N-(2-Aminoethyl)dithiocarbamic acid

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The title compound, $C_3H_8N_2S_2$, exists as a zwitterion, $H_3N^+(CH_2)_2NHCS_2^-$. The lengths of the two C—S bonds in the planar NCS_2 dithiocarbamate group are essentially equal, which suggests that these bonds have almost equal double-bond character. Four N—H$\cdots$S interactions link the molecules in the crystal into an infinite three-dimensional network.

Comment

Studies on dithiocarbamic acids of the $NH_3(CH_2)_nNHCS_2$ type are relatively scarce compared with their hydrazine analogues RNHNHCS$_2$H or $[R$NHNH$_3]^+[R$NHNHCS$_2]^-$ (Battistoni *et al.*, 1971; Iskander & El-Syed, 1971). This is rather surprising, taking into account that pyrolysis of N-(2-aminoethyl)dithiocarbamic acid provides a convenient method for the preparation of ethylenethiourea. Alkyl-substituted N-(2-aminoethyl)dithiocarbamic acid, namely zwitterionic alkylaminoalkyldithiocarbamates, have also been of interest in an attempt to determine the effect of the alkyl substituent on the structure of thiocarbamate ligands (Kokkou *et al.*, 1988; Stergioudis *et al.*, 1989). This interest prompted us to study the structure of the title compound, (I).

$$^-S_2C\text{---}NH\text{----}CH_2\text{---}CH_2\text{---}NH_3^+$$
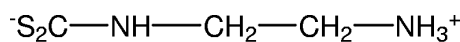
(I)

The molecule exists as a zwitterion, $H_3N^+(CH_2)_2NHCS_2^-$. The NCS_2 dithiocarbamate group is planar with a maximum deviation of 0.004 (2) Å for the C1 atom. The N1—C1 bond length of 1.339 (3) Å (Table 1) is that of a typical Csp^2—Nsp^2 bond (Allen *et al.*, 1987), and is close to the analogous bond lengths in the reported thiocarbamates with alkyl substituents [C—N = 1.345 (5) and 1.340 (6) Å; Kokkou *et al.*, 1988; Stergioudis *et al.*, 1989] and to the corresponding distance of 1.339 (4) Å in sodium dimethylaminodithiocarbamate hydrate (Oskarsson & Ymén, 1983). The C1—S1 and C1—S2 bond lengths of 1.720 (2) and 1.712 (2) Å are typical of the CS_2^- anion (Allen *et al.*, 1987). The difference of 0.008 (4) Å is negligible compared with that in dimethylaminoethyldithiocarbamate [0.048 (6) Å; Stergioudis *et al.*, 1989] or diethylaminoethyldithiocarbamate [0.032 (7) Å; Kokkou *et al.*, 1988]. This implies that the two C—S bonds in the title compound have almost equal partial double-bond character. The bond length N2—C3, 1.486 (3) Å, is within the normal range for the C—N$^+$ distance. The conformation about the N2—C3 bond is staggered.
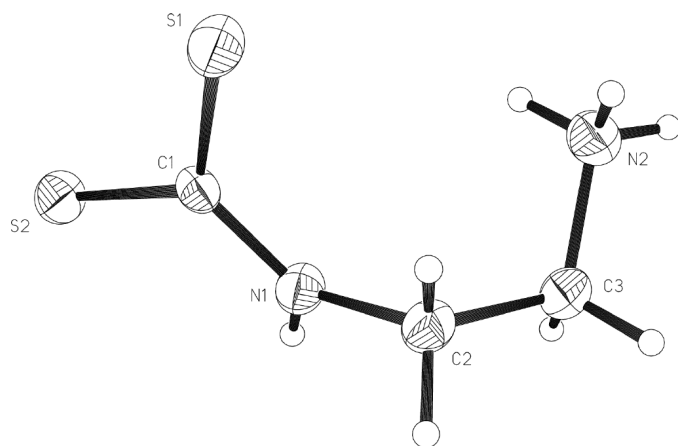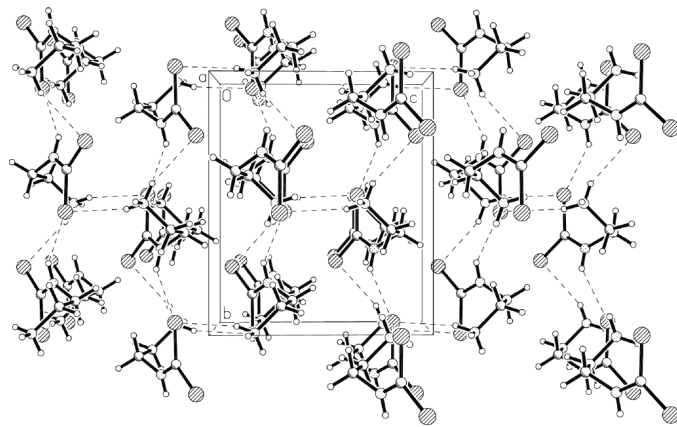
Figure 1
The molecular structure of the title compound with 50% probability displacement ellipsoids.

