Table 2. Conformations of the saturated rings: asymmetry and pucker parameters

The numerical position of a ring atom in the sequences of the first column is used as an identifier in the conformational symbols of the last column.

| | Asymmetry parameters* | | Pucker parameters† | |
	Mol. (a)	Mol. (b)		Mol. (a)	Mol. (b)
C(1)–C(2)–C(3)– C(4)–C(5)–C(6)	$\Delta C_s[C(2)]$ 1·4	$\Delta C_2[C(1)-C(2)]$ 1·5	$Q(\text{Å})$ $\varphi(°)$ $\theta(°)$	0·536 (5) 247 (3) 168·3 (5) $^4C_1$	0·535 (5) 213 (2) 165·6 (5) $^4C_1$
O(5)–C(5)–C(6)– C(7)–C(8)	$\Delta C_s[C(5)]$ 6·6	$\Delta C_s[C(5)]$ 3·3	$Q(\text{Å})$ $\varphi(°)$	0·435 (4) 47·0 (5) E_2:$^3H_2$ 1:1	0·436 (4) 43·1 (5) E_2:$^3H_2$ 1:1
O(8)–C(8)–C(9)– C(10)–C(11)–C(12)	$\Delta C_2[O(8)-C(12)]$ 1·3	$\Delta C_2[O(8)-C(12)]$ 1·3	$Q(\text{Å})$ $\varphi(°)$ $\theta(°)$	0·546 (5) 132 (5) 173·1 (6) $^4C_1$	0·523 (3) 126 (3) 173·5 (3) $^4C_1$

* In each case, only the parameter of lowest magnitude has been reported. Standard deviations are in the range 0·3–0·7°.

† The total degree of pucker is described by the radial coordinate Q, and the angular coordinates φ and θ (six-membered rings), or φ (five-membered rings) describe the shape of the ring.

hydrogens were not revealed in the final difference maps, we may only postulate their locations in an indication of the H-bonding possibilities.

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Structure of N-(3-Dimethylaminopropyl)dithiocarbamic Acid, C6H14N2S2

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Abstract. $M_r = 178·3$, monoclinic, $P2_1/n$ (z-axis unique), $a = 6·9882$ (2), $b = 10·9995$ (5), $c = 12·3087$ (5) Å, $\gamma = 96·830$ (5)°, $V = 939·42$ Å³, $Z = 4$, $D_m = 1·250$, $D_x = 1·261$ Mg m⁻³, m.p. $= 433–434$ K, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·576$ mm⁻¹, $F(000) = 384$, $T = 295$ K, $R = 0·048$ for 1444 independent non-zero reflexions. In the planar thioureide group $-NCS_2$, the C–N bond, 1·338 (5) Å, has strong double-bond character and the two C–S bonds,

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1·727 (3) and 1·699 (3) Å, with a difference in length of 6·6σ, are not equivalent. The molecule exists as a zwitterion $(CH_3)_2N^+H(CH_2)_3NHCS_2^-$, the bonding at the protonated N atom being approximately tetrahedral.

Introduction. Although considerable work has been done on the structure of metal dithiocarbamates very little is known about the free dithiocarbamate ligands themselves. More than one reason for their complexation behaviour has been given in the literature.
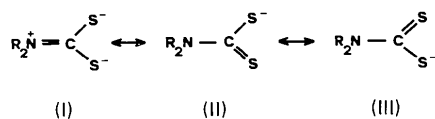
The IR spectral evidence that a significant contribution of a resonance structure of type (I) is necessary to describe the electronic structure of the dithiocarbamate ligand in complexes is generally accepted. This is attributed to the influence of the substituents R, because of the mesomeric effect of the $-NR_2$ group (Chatt, Duncanson & Venanzi, 1956; Coucouvanis & Fackler, 1967; Merlino, 1969). However, some authors, also on the basis of IR spectra, have suggested that the stereochemistry of the complex and probably the oxidation state of the metal (Cotton & McCleverty, 1964; Jensen, Dahl, Nielsen & Borch, 1972; Octavec, Beinrohr, Sileš, Štefanec & Garaj, 1979) influence the C—N stretching frequency and consequently affect the behaviour of the dithiocarbamate ligands as monodentate or bidentate.

With the aim of gaining more structural data for free dithiocarbamate ligands and additional information on their complexation behaviour we have carried out an X-ray crystal structure analysis of the title compound.

