3-Benzyl-5-methylthio-3*H*,7*H*-1,2,3-triazolo[4,5-*d*][1,3]thiazine

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Abstract. $C_{12}H_{12}N_4S_2$, $M_r = 276.41$, triclinic, $P\bar{1}$, $a = 8.742$ (3), $b = 9.717$ (3), $c = 9.823$ (3) Å, $\alpha = 110.09$ (2), $\beta = 113.70$ (2), $\gamma = 102.17$ (2)°, $U = 655.9$ Å^3, $Z = 2$, $D_m = 1.38$, $D_c = 1.400$ Mg m^{-3}, $F(000) = 288$, μ(Mo $K\alpha$) = 0.384 mm^{-1}. The structure was refined to $R = 0.051$ for 1469 observed diffractometer data. The 1,3-thiazine ring has a distorted boat-like conformation characterized by the torsion angles C(9)–N(4)–C(5)–S(6), 2.6 (5)° and S(6)–C(7)–C(8)–C(9), −30.4 (5)°. The fused 1,2,3-triazole ring is planar.

Introduction. Recrystallization of the title compound from cyclohexane afforded colourless, thin rectangular-shaped crystals, with a bi-convex cross-section from which a fragment of dimensions 0.38 × 0.58 mm was cut. It had a maximum thickness of about 15 μm. Reflection intensities were measured on a Picker FACS-1 diffractometer in θ–2θ continuous scan mode [3° < 2θ < 50°, Mo $K\bar{\alpha}$ radiation, graphite-crystal monochromator, forms recorded $h, \pm k, \pm l$, 2524 reflections including standards (3 every 97 data, no significant degradation)]. Sorting and averaging yielded 1469 unique data having $I \geq 3\sigma(I)$. R_s for this data set (Robertson & Whimp, 1975) was 0.028. The unit-cell dimensions were determined by least-squares analysis of the angular settings for 12 widely separated reflections with 27° < 2θ < 34°.

The positions of all non-H atoms were determined using *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). After partial refinement, H atoms were included in the scattering model at their expected locations. The structure was then refined to convergence by full-matrix least-squares analysis with anisotropic thermal parameters for C, N and S atoms, isotropic thermal parameters for H atoms, and σ_F^{-2} weights ($p^2 = 0.002$ assumed; Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967). The final agreement indices were $R = 0.051$ and $R_w = 0.061$ with $[\sum \Delta^2/(n - s)]^{1/2} = 1.89$. A difference synthesis after the final refinement cycle showed fluctuations of up to 0.79 and

Table 1. *Atom coordinates* ($\times 10^4$ *for* C, N *and* S *atoms and* $\times 10^3$ *for* H *atoms*) *with their e.s.d.'s in parentheses and isotropic thermal parameters*

	x	y	z	B_{eq}* (Å^2)
N(1)	2847 (7)	5452 (5)	3607 (5)	5.75
N(2)	1427 (6)	4097 (5)	2865 (4)	5.66
N(3)	1280 (4)	3887 (4)	4100 (4)	4.01
N(4)	2803 (4)	5241 (4)	7121 (4)	3.89
C(5)	3892 (5)	6610 (5)	8418 (5)	4.30
S(6)	5109 (2)	8365 (1)	8474 (2)	5.85
C(7)	5255 (7)	7548 (6)	6610 (5)	5.88
C(8)	3589 (6)	6092 (5)	5282 (6)	4.35
C(9)	2617 (5)	5109 (4)	5624 (4)	3.34
S(10)	4219 (2)	7025 (2)	10401 (1)	6.63
C(11)	2490 (11)	5266 (9)	9891 (9)	7.42
C(12)	−61 (6)	2409 (5)	3711 (6)	4.81
C(13)	643 (5)	1113 (4)	3549 (4)	3.58
C(14)	127 (6)	−65 (5)	1997 (6)	4.96
C(15)	803 (7)	−1236 (5)	1850 (7)	6.00
C(16)	1998 (7)	−1232 (5)	3271 (6)	5.48
C(17)	2512 (6)	−78 (5)	4822 (6)	5.00
C(18)	1846 (6)	1097 (5)	4972 (5)	4.42
H1(C7)	644 (7)	748 (6)	697 (6)	7.6 (13)
H2(C7)	524 (6)	827 (5)	618 (5)	6.2 (11)
H1(C11)	257 (7)	551 (6)	1090 (7)	8.1 (13)
H2(C11)	110 (10)	506 (8)	903 (9)	12.9 (22)
H3(C11)	258 (7)	437 (6)	931 (6)	7.1 (14)
H1(C12)	−113 (5)	208 (4)	266 (5)	4.6 (9)
H2(C12)	−29 (6)	278 (5)	478 (5)	6.7 (11)
H(C14)	−73 (6)	−5 (5)	109 (5)	5.6 (10)
H(C15)	44 (6)	−196 (6)	82 (6)	6.9 (12)
H(C16)	242 (5)	−193 (5)	317 (5)	4.9 (10)
H(C17)	340 (6)	−8 (5)	591 (5)	6.3 (10)
H(C18)	223 (5)	193 (4)	609 (5)	4.4 (8)

