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Structure of *N*-(Diethylaminothiocarbonyl)benzamidine

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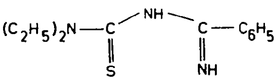
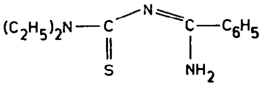
Abstract. $C_{12}H_{17}N_3S$, $M_r = 235{\cdot}4$, monoclinic, $P2_1$, $a = 5{\cdot}353\ (2)$, $b = 8{\cdot}440\ (3)$, $c = 14{\cdot}380\ (8)$ Å, $\beta = 95{\cdot}06\ (3)^\circ$, $V = 647{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}21$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 1{\cdot}88$ cm^{-1}, $F(000) = 252$, room temperature. Final $R = 0{\cdot}079$ for 1164 unique observed reflections. The molecules have an approximate *Z,Z'* configuration. Both H atoms are bonded to the terminal N atom (enamine form). The C—S bond is intermediate between a double and a single bond. There exist two types of C—N bonds inside the molecule.

Introduction. Recently we reported the structure of 1,1-diethyl-3-thiobenzoylthiourea (Braun, Richter, Sieler, Beyer, Lindqvist, Yanovsky & Struchkov, 1987). As part of our study on the structure of *N*-chalcogenoacylthioureas we report here the structure of the title compound in which the chalcogen atom is formally substituted by an NH group which is isoelectronic to the chalcogen atom O [(I)]. The solution of the structure should provide information on the configuration and the tautomerism [(I) or (II)] as well as the bonding parameters.



$(C_2H_5)_2N{-}C({=}S){-}NH{-}C({=}NH){-}C_6H_5$

(I)



$(C_2H_5)_2N{-}C({=}S){-}N{=}C(NH_2){-}C_6H_5$

(II)

Experimental. The title compound was prepared according to the method of Beyer, Hartung & Widera

(1984). Suitable crystals were obtained by recrystallization from ethanol; m.p. 372–373 K. Crystal dimensions 0·4 × 0·3 × 0·2 mm. Nonius CAD-4 diffractometer, graphite monochromator, $\omega/2\theta$ scans, lattice parameters by least-squares fit of 16 reflections, systematic absences $0k0$, $k = 2n + 1$, Lp corrections, no absorption corrections, $0 < \theta \leq 29{\cdot}8°$, h −7→6, k 0→11, l 0→18, 1535 unique reflections, 1164 with $F_o > 3\sigma(F_o)$, three standard reflections, 3% intensity variation, direct methods, full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, unit weights, anisotropic for all non-H atoms, all H atoms were obtained from a difference map, contribution of scattering amplitudes of all H atoms in their calculated positions (C—H = 1·05 Å) except for H(1) and H(2), included in the last cycle of the refinement, with assigned isotropic thermal parameters $U_{\rm iso}$ of the attached atom, no refinement of hydrogen coordinates. Final $R = 0{\cdot}079$ (rather high owing to the poor quality of the crystal), maximum and minimum peaks in the final difference map 0·39 and $-0{\cdot}43$ e Å^{-3}, respectively; maximum least-squares shift-to-e.s.d. ratio in the final cycle 0·82; average shift-to-e.s.d. ratio 0·17; atomic scattering factors from *SHELX76* (Sheldrick, 1976) used, all calculations performed with *SHELX76*. The stereoscopic view of the molecule was drawn with the program *ORTEP* (Johnson, 1965).

Discussion. Table 1 lists the fractional coordinates and Table 2 lists bond lengths and angles involving non-H atoms.* Fig. 1 shows the atomic numbering scheme. A stereoscopic view of the molecule is shown in Fig. 2. The molecule adopts an approximate *Z,Z′* configuration which has already been found for the planar molecule of *N*-(pivaloyl)pivalamidine, in which an intramolecular N—H···O bridge is formed (Hvoslef, Tracy & Nash, 1986). The S,C(2),N(1),C(1),N(3) unit deviates extensively from planarity and the torsion angles ω_1[S—C(2)—N(1)—C(1)] and ω_2[C(2)—N(1)—C(1)—N(3)] described by Braun *et al.* (1987) are 65·0 (4) and 5·3 (4)°, respectively. The C(2),N(2),C(3),C(5) unit is planar within 3σ indicating sp^2 hybridization of N(2).

