Methyl 2-[2-(Diethylamino)ethyl]amino-1-cyclopentenecarbodithioate, $C_{13}H_{24}N_2S_2$

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Abstract. $M_r = 272.48$, monoclinic, *Cc*, $a = 7.571$ (5), $b = 17.772$ (9), $c = 11.505$ (7) Å, $\beta = 92.87$ (5)°, $V = 1546.0$ Å³, $D_x = 1.17$ Mg m⁻³, $Z = 4$, $F(000) = 592$, graphite-monochromated Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.309$ mm⁻¹, room temperature, $R_F = 0.061$ for 1006 observed reflections. Intramolecular hydrogen bonding [N—H⋯S = 3.030 (7) Å] is present. Another significant observation is the partial delocalization of the N lone pair in the conjugated system N—C=C—C; as a result the double bond C=C = 1.402 (11) Å is longer than its normal value of 1.34 Å and the single bonds C—C = 1.391 (10) Å and C—N = 1.332 (10) Å are noticeably shortened. The five-membered ring has an envelope conformation with pseudorotational phase angle $\Delta = 38.7°$.

Introduction. The title compound contains three potential donor sites which are capable of forming strong metal–ligand bonds. Our particular interest is to investigate whether there exists any intramolecular hydrogen bonding through the thiocarbonyl S atom and secondary amino N. If verified this would lead to the formation of deprotonated metal complexes of the ligand.

Experimental. Brownish plate-shaped single crystals from petroleum ether solution by slow evaporation at room temperature. D_m not determined. Crystal 0.23 × 0.20 × 0.15 mm. Enraf–Nonius CAD-4 diffractometer. 1359 unique reflections. $\omega/2\theta$ scan mode; θ from 2 to 25° ($h = -9$ to 9, $k = 0$ to 21, $l = 0$ to 13); variable scan speeds with max. scan time 75 s. Cell dimensions and standard errors from least-squares analysis of setting angles for 25 reflections with $9° < \theta < 15°$. Intensities of three reflections monitored after every hour of exposure showed no crystal decomposition. Intensities corrected for Lorentz and polarization effects only. 1025 reflections observed with $F_o > 2\sigma(F_o)$. Intensities placed on an absolute scale by Wilson's method. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); the best *E* map revealed the two S and six non-hydrogen atoms; S positions also confirmed from Patterson map; remaining non-hydrogen atoms from a weighted Fourier synthesis. Positional and anisotropic thermal

parameters for all non-H atoms were refined by block-diagonal least squares; $\sum w(|F_o| - |F_c|)^2$ minimized; weights $w = 1/\sigma^2$ calculated according to Seal & Ray (1981). 18 H atoms from difference Fourier map, remaining H atoms assigned geometrically. Subsequent refinement including H atoms with fixed positional and isotropic temperature factors led to $R = 0.063$, $R_w = 0.068$ for observed data. 19 reflections excluded from observed data due to poor agreement of F_o and F_c resulting in final $R_F = 0.061$, $R_w = 0.065$. In final cycle of refinement $(\Delta/\sigma)_{max} = 0.33$; max. peak on final difference map 0.20 e Å⁻³. Atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). Computer programs used were those of the *XRAY ARC* program package (Vickery, Bright & Mallinson, 1971).

Discussion. A perspective view of the molecule with the atomic numbering scheme and thermal ellipsoids is shown in Fig. 1. Fig. 2 shows the packing of the molecules in the unit cell viewed down **a**. Table 1 contains the final positional parameters with equivalent isotropic thermal parameters and Table 2 the intramolecular bond distances and angles.* On comparing the bond lengths and valency angles in this structure with those found in similar compounds (Sarkar & Sen Gupta 1981, 1982*a,b*), good agreement is observed when experimental errors are taken into account. A unique and common feature that exists in all these structures is the intramolecular N—H⋯S bonding. For the present structure the hydrogen-bonding distances are S(1)⋯H—N(1) = 3.030 (7) and S(1)—HN(1) = 2.304 (3) Å. N(1) shows a significant deviation from the expected sp^3 hybridization. The bond length N(1)—C(7) = 1.332 (10) Å is significantly shorter than the normal value of 1.426 Å for a C(sp^2)—N single bond, thus showing partial double-bond character.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39647 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Again, the C(7)—N(1)—C(8) angle of 122·9 (7)° is very close to 120° and creates the impression that the N(1) atom is sp^2 hybridized. This strongly suggests partial delocalization of the N(1) lone pair in the conjugated system N(1)—C(7)=C(3)—C(2); as a result the double bond C(7)=C(3) is extended from its normal value of 1·34 Å and the single bonds C(2)—C(3) and C(7)—N(1) are noticeably shortened. The five-membered ring has an envelope conformation with pseudorotational phase angle $\Delta = 38·7°$ (Altona, Geise & Romers, 1968).
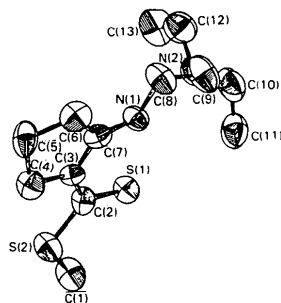
Fig. 1. A perspective view of the molecule with the atomic numbering scheme and 50% probability ellipsoids of the atoms. N(2) is connected to C(9), C(10) and C(12).
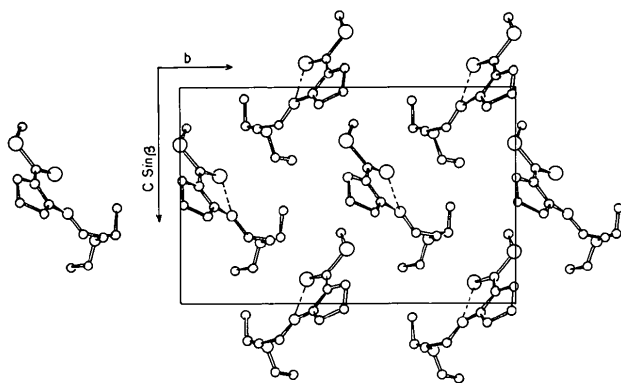