* $B_{eq} = \frac{4}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$; actual B values for H atoms.

−1.65 e Å^{-3}. All features above 0.20 e Å^{-3} occurred in the vicinity of the S atoms. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 1.† Bond distances, angles and torsion angles are in Tables 2, 3 and 4 respectively.

† Lists of structure factors, anisotropic thermal parameters and deviations from mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36822 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$$C_{12}H_{12}N_4S_2$$

Table 2. Bond lengths (Å)

N(1)–N(2)	1·316 (5)	C(12)–C(13)	1·502 (5)
N(1)–C(8)	1·336 (5)	C(13)–C(14)	1·367 (5)
N(2)–N(3)	1·347 (4)	C(13)–C(18)	1·378 (5)
N(3)–C(9)	1·343 (4)	C(14)–C(15)	1·380 (6)
N(3)–C(12)	1·462 (5)	C(15)–C(16)	1·365 (6)
N(4)–C(5)	1·275 (5)	C(16)–C(17)	1·358 (6)
N(4)–C(9)	1·369 (4)	C(17)–C(18)	1·378 (6)
C(5)–S(6)	1·779 (4)	C(7)–H1(C7)	0·93 (4)
C(5)–S(10)	1·733 (4)	C(7)–H2(C7)	0·98 (5)
S(6)–C(7)	1·798 (5)	C(11)–H	0·90–1·09 (6)
C(7)–C(8)	1·470 (6)	C(12)–H1(C12)	0·95 (4)
C(8)–C(9)	1·362 (5)	C(12)–H2(C12)	1·10 (4)
S(10)–C(11)	1·781 (7)	C(phenyl)–H	0·83–1·04 (4)

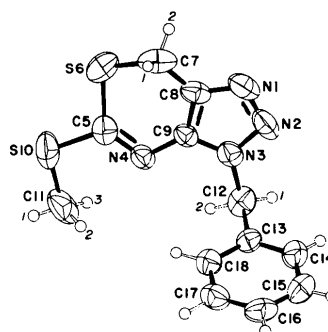Fig. 1. Atom numbering in 3-benzyl-5-methylthio-3H,7H-1,2,3-triazolo[4,5-d][1,3]thiazine. Thermal ellipsoids depict 50% probability surfaces and H atoms are shown as 0·1 Å spheres.

Table 3. Bond angles (°)

