Crystal structure of 3-(1-naphthylmethyl)-6-phenyl-7*H*-1,2,4-triazolo[3,4-*b*][1,3,4]-thiadiazine, $C_{21}H_{16}N_4S$

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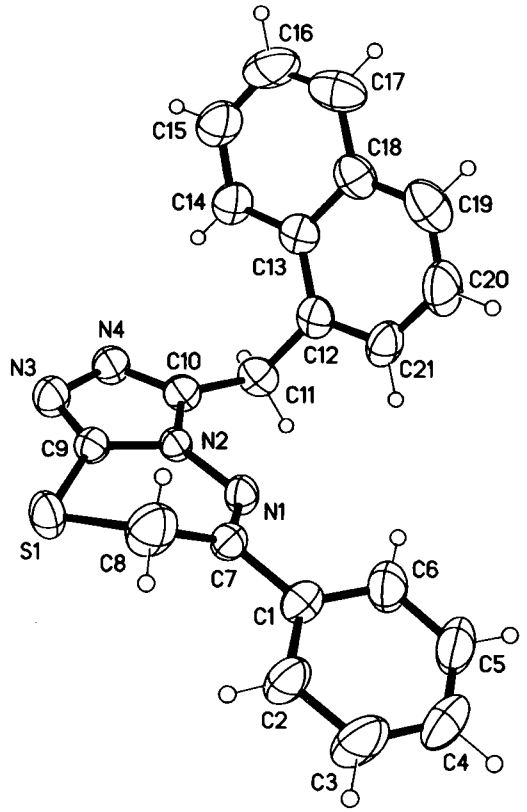

Abstract

$C_{21}H_{16}N_4S$, orthorhombic, *Pbca* (no. 61), a = 12.886(4) Å, b = 10.226(3) Å, c = 26.694(7) Å, V = 3517.5 Å^3, Z = 8, $R_{gt}(F)$ = 0.077, $wR_{ref}(F^2)$ = 0.257, T = 273 K.

Source of material

4-amino-5-mercapto-3-(1-naphthylmethyl)-1,2,4-triazole was prepared by the reaction of acetic acid and thiocarbohydrazide, followed the literature [1]. To a solution of 4-amino-5-mercapto-3-(1-naphthylmethyl)-1,2,4-triazole (0.001 mol) in absolute ethanol was added 2-bromoacetophenone (0.001 mol). The mixture was refluxed for 7 h. The solid obtained on cooling was filtered, washed with cold water, dried and recrystallized from ethanol to give the title compound. The purified product was dissolved in 95 % ethanol and kept at room temperature for six days, and brown single crystals were formed.

Experimental details

An exact explanation for the large R values could not be found. Those possibly are caused by the imperfect crystals. Co-crystallizing solvents were not analyzed.

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Discussion

1,2,4-triazoles fused with six-membered ring systems are found to possess diverse applications in the fields of medicine, agriculture and industry. The commonly known systems are triazoles fused with pyridine, pyridazine, pyrimidine, pyrazines and triazines. A literature survey reveals that there are not many examples of triazoles fused with thiadiazines. Moreover, a large number of triazolothiazines have been shown to exhibit antimicrobial activity [2]. In the title compound, the five-membered triazole ring (N2, N3, N4, C9, C10) and the benzene ring (C1 - C6) are essentially planar, while the six-membered thiadiazine ring (N1, N2, C7, C8, C9 and S1), is distorted from planarity with an r.m.s. deviation of 0.1748 Å. Both the S—C (with mean distance 1.775 Å) and C—N bond lengths are in line with this observation in related complexes [3]. The C and N atoms are involved in the conjugated form of the five-membered triazole ring and its bond lengths show normal values [4-5]. The dihedral angle between the thiadiazine ring and the triazole ring is 173.2(1)° and that between the benzene ring and the thiadiazine ring is 158.9(2)° and the naphthalene ring is rotated by 70.6(1)° with respect to the triazole ring.

Table 1. Data collection and handling.