Both H(1) and H(2) are bonded to the terminal nitrogen atom N(3). Thus the molecule exists in the tautomeric enamine form which is consistent with ESCA spectroscopic investigations by Härtung, Weber, Beyer & Szargan (1985). The C(2)—S distance of 1·700 (8) Å is intermediate between a double (1·61 Å) and a single bond (1·81 Å) (Pauling, 1968) and is in accordance with those of other compounds containing —N—C(S)—N— elements, *e.g.* thiourea [1·720 (9) Å] (Truter, 1967) and thiosemicarbazide [1·701 (5) Å] (Hansen & Hazell, 1969).

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2× 10^3)

	x	y	z	$U_{\rm eq}$*
S	4539 (5)	4549	1567 (2)	59 (1)
N(1)	4861 (13)	6679 (8)	2965 (4)	39 (4)
N(2)	3514 (13)	7638 (9)	1508 (4)	43 (4)
N(3)	9056 (17)	6116 (14)	2936 (6)	61 (5)
C(1)	7049 (13)	6484 (9)	3380 (5)	34 (4)
C(2)	4329 (15)	6402 (10)	2018 (5)	37 (4)
C(3)	2793 (19)	7546 (12)	0494 (5)	55 (5)
C(4)	0071 (20)	7182 (15)	0265 (5)	63 (6)
C(5)	3439 (20)	9236 (11)	1923 (6)	55 (6)
C(6)	5944 (21)	10117 (12)	1870 (8)	65 (6)
C(7)	7431 (14)	6767 (10)	4391 (5)	36 (4)
C(8)	9406 (18)	6054 (14)	4917 (6)	59 (6)
C(9)	9699 (20)	6300 (16)	5878 (7)	68 (7)
C(10)	8075 (21)	7199 (13)	6319 (6)	59 (6)
C(11)	6042 (21)	7885 (13)	5803 (6)	63 (6)
C(12)	5753 (17)	7671 (11)	4846 (6)	49 (5)

* $U_{\rm eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

S—C(2)	1·700 (8)	C(3)—C(4)	1·498 (14)
N(1)—C(1)	1·278 (9)	C(5)—C(6)	1·541 (14)
N(1)—C(2)	1·386 (9)	C(7)—C(12)	1·386 (11)
N(2)—C(2)	1·326 (9)	C(7)—C(8)	1·382 (11)
N(2)—C(3)	1·476 (10)	C(8)—C(9)	1·392 (13)
N(2)—C(5)	1·478 (11)	C(9)—C(10)	1·353 (14)
N(3)—C(1)	1·334 (10)	C(10)—C(11)	1·389 (14)
C(1)—C(7)	1·469 (10)	C(11)—C(12)	1·383 (12)
C(1)—N(1)—C(2)	122·5 (7)	N(2)—C(3)—C(4)	113·1 (7)
C(2)—N(2)—C(3)	123·3 (7)	N(2)—C(5)—C(6)	111·4 (8)
C(2)—N(2)—C(5)	120·9 (6)	C(1)—C(7)—C(8)	120·3 (8)
C(3)—N(2)—C(5)	115·7 (7)	C(1)—C(7)—C(12)	121·1 (7)
N(1)—C(1)—N(3)	123·4 (7)	C(8)—C(7)—C(12)	118·5 (7)
N(1)—C(1)—C(7)	118·9 (6)	C(7)—C(8)—C(9)	119·5 (9)
N(3)—C(1)—C(7)	117·6 (7)	C(8)—C(9)—C(10)	121·9 (10)
S—C(2)—N(1)	121·0 (6)	C(9)—C(10)—C(11)	119·2 (8)
S—C(2)—N(2)	122·8 (5)	C(10)—C(11)—C(12)	119·4 (10)
N(1)—C(2)—N(2)	116·1(7)	C(11)—C(12)—C(7)	121·4 (9)

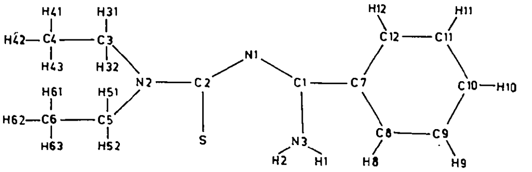


Fig. 1. The atom-numbering scheme.

