Crystal structure of *N*-nitroso-2,3,4,5-tetrahydro-2,2,4-trimethyl-1,5-benzothiazepine, $C_{12}H_{16}N_2OS$

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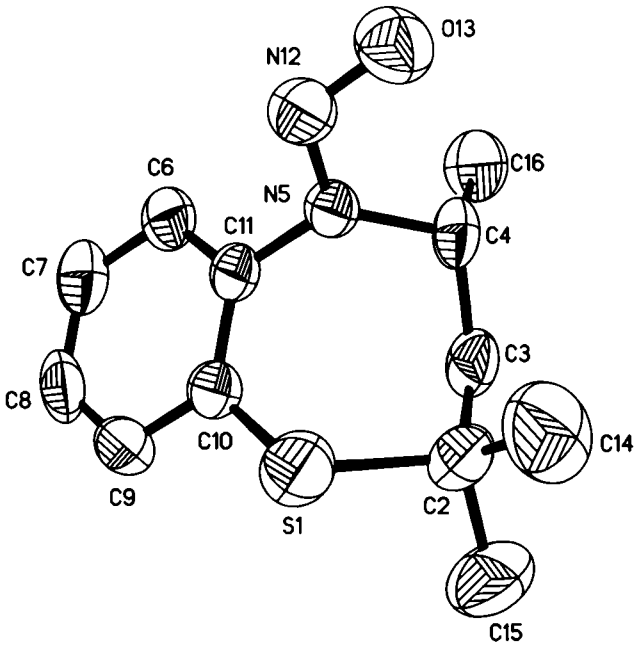

Abstract

$C_{12}H_{16}N_2OS$, monoclinic, *C*12/*c*1 (No. 15), $a = 31.342(5)$ Å, $b = 6.927(1)$ Å, $c = 12.322(2)$ Å, $\beta = 110.741(4)°$, $V = 2501.7$ Å^3, $Z = 8$, $R_{gt}(F) = 0.073$, $wR_{ref}(F^2) = 0.225$, $T = 295$ K.

Source of material

The title compound was prepared by the nitrosation [1] of 2,3,4,5-tetrahydro-2,2,4-trimethyl-1,5-benzothiazepine. Diffraction quality crystals were obtained by recrystallization of the crude product from ethanol.

Discussion

Quantitative Structure Activity Relationship (QSAR) study reveals that 1,5-benzothiazepine derivatives possess specific mitochondrial activity [2]. This activity depends *inter alia* on the substituents in the 1,5-benzothiazepine ring and conjugation of the fused heterocyclic ring at the nitrogen site. Such derivatives containing *N*-substituents [3] structurally resemble Diltiazem, the well known calcium antagonistic drug [4]. *N*-Nitroso derivatives are known to possess anticancer and carcinogenic properties [5]. The present structure is determined as a forerunner for assessing the biological functions of the title compound.

The conformation of the seven-membered ring is best described as a *boat* with the four atoms, C2, S1, C4, N5 lying approximately (within 0.02 Å) in one plane. The C3, C10, and C11 atoms are displaced from the above plane by –0.633(6) Å, –1.203(5) Å and –1.062(5)Å, respectively. The torsion angles in the seven-membered ring also suggest a *boat* conformation, with significant torsional distortion around the S1—C2 bond. This deviation from –34.4° [6] is attributed to the presence of sulfur atom, the bond angle around which deviates from the ideal tetrahedral angle of 109°. This conformation is in contrast to the twist boat conformation observed in similar molecules [7-10]. The sp^2 and sp^3 hybridized states for C10 and C2, respectively cause the difference in the S—C bond lengths in the title molecule. The S1···N5 intramolecular distance 3.007(3) Å is shorter than the sum of the van der Waals radii of 3.35 Å. The presence of the nitroso group in the predominant polarized form is evident from the distance *d*(N5—N12) = 1.318(4) Å, which is significantly shorter than the expected distance between the pyramidal and planar nitrogen (1.420(2) Å) [11]. The N–N=O moiety is non-coplanar with the fused benzene ring and suspends a dihedral angle of 67.1°, suggesting no conjugative interaction of N–N=O with the fused benzene ring. There is a significant intramolecular C-H···O interaction between C4 and O13 [*d*(C4···O13) = 2.646(6) Å, ∠C4–H4···O13 = 101(3)°] which may favour the *syn* orientation of the nitroso group with respect to the N5—C4 bond. The equatorial orientation of the C4-methyl group is deduced from the ∠C2–C3–C4–C16 torsion angle of 177.2(4)°.

Table 1. Data collection and handling.