Experimental. Crystals prepared by one of us (PK), 0·35 × 0·37 × 0·44 mm, D_m by flotation in KBr solution, computer-controlled Phillips PW 1100 four-circle single-crystal diffractometer, cell parameters and standard deviations by least-squares analysis of measured θ angles of the 24 strongest reflexions, $P2_1/n$ (z-axis unique) from systematic absences ($hk0$, $h + k$ odd; $00l$, l odd), 3D data, Nb-filtered Mo $K\alpha$, ω–2θ scan, scan width $\Delta\omega = (1·0 + 0·35\tan\theta)°$, 3 standard reflexions without significant intensity variation, $\theta = 3$–25° (max. $hkl = \pm8,13,14$), 1653 unique reflexions, 1444 with $I > 2\sigma(I)$, no absorption correction; direct methods with SHELX76 (Sheldrick, 1976), phases of 227 reflexions with $E > 1·2$; best solution (PARACHOR = 3·26 and NQT = −0·50) revealed all non-hydrogen atoms, full-matrix least-squares refinement, first with a version of ORFLS (Busing, Martin & Levy, 1962) and later with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), atomic

scattering factors from *International Tables for X-ray Crystallography* (1974), H atoms located on difference Fourier map, refined with isotropic temperature coefficients, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1$ if $F_o \leq A$ else $w = (A/F_o)^2$, where $A = 30$; $R = 0·048$, $R_w = 0·053$, $S = 0·68$, max. $\Delta/\sigma = 1·70$, average $\Delta/\sigma = 0·28$ (0·62 and 0·18 respectively if H atoms excluded), max. and min. $\Delta\rho$ excursions in final difference Fourier 0·39 and −0·32 e Å^{-3}.

Discussion. The final positional parameters are given in Table 1.* Interatomic distances and angles are given in Table 2.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths involving H atoms and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38866 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and isotropic temperature factors (Å^2) with e.s.d.'s in parentheses*

	x	y	z	B_{eq}/B_{iso}*
S(1)	0·8041 (1)	0·1340 (1)	−0·0665 (1)	4·1
S(2)	1·0624 (1)	0·3638 (1)	−0·1212 (1)	3·6
N(1)	0·8280 (4)	0·3417 (3)	0·0449 (2)	4·2
N(2)	0·3560 (4)	0·4130 (3)	0·2658 (2)	3·5
C(1)	0·8900 (4)	0·2823 (3)	−0·0407 (3)	3·2
C(2)	0·6700 (5)	0·2992 (4)	0·1187 (3)	4·3
C(3)	0·4942 (6)	0·3583 (4)	0·0830 (3)	4·9
C(4)	0·3250 (5)	0·3461 (4)	0·1598 (3)	4·5
C(5)	0·4288 (6)	0·5450 (4)	0·2578 (4)	5·0
C(6)	0·1704 (6)	0·3977 (4)	0·3287 (4)	4·6
H(N1)	0·876 (6)	0·425 (4)	0·054 (4)	2·5 (1·1)
H(N2)	0·447 (6)	0·382 (4)	0·306 (4)	2·1 (1·0)
H1(C2)	0·634 (5)	0·209 (4)	0·114 (3)	2·6 (0·8)
H2(C2)	0·704 (6)	0·331 (4)	0·202 (4)	3·9 (1·1)
H1(C3)	0·460 (8)	0·308 (5)	0·011 (5)	5·5 (1·4)
H2(C3)	0·534 (8)	0·459 (6)	0·082 (5)	5·0 (1·6)
H1(C4)	0·208 (6)	0·386 (4)	0·118 (3)	4·0 (1·0)
H2(C4)	0·296 (5)	0·250 (4)	0·175 (3)	2·4 (0·8)
H1(C5)	0·557 (7)	0·554 (4)	0·224 (4)	4·1 (1·0)
H2(C5)	0·428 (6)	0·582 (4)	0·334 (4)	3·1 (1·0)
H3(C5)	0·341 (8)	0·581 (5)	0·209 (4)	4·6 (1·3)
H1(C6)	0·123 (5)	0·312 (4)	0·335 (3)	2·6 (0·8)
H2(C6)	0·199 (6)	0·437 (4)	0·405 (3)	2·6 (0·8)
H3(C6)	0·082 (6)	0·444 (4)	0·293 (3)	3·1 (0·9)

* $B_{eq} = \frac{8}{3}\pi^2$ trace $\tilde{U}$.