Crystal:	brown prism, size 0.25 x 0.33 x 0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.96 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16177, 3097
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2784
$N(param)_{refined}$:	235
Program:	SHELX-97 [6]

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

Atom	Site	x	y	z	U_{iso}
H(2)	8c	0.9624	0.4112	0.0441	0.062
H(3)	8c	1.1027	0.5213	0.0767	0.084
H(4)	8c	1.0828	0.6631	0.1420	0.073
H(5)	8c	0.9229	0.6986	0.1745	0.082
H(6)	8c	0.7817	0.5867	0.1456	0.074
H(8A)	8c	0.7651	0.2220	0.0740	0.078
H(8B)	8c	0.8514	0.2771	0.0384	0.078
H(11A)	8c	0.3883	0.5780	0.0945	0.051
H(11B)	8c	0.5043	0.6208	0.1006	0.051
H(14)	8c	0.2822	0.4115	0.1129	0.058
H(15)	8c	0.1544	0.2810	0.1451	0.077
H(16)	8c	0.1650	0.2050	0.2265	0.085
H(17)	8c	0.2970	0.2627	0.2763	0.079
H(19)	8c	0.4671	0.3812	0.2886	0.080
H(20)	8c	0.5934	0.5108	0.2582	0.081
H(21)	8c	0.5893	0.5847	0.1763	0.061

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)	8c	0.6975(1)	0.2534(2)	−0.00554(5)	0.0391(9)	0.061(1)	0.0424(8)	0.0053(6)	0.0010(6)	−0.0201(7)
N(1)	8c	0.6755(3)	0.4702(4)	0.0787(2)	0.031(2)	0.045(3)	0.034(2)	0.001(2)	−0.004(2)	−0.008(2)
N(2)	8c	0.5898(3)	0.4097(4)	0.0577(1)	0.022(2)	0.045(2)	0.028(2)	−0.001(2)	−0.002(2)	−0.006(2)
N(3)	8c	0.4899(4)	0.2978(5)	0.0066(2)	0.035(3)	0.057(3)	0.042(3)	−0.002(2)	−0.002(2)	−0.010(2)
N(4)	8c	0.4287(3)	0.3813(5)	0.0359(2)	0.028(2)	0.062(3)	0.042(2)	−0.004(2)	−0.002(2)	−0.007(2)
C(1)	8c	0.8553(4)	0.4872(5)	0.0909(2)	0.034(3)	0.035(3)	0.045(3)	0.002(2)	−0.009(2)	0.004(2)
C(2)	8c	0.9533(4)	0.4685(6)	0.0708(3)	0.033(3)	0.053(4)	0.069(4)	−0.004(3)	−0.006(3)	−0.013(3)
C(3)	8c	1.0371(5)	0.5347(8)	0.0903(3)	0.033(3)	0.077(5)	0.100(6)	−0.007(3)	−0.006(3)	−0.015(4)
C(4)	8c	1.0255(5)	0.6193(7)	0.1290(3)	0.052(4)	0.059(4)	0.073(4)	−0.013(3)	−0.028(3)	0.000(3)
C(5)	8c	0.9310(6)	0.6391(8)	0.1484(3)	0.067(5)	0.080(5)	0.059(4)	−0.011(4)	−0.017(3)	−0.023(4)
C(6)	8c	0.8462(5)	0.5734(8)	0.1308(2)	0.049(4)	0.088(5)	0.049(4)	−0.006(3)	−0.005(3)	−0.020(3)
C(7)	8c	0.7631(4)	0.4209(5)	0.0696(2)	0.033(3)	0.042(3)	0.043(3)	−0.005(2)	0.007(2)	−0.013(2)
C(8)	8c	0.7793(5)	0.2864(7)	0.0482(3)	0.046(4)	0.069(5)	0.080(5)	−0.001(3)	−0.003(3)	−0.015(4)
C(9)	8c	0.5855(4)	0.3191(5)	0.0205(2)	0.032(3)	0.042(3)	0.032(3)	−0.003(2)	−0.002(2)	−0.003(2)
C(10)	8c	0.4890(4)	0.4463(5)	0.0658(2)	0.031(3)	0.044(3)	0.037(3)	0.003(2)	−0.001(2)	0.000(2)
C(11)	8c	0.4572(4)	0.5471(6)	0.1030(2)	0.035(3)	0.047(3)	0.045(3)	0.010(2)	0.002(2)	0.000(3)
C(12)	8c	0.4564(4)	0.4986(6)	0.1569(2)	0.035(3)	0.043(3)	0.046(3)	0.010(2)	0.003(2)	−0.013(2)
C(13)	8c	0.3738(4)	0.4204(5)	0.1750(2)	0.029(3)	0.043(3)	0.048(3)	0.012(2)	0.006(2)	−0.007(2)
C(14)	8c	0.2873(4)	0.3826(6)	0.1459(2)	0.030(3)	0.059(4)	0.057(3)	0.002(3)	0.000(3)	−0.010(3)
C(15)	8c	0.2107(5)	0.3043(8)	0.1650(3)	0.039(4)	0.076(5)	0.078(5)	−0.008(3)	0.007(3)	−0.017(4)
C(16)	8c	0.2169(6)	0.2593(7)	0.2141(3)	0.046(4)	0.068(5)	0.099(6)	−0.012(3)	0.024(4)	−0.004(4)
C(17)	8c	0.2953(6)	0.2928(8)	0.2435(3)	0.061(5)	0.066(4)	0.071(5)	0.010(4)	0.027(4)	0.012(4)
C(18)	8c	0.3774(5)	0.3745(6)	0.2255(2)	0.047(3)	0.057(4)	0.045(3)	0.011(3)	0.005(3)	−0.004(3)
C(19)	8c	0.4632(6)	0.4108(8)	0.2558(2)	0.069(5)	0.089(6)	0.043(4)	0.011(4)	−0.004(3)	0.005(3)
C(20)	8c	0.5384(6)	0.4870(8)	0.2376(3)	0.054(4)	0.097(6)	0.050(4)	−0.001(4)	−0.017(3)	−0.015(4)
C(21)	8c	0.5360(4)	0.5317(6)	0.1881(2)	0.032(3)	0.063(4)	0.057(4)	−0.003(3)	−0.003(3)	−0.019(3)