All H atoms bonded to N (one at N1 and three at N2) participate in N—H···S hydrogen bonding (Table 2). The N1—H1A···S1^i, N2—H2C···S1^{ii} and N2—H2D···S2^{iii} bonds link the molecules into layers parallel to the ab crystal plane [symmetry codes: (i) $1-x$, $y-1/2$, $1/2-z$; (ii) $x-1$, y, z; (iii) $1-x$, $y+1/2$, $1/2-z$]. A fourth N2—H2E···S1^{iv} bond interconnects the layers into a three-dimensional infinite network [symmetry code: (iv) $1-x$, $1-y$, $1-z$].

Experimental

Carbon disulfide (25.2 g, 0.33 mol) was added dropwise to a solution of ethylenediamine (12.0 g, 0.33 mol) in 95% ethanol at a temperature below 273 K. Mixing was carried out under constant stirring with a magnetic stirrer. The white precipitate which formed was filtered off and washed first with cold ethanol and then with petroleum ether. The dried precipitate was dissolved in hot water, poured into a crystalizing dish and covered with aluminum foil to allow evaporation of the solvent. After one day, white single crystals were obtained and washed with ethanol.

Figure 2
The packing diagram for the crystal of the title compound, viewed down the a axis. The dashed lines denote the N—H···S hydrogen bonds.

Crystal data

$C_3H_8N_2S_2$	$D_x = 1.449$ Mg m^{-3}
$M_r = 136.23$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3039
$a = 7.0173$ (3) Å	reflections
$b = 10.2294$ (4) Å	$\theta = 3.1$–28.3°
$c = 8.7064$ (4) Å	$\mu = 0.73$ mm^{-1}
$\beta = 92.561$ (2)°	$T = 293$ (2) K
$V = 624.35$ (5) Å^3	Block, colorless
$Z = 4$	$0.30 \times 0.20 \times 0.20$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	1513 independent reflections
	1235 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.079$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 28.2°$
	$h = -9 \rightarrow 9$
$T_{min} = 0.810$, $T_{max} = 0.867$	$k = -13 \rightarrow 13$
3678 measured reflections	$l = -8 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.159$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.09$	$\Delta\rho_{max} = 0.97$ e Å^{-3}
1513 reflections	$\Delta\rho_{min} = -1.03$ e Å^{-3}
65 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.21 (2)

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.720 (2)	N1—C2	1.458 (3)
S2—C1	1.712 (2)	N2—C3	1.486 (3)
N1—C1	1.339 (3)		
C1—N1—C2	127.6 (2)	S2—C1—S1	122.03 (13)
N1—C1—S2	117.81 (17)	N1—C2—C3	113.4 (2)
N1—C1—S1	120.16 (17)	N2—C3—C2	111.7 (2)
C2—N1—C1—S2	−167.90 (18)	C1—N1—C2—C3	−116.4 (3)
C2—N1—C1—S1	12.9 (3)	N1—C2—C3—N2	73.5 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···S1^i	0.86	2.53	3.275 (2)	145
N2—H2C···S1^{ii}	0.89	2.41	3.278 (2)	166
N2—H2D···S2^{iii}	0.89	2.57	3.393 (2)	155
N2—H2E···S1^{iv}	0.89	2.53	3.360 (3)	154

Symmetry codes: (i) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x-1, y, z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1-x, 1-y, 1-z$.

After checking their presence in a difference map, all H atoms were fixed geometrically and allowed to ride on their parent C or N atoms, with C—H = 0.97 Å and N—H = 0.89 Å. Their U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for the NH$_3$ group H atoms and $1.2U_{eq}$ for the remaining H atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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