Fig. 2. Packing of the molecules viewed down a.

Table 1. *Atomic coordinates for non-hydrogen atoms* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2$)

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S(2)	1557	4993 (1)	2585	5·48
S(1)	−243 (3)	3793 (1)	1114 (3)	4·97
N(1)	2465 (8)	3420 (4)	−651 (6)	4·14
C(3)	3011 (9)	4427 (4)	769 (6)	3·70
C(2)	1499 (10)	4383 (5)	1405 (8)	4·39
C(6)	5250 (10)	4159 (5)	−551 (8)	5·04
C(1)	−386 (12)	4795 (6)	3345 (10)	6·83
C(7)	3444 (9)	3970 (4)	−168 (7)	4·21
N(2)	−121 (9)	2588 (4)	−2003 (7)	5·27
C(4)	4550 (11)	4959 (5)	1047 (8)	5·02
C(9)	1690 (14)	2325 (6)	−1809 (11)	7·83
C(8)	3043 (11)	2963 (5)	−1602 (9)	5·93
C(13)	−1727 (17)	1937 (6)	−527 (12)	8·28
C(10)	−419 (16)	2839 (7)	−3184 (10)	8·25
C(5)	5665 (11)	4914 (5)	−10 (9)	5·60
C(12)	−1362 (16)	1979 (6)	−1759 (11)	8·34
C(11)	−2012 (17)	3367 (8)	−3364 (13)	9·96

Table 2. *Intramolecular bond distances* (Å) *and angles* (°)

C(1)—S(2)	1·783 (10)	C(7)—N(1)	1·332 (10)
S(2)—C(2)	1·737 (9)	N(1)—C(8)	1·448 (12)
S(1)—C(2)	1·705 (8)	C(8)—C(9)	1·539 (14)
C(2)—C(3)	1·391 (10)	C(9)—N(2)	1·455 (13)
C(3)—C(4)	1·522 (11)	N(2)—C(10)	1·437 (14)
C(4)—C(5)	1·516 (13)	N(2)—C(12)	1·470 (14)
C(5)—C(6)	1·506 (13)	C(10)—C(11)	1·535 (18)
C(6)—C(7)	1·496 (10)	C(12)—C(13)	1·459 (19)
C(3)—C(7)	1·402 (11)		

C(1)—S(2)—C(2)	105·7 (4)	C(3)—C(7)—N(1)	126·8 (7)
S(2)—C(2)—S(1)	121·8 (5)	C(6)—C(7)—N(1)	122·7 (7)
C(3)—C(2)—S(1)	125·5 (6)	C(7)—N(1)—C(8)	122·9 (7)
C(3)—C(2)—S(2)	112·7 (6)	N(1)—C(8)—C(9)	107·8 (8)
C(2)—C(3)—C(4)	124·5 (7)	C(8)—C(9)—N(2)	113·7 (9)
C(2)—C(3)—C(7)	127·0 (7)	C(9)—N(2)—C(10)	110·3 (8)
C(4)—C(3)—C(7)	108·3 (6)	C(9)—N(2)—C(12)	109·9 (8)
C(3)—C(4)—C(5)	104·5 (7)	C(10)—N(2)—C(12)	109·7 (8)
C(4)—C(5)—C(6)	105·4 (7)	N(2)—C(10)—C(11)	113·7 (9)
C(5)—C(6)—C(7)	104·6 (7)	N(2)—C(12)—C(13)	112·1 (9)
C(6)—C(7)—C(3)	110·4 (7)		

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