF/3-21G) calculations.

| | (I) | HF/3-21G |
|---|---|---|
| S1—C3 | 1.790 (3) | 1.856 |
| S1—C2 | 1.812 (3) | 1.873 |
| S2—C3 | 1.655 (3) | 1.713 |
| S3—C6 | 1.783 (3) | 1.841 |
| S3—C2 | 1.799 (3) | 1.856 |
| S4—C6 | 1.661 (3) | 1.720 |
| O1—C1 | 1.313 (3) | 1.312 |
| O2—C1 | 1.214 (3) | 1.214 |
| N1—C3 | 1.332 (3) | 1.332 |
| N1—C5 | 1.463 (4) | 1.461 |
| N1—C4 | 1.467 (4) | 1.469 |
| N2—C6 | 1.326 (3) | 1.327 |
| N2—C8 | 1.462 (4) | 1.462 |
| N2—C7 | 1.465 (3) | 1.462 |
| C1—C2 | 1.531 (4) | 1.529 |
| | | |
| C3—S1—C2 | 102.2 (1) | 103.1 |
| C6—S3—C2 | 102.4 (1) | 101.5 |
| C3—N1—C5 | 123.8 (2) | 123.0 |
| C3—N1—C4 | 119.7 (2) | 118.8 |
| C5—N1—C4 | 116.5 (2) | 118.2 |
| C6—N2—C8 | 123.4 (2) | 122.4 |
| C6—N2—C7 | 120.7 (2) | 119.1 |
| C8—N2—C7 | 115.8 (2) | 118.5 |
| O2—C1—O1 | 124.9 (3) | 123.8 |
| O2—C1—C2 | 123.0 (2) | 126.8 |
| O1—C1—C2 | 112.0 (2) | 109.3 |
| C1—C2—S3 | 113.9 (2) | 113.0 |
| C1—C2—S1 | 105.0 (2) | 106.7 |
| S3—C2—S1 | 106.4 (1) | 107.1 |
| N1—C3—S2 | 124.9 (2) | 124.9 |
| N1—C3—S1 | 111.4 (2) | 112.5 |
| S2—C3—S1 | 123.7 (2) | 122.5 |
| N2—C6—S4 | 125.6 (2) | 124.8 |
| N2—C6—S3 | 113.0 (2) | 114.0 |
| S4—C6—S3 | 121.4 (1) | 121.2 |

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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## References

Fawcett, C. H., Wain, R. L. & Wrightman, F. (1956). *Nature* (*London*), **178**, 972–974.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T. A., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Peng, C. Y., Ayala, P. Y., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C. & Pople, J. A. (1995). *GAUSSIAN*-94. Revision A.1. Gaussian Inc., Pittsburgh, PA, USA.

Janssen, M. J. (1962). *Recuiel*, **81**, 650–660.

Janssen, M. J. (1963). *Recuiel*, **82**, 931–940.

Kerk, G. J. M. van der, van Raalte, M. H., Kaars Sijpesteijn, A. & van der Veen, R. (1995). *Nature* (*London*), **176**, 308–310.

Nachmias, G. (1952). *Ann. Chim.* (*Paris*), **12**, 584–631.

Ng, S. W. (1996). *Acta Cryst.* C**52**, 181–183.

Ng, S. W. (1997). *Acta Cryst.* C**53**, 1111–1113.

Pluijgers, C. W. (1959). PhD dissertation, University of Utrecht, The Netherlands.

Pluijgers, C. W. & van der Kerk, G. J. M. (1961). *Recuiel*, **90**, 1089–1100.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXS*97. University of Göttingen, Germany.

Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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