N(2)–N(1)–C(8)	108·9 (3)	C(12)–C(13)–C(18)	120·5 (4)
N(1)–N(2)–N(3)	107·1 (3)	C(14)–C(13)–C(18)	118·4 (4)
N(2)–N(3)–C(9)	110·2 (3)	C(13)–C(14)–C(15)	121·1 (4)
N(2)–N(3)–C(12)	121·0 (4)	C(14)–C(15)–C(16)	119·8 (5)
C(9)–N(3)–C(12)	128·5 (3)	C(15)–C(16)–C(17)	119·8 (5)
C(5)–N(4)–C(9)	115·6 (3)	C(16)–C(17)–C(18)	120·5 (5)
N(4)–C(5)–S(6)	127·2 (3)	C(13)–C(18)–C(17)	120·4 (4)
N(4)–C(5)–S(10)	122·0 (3)	S(6)–C(7)–H1(C7)	107 (3)
S(6)–C(5)–S(10)	110·5 (2)	S(6)–C(7)–H2(C7)	109 (3)
C(5)–S(6)–C(7)	102·3 (2)	C(8)–C(7)–H1(C7)	119 (3)
S(6)–C(7)–C(8)	109·2 (3)	C(8)–C(7)–H2(C7)	105 (3)
N(1)–C(8)–C(7)	127·8 (4)	H1(C7)–C(7)–H2(C7)	108 (4)
N(1)–C(8)–C(9)	109·0 (4)	S(10)–C(11)–H	102–114 (3)
C(7)–C(8)–C(9)	123·0 (4)	H–C(11)–H	102–122 (3)
N(3)–C(9)–N(4)	123·5 (3)	N(3)–C(12)–H1(C12)	107 (2)
N(3)–C(9)–C(8)	104·9 (3)	N(3)–C(12)–H2(C12)	103 (2)
N(4)–C(9)–C(8)	131·6 (4)	C(13)–C(12)–H1(C12)	110 (2)
C(5)–S(10)–C(11)	101·0 (3)	C(13)–C(12)–H2(C12)	113 (2)
N(3)–C(12)–C(13)	111·4 (3)	H1(C12)–C(12)–H2(C12)	113 (3)
C(12)–C(13)–C(14)	121·1 (4)	C–C(phenyl)–H	115–123 (3)

Table 4. Torsion angles in the 1,3-thiazine ring (°)

C(9)–N(4)–C(5)–C(6)	2·6 (5)	S(6)–C(7)–C(8)–C(9)	−30·4 (5)
N(4)–C(5)–S(6)–C(7)	−24·6 (4)	N(1)–C(8)–C(9)–N(4)	−178·7 (3)
N(4)–C(5)–S(10)–C(11)	−8·2 (4)	C(7)–C(8)–C(9)–N(4)	5·3 (6)
S(6)–C(5)–S(10)–C(11)	167·0 (3)	C(7)–C(8)–C(9)–N(3)	−176·5 (3)
C(5)–S(6)–C(7)–C(8)	34·2 (4)	C(8)–C(9)–N(4)–C(5)	11·8 (6)

Discussion. Heating 4-amino-5-aminomethyl-3-benzyl-1,2,3-triazole with carbon disulphide and a base did not lead to the expected product (9-benzyl-1,6-dihydro-8-azapurine-2-thione). Instead a triazolothiazine was obtained (Albert, 1980). It contains a completely new heterocyclic system. Such a nucleus is attractive to synthetic chemists who seek candidate drugs for experimental testing (in this case for anticancer activity). A single-crystal X-ray analysis was required to establish which of two isomers, with the locations of the N and S atoms reversed, was formed. Since the parent compound did not yield suitable crystals, the S-methyl derivative was prepared and the analysis furnished the structure: 3-benzyl-5-methylthio-3H,7H-1,2,3-triazolo[4,5-d][1,3]thiazine. A preliminary account of this work and of the chemistry of the system has appeared elsewhere (Albert & Dunand,

1980). The atom nomenclature is defined in Fig. 1, drawn using ORTEP (Johnson, 1976).

The 6H-1,3-thiazine system has a distorted boat conformation. The C atoms opposite the C=N bond [C(7) and C(8)] are each displaced in the same direction [by 0·680 (7) and 0·249 (6) Å respectively] from the best plane through the remaining atoms. That conformation is in contrast with the distorted half-chair conformation adopted in a 2-benzylthio-4,5-dihydro-6H-1,3-thiazine derivative (Martinez, Cano & Garcia-Blanco, 1977), in which the respective C atoms are displaced in opposite directions (+0·32 and −0·43 Å) from the C–N=C–S plane. Otherwise, both molecules exhibit similar geometry in the N=C(–S–C)₂ fragment. Constraints in the six-membered ring result in strained endocyclic N–C–S angles [127·2 (3)° in the title compound, 130·1 (2)° in the other]. In contrast, the exocyclic N–C–S angles [122·0 (3) and 122·8 (2)° respectively] are close to those found in the unstrained −N=C(S–Me)₂ system of 3,6-bis(methylthio)-4,5-diaza-2,7-dithiaocta-3,5-diene, 120·7–121·5 (6)° (Lanfredi, Tiripicchio & Camellini, 1975). It follows that the S–C–S angles in the 1,3-thiazine derivatives [110·5 (2) and 107·2 (9)° respectively] are significantly smaller than in the unstrained system [117·8 (4)°]. Presumably because of ring strain, the endocyclic C–S bonds in the present molecule are longer than the corresponding exocyclic ones, C(5)–S(6) = 1·779 (4) and C(7)–S(6) = 1·798 (5) Å versus C(5)–S(10) = 1·733 (4) and C(11)–S(10) = 1·781 (7) Å. The C–S–C bond angles [endocyclic, 102·3 (2)°; exocyclic, 101·0 (3)°] are in good agreement with those in 3,6-bis(methylthio)-4,5-diaza-2,7-dithiaocta-3,5-diene [102·1–103·3 (4)°].