Table 2. *Interatomic distances (Å) and angles (°)*

S(1)–C(1)	1·699 (3)	C(3)–C(4)	1·508 (6)
S(2)–C(1)	1·727 (3)	C(4)–N(2)	1·501 (5)
C(1)–N(1)	1·338 (5)	N(2)–C(5)	1·483 (5)
N(1)–C(2)	1·464 (5)	N(2)–C(6)	1·503 (5)
C(2)–C(3)	1·521 (6)		
S(1)–C(1)–S(2)	122·4 (2)	N(2)–C(4)–C(3)	115·8 (3)
S(1)–C(1)–N(1)	121·2 (2)	C(1)–N(1)–C(2)	127·5 (3)
S(2)–C(1)–N(1)	116·4 (2)	C(4)–N(2)–C(5)	115·8 (3)
N(1)–C(2)–C(3)	107·5 (3)	C(4)–N(2)–C(6)	108·7 (3)
C(2)–C(3)–C(4)	116·5 (4)	C(5)–N(2)–C(6)	109·5 (3)

A clinographic projection of the molecule, with atom labelling, is shown in Fig. 1. The molecule exists as a zwitterion $(CH_3)_2N^+H(CH_2)_3NHCS_2^-$. The thioureide group $-NCS_2$ is planar to within 0·004 (3) Å. The C—N and C—S bond lengths compare very well with the values found in sodium N,N-diethyldithiocarbamate trihydrate (Colapietro, Domenicano & Vaciago, 1968). The C(1)—N(1) distance, 1·338 (5) Å, implies that this bond has strong double-bond character. The C—S bonds, lengths 1·727 (3) and 1·699 (3) Å, have partial double-bond character. A calculation of the contributions of the resonance structures (I)–(III), based on the bond lengths above and carried out according to valence-bond theory (Pauling, 1960), gives 38% for (I) and 31% for each of (II) and (III).

The difference in length, equal to 6·6σ, between the bonds C(1)—S(1) = 1·699 (3) and C(1)—S(2) = 1·727 (3) Å implies that they are not equivalent. Because of this the IR spectrum of the compound exhibits two discrete bands, at 995(s) and 1035(m) cm^{-1}. Similar bands are observed in the IR spectra of the Ni^{II} [at 980(s) and 1050(m) cm^{-1}] and the Cu^I [at 980(s) and 1030(m) cm^{-1}] complexes of the compound, which are also attributed to the non-equivalence of the C—S bonds. All IR spectra were measured on the compounds in the solid state. As a consequence, it might be concluded that the character of these bonds is influenced mainly by the electron-donating capacity of the R group $(CH_3)_2N(CH_2)_3-$ but is not affected substantially by complex formation. Undoubtedly, exact quantitative conclusions can only be drawn after X-ray crystal structure analysis of the metal complexes.

N(2) is bonded to three C atoms and one H atom in an approximately tetrahedral arrangement. None of the bond angles differ from 109° by more than 7$^\delta$ and four have values very near to 109°. The C—N(2) bond lengths are close to the accepted C—N distance, 1·48 Å, for four-covalent nitrogen (*International Tables for X-ray Crystallography*, 1968). The distance of N(2) from the plane of the three C atoms to which it is bonded is 0·449 (3) Å. H(N2) is closely approached by the sulphur atoms, S(1^i) and S(2^i), of a symmetry-equivalent molecule situated at $\frac{3}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$. The distance H(N2)$\cdots$S(1^i) = 2·37 (5) Å and the angle N(2)—H(N2)$\cdots$S(1^i) = 161 (3)° indicate the existence of a hydrogen bond. The distance H(N2)$\cdots$S(2^i) = 2·84 (4) Å. These distances may be compared with the sum of the corresponding van der Waals radii, 2·86 Å (Bondi, 1964).

Another hydrogen bond occurs between the molecule and its symmetry equivalent at $2 - x$, $1 - y$, $-z$. The distance H(N1)$\cdots$S(2^{ii}) is 2·46 (5) Å and the angle N(1)—H(N1)$\cdots$S(2^{ii}) is 164 (4)°.

All other intermolecular contact distances are normal within the limits of experimental error.

The molecular packing is illustrated in a stereoview of the unit cell (Fig. 2).
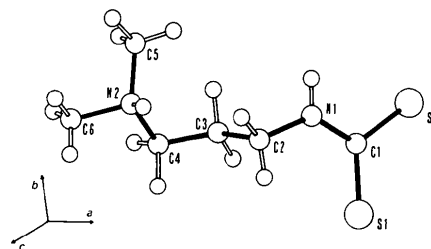

Fig. 1. Clinographic projection of an N-(3-dimethylaminopropyl)-dithiocarbamic acid molecule.
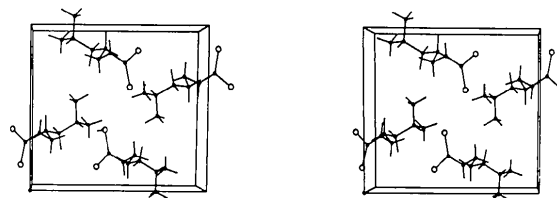

Fig. 2. Stereo plot of the unit cell.

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