Crystal:	colorless irregular chunk, size 0.20 × 0.22 × 0.28 mm
Wavelength:	Ag K_α radiation (0.56085 Å)
μ:	1.3 cm^{-1}
Diffractometer, scan mode:	Siemens SMART 2K CCD, $\omega/2\theta$
$2\theta_{max}$:	44°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11296, 3122
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1121
$N(param)_{refined}$:	162
Programs:	SIR97 [12], SHELXL-97 [13], ZORTEP [14]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3A)	8f	0.3604(2)	0.559(1)	0.301(2)	0.067(5)
H(3B)	8f	0.3498(2)	0.735(4)	0.2113(4)	0.067
H(6)	8f	0.475(1)	0.260(2)	0.4338(7)	0.067
H(7)	8f	0.462(1)	0.060(2)	0.575(3)	0.067
H(8)	8f	0.3873(3)	–0.045(4)	0.540(3)	0.067
H(9)	8f	0.330(1)	0.035(2)	0.3700(7)	0.067
H(14A)	8f	0.308(1)	0.650(4)	–0.0025(9)	0.105(6)
H(14B)	8f	0.285(1)	0.454(4)	–0.034(2)	0.105

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(14C)	8f	0.3369(9)	0.471(4)	–0.0003(9)	0.105
H(15A)	8f	0.2692(6)	0.678(4)	0.146(3)	0.105
H(15B)	8f	0.2776(4)	0.515(4)	0.238(2)	0.105
H(15C)	8f	0.2489(8)	0.474(4)	0.109(2)	0.105
H(16A)	8f	0.4412(7)	0.671(3)	0.374(2)	0.105
H(16B)	8f	0.4316(6)	0.832(4)	0.279(2)	0.105
H(16C)	8f	0.4687(8)	0.676(3)	0.291(2)	0.105
H(4)	8f	0.401(1)	0.598(5)	0.134(3)	0.04(1)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	8f	0.32293(4)	0.2200(2)	0.1600(1)	0.0593(7)	0.0562(9)	0.092(1)	–0.0042(6)	0.0074(6)	–0.0065(8)
C(2)	8f	0.3173(1)	0.4853(7)	0.1390(4)	0.051(2)	0.066(3)	0.069(3)	0.015(2)	0.019(2)	0.012(3)
C(3)	8f	0.3576(1)	0.5946(6)	0.2207(4)	0.066(3)	0.035(2)	0.072(3)	0.014(2)	0.029(2)	0.006(2)
C(4)	8f	0.4042(1)	0.5717(6)	0.2117(4)	0.068(3)	0.029(2)	0.057(3)	0.009(2)	0.022(2)	0.007(2)
N(5)	8f	0.4193(1)	0.3668(4)	0.2311(3)	0.049(2)	0.030(2)	0.056(2)	0.001(1)	0.025(2)	–0.004(2)
C(6)	8f	0.4455(2)	0.2115(6)	0.4198(4)	0.058(2)	0.033(2)	0.067(3)	–0.003(2)	0.020(2)	–0.007(2)
C(7)	8f	0.4366(2)	0.0961(7)	0.5016(4)	0.086(3)	0.039(3)	0.066(3)	0.009(2)	0.027(3)	0.002(2)
C(8)	8f	0.3933(2)	0.0325(7)	0.4819(5)	0.094(4)	0.032(3)	0.091(4)	0.009(2)	0.053(3)	0.014(3)
C(9)	8f	0.3584(2)	0.0768(6)	0.3809(4)	0.059(3)	0.046(3)	0.096(4)	–0.003(2)	0.042(3)	0.004(3)
C(10)	8f	0.3664(1)	0.1865(6)	0.2951(4)	0.050(2)	0.033(2)	0.079(3)	0.004(2)	0.031(2)	0.001(2)
C(11)	8f	0.4105(1)	0.2531(5)	0.3176(3)	0.050(2)	0.028(2)	0.058(2)	0.006(2)	0.024(2)	–0.001(2)
N(12)	8f	0.4466(1)	0.2892(6)	0.1827(3)	0.063(2)	0.046(2)	0.070(2)	0.000(2)	0.034(2)	–0.008(2)
O(13)	8f	0.4563(1)	0.3950(5)	0.1140(3)	0.088(2)	0.067(2)	0.081(2)	0.001(2)	0.050(2)	0.000(2)
C(14)	8f	0.3114(2)	0.518(1)	0.0137(4)	0.106(4)	0.128(6)	0.076(4)	–0.018(4)	0.010(3)	0.027(4)
C(15)	8f	0.2743(2)	0.5435(9)	0.1601(6)	0.070(3)	0.091(5)	0.165(6)	0.024(3)	0.043(4)	0.004(5)
C(16)	8f	0.4397(2)	0.6995(7)	0.2967(4)	0.078(3)	0.037(3)	0.094(3)	–0.002(2)	0.033(3)	–0.010(3)

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