The 1,2,3-triazole ring is planar to within experimental error and its geometry is consistent with that in benzotriazole (Escande, Galigné & Lapasset, 1974). The methylene atom C(12) lies 0·129 (6) Å from the plane of the triazole ring on the same side as the aromatic ring, and N(3) has a slightly pyramidal conformation, lying 0·048 (4) Å from the N(2)C(9)C(12) plane. The conformation about the

N(3)–C(12) and C(12)–C(13) bonds is approximately 'perpendicular' with torsion angles N(2)–N(3)–C(12)–C(13) = 83·0 (4), C(9)–N(3)–C(12)–C(13) = –89·4 (5), N(3)–C(12)–C(13)–C(14) = –99·7 (4) and N(3)–C(12)–C(13)–C(18) = 79·5 (5)°. The C(11) methyl H atoms are staggered relative to the S(10)–C(5) bond.

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N-Cyclohexylbicyclo[3.2.1]octane-3-spiro-3'-succinimide

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Abstract. $C_{17}H_{25}NO_2$, $M_r = 275·39$, orthorhombic, *Pbca*, $a = 24·520$ (7), $b = 11·795$ (2), $c = 10·577$ (2) Å, $V = 3059$ (1) Å^3, $Z = 8$, $D_x = 1·196$ g cm^{-3}, $\mu = 0·7226$ cm^{-1}, $\lambda = 0·7107$ Å. The structure was solved by direct methods and refined to an R value of 0·078 for 1528 observed reflections. The bicyclic system adopts an envelope–boat conformation.

Introduction. The compound was prepared and crystallized by P. Ballesteros and E. De la Cuesta of the Facultad de Farmacia de la Universidad Complutense de Madrid, Spain. The crystal used for data collection was a parallelepiped of dimensions 0·20 × 0·30 × 0·35 mm. Cell parameters and intensities were obtained on a four-circle automatic Nonius CAD-4 diffractometer with the θ–2θ scan method and graphite-monochromatized Mo $K\alpha$ radiation. 3611 reflections were collected up to $2\theta = 60°$. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The crystal structure was solved with *MULTAN* 80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The complete non-H skeleton was found and the refinement of these atoms with isotropic temperature factors by the least-squares full-matrix methods gave $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0·130$. H atoms were located from a difference map. The final refinement ($R = 0·078$) was based on 1528 observed reflections having $I > 2\sigma(I)$ and included isotropic and anisotropic thermal parameters for the H and non-H atoms respectively. The weights were calculated (Martínez-Ripoll & Cano, 1975) as $W = K/\sigma^2$, $\sigma = a + b|F_o|$ and $K = 0·575$ ($a = 6·111$, $b = -5·380$ when $|F_o| = 0·30-0·84$; $a = 1·526$, $b = 0·149$ when $|F_o| = 0·85-5·89$; $a = 4·284$, $b = 0·264$ when $|F_o| > 5·89$). No trends in $\sin\theta/\lambda$ were observed.
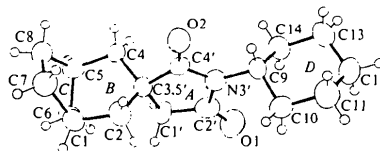

Fig. 1. Perspective view and labelling of the molecule with H atoms.