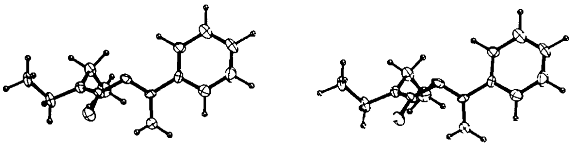


Fig. 2. Stereoview of the molecule.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44471 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

There exist two significantly different C—N bonds within the C(1)—N(1)—C(2) unit. While C(1)—N(1) [1·278 (9) Å] is a double bond, C(2)—N(1) [1·386 (9) Å] has a value halfway between a single and a double bond. In the *S*-methyl ester of guanidinodithioformic acid one can note the opposite effect. Here C(2)—N(1) [1·295 (5) Å] is a double bond whereas C(1)—N(1) [1·370 (5) Å] lies between a single and a double bond (Kiel, Gattow & Eul, 1984). The other C—N bonds C(1)—N(3) [1·334 (10)] and C(2)—N(2) [1·326 (9) Å] also have values between a single and a double bond. The C—N bond lengths involving C(1) are in good agreement with those found in acetamidine [C(1)—N(1) 1·298 (1), C(1)—N(3) 1·344 (1) Å] (Norrestam, Mertz & Crossland, 1983). The atoms of the phenyl ring C(7)—C(12) are coplanar within the experimental error. The least-squares plane defined by these atoms makes a dihedral angle of 23·3 (4)° with the plane defined by the atoms N(1), C(1), N(3).

The crystal structure is built up from isolated molecules. Surprisingly the molecule does not form an intermolecular hydrogen bridge. However, there are relatively short intramolecular S···H(2) (2·68 Å) and S—N(3) (3·26 Å) distances. The angle S—H(2)—N(3) has a value of 131°. In contrast to *N*-(pivaloyl)-pivalamidine a planar arrangement of the S—C(2)—N(1)—C(1)—N(3)—H(2) unit is not possible because of the greater van der Waals radius of S compared with O.

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Structure of 3-Methoxy-2-phenyl-4*H*-1-benzopyran-4-one (3-Methoxyflavone)

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Abstract. $C_{16}H_{12}O_3$, $M_r = 252·27$, monoclinic, $P2_1/c$, $a = 10·267$ (3), $b = 14·679$ (4), $c = 8·738$ (2) Å, $\beta = 111·9$ (1)°, $Z = 4$, $D_m = 1·3$, $D_x = 1·37$ g cm^{-3}, $V = 1222$ (1) Å^3, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·883$ cm^{-1}, $F(000) = 528$, $T = 293$ K, $R = 0·044$ for 1005 reflections. The torsion angle between the phenyl ring and the fused two-ring system is 37·2° due to the steric interaction between the methoxy C(3) and adjacent hydrogen atoms on the phenyl ring. A comparison is made with three other 3-substituted flavones reported earlier.

Introduction. Owing to the pharmacological interest of the flavonoids a certain number of crystal structures have been resolved. A recent review has been published by Cantrell (1986). The structure of 5-hydroxy-6′,8-dimethoxy-2′,5′,7-triethoxyflavone has been elucidated by X-ray methods (Kimura, Okuda, Taira, Shoji, Takemoto & Arichi, 1984) as has that of 5,3′-dihydroxy-6,7,8,2′,4′,5′-hexamethoxyflavone (Quijano, Calderon, Gomez, Escobar & Rios, 1985) but in the latter case no crystallographic data were available.

In order to collect conformational information about methoxyflavones and to find relationships between chemical structure, chromatographic behaviour and

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