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References

1. Zhang, L. X.; Zhang, A. J.; Chen, G.; Chen, F. Y.; Jiang, Y. P.; Zhang, Z. Y.: Preparation and Spectral Characterization of 3-Benzyl-6-aryl-1,2,4-triazolothiadiazoles. Chem. Res. Chin. Univ. **18** (2002) 280-283.
2. Feng, X. M.; Chen, R.; Yang, W. D.; Zhang, Z. Y.: Synthesis of Bis(1-acetyl-4-aroylthiosemicarbazides) and Their Derivatives. Chem. J. Chin. Univ. **13** (1992) 187-194.
3. Xiang, G. Q.; Zhang, L. X.; Zhang, A. J.; Cai, X. Q.; Hu, M. L.: 6-(2,4-Difluorophenyl)-3-(3-methylphenyl)-7*H*-1,2,4-triazolo[3,4-*b*]-[1,3,4]thiadiazine. Acta Crystallogr. **E60** (2004) o1736-o1738.
4. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R.: Tables of bond lengths determined by X-ray and neutron diffraction. Part 1. Bond lengths in organic compounds. J. Chem. Soc., Perkin Trans. 2 (1987) 1-19.
5. Jin, Z. M.; Li, L.; Li, M. C.; Hu, M. L.; Shen, L.: Diethyl 3,8-dimethyl-4,7-diazadeca-2,8-dienedioate. Acta Crystallogr. **C60** (2004) o642-o643.
6. Sheldrick, G. M.: SHELX-97. Programs for the Analysis of Crystal Structures. Release 97-2. University of Göttingen, Germany 1997.