Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O1	0.14279 (15)	0.29429 (9)	0.05084 (9)	0.0573 (3)
N1	−0.5442 (3)	−0.2015 (2)	−0.1738 (2)	0.0944 (6)
C1	0.0587 (2)	0.16772 (12)	−0.04813 (12)	0.0469 (3)
C2	−0.1322 (2)	0.08593 (13)	−0.05789 (12)	0.0471 (3)
C3	−0.1982 (2)	−0.04148 (13)	−0.16375 (13)	0.0509 (3)
C4	−0.0785 (3)	−0.08442 (15)	−0.25690 (15)	0.0648 (4)
C5	0.1131 (3)	−0.0010 (2)	−0.2429 (2)	0.0730 (5)
C6	0.1821 (3)	0.12440 (15)	−0.13873 (15)	0.0614 (4)
C7	−0.3928 (3)	−0.1303 (2)	−0.17104 (15)	0.0642 (4)
C8	0.0133 (2)	0.35420 (13)	0.13228 (13)	0.0495 (3)
C9	0.1358 (2)	0.49633 (11)	0.22773 (11)	0.0400 (3)
C10	0.3776 (2)	0.52616 (13)	0.27737 (13)	0.0484 (3)
B1	0.3117 (2)	0.5938 (2)	0.17760 (15)	0.0501 (4)
B2	0.0886 (2)	0.63598 (15)	0.22530 (14)	0.0477 (3)
B3	0.0228 (2)	0.58566 (14)	0.34845 (13)	0.0449 (3)
B4	0.2085 (2)	0.51669 (14)	0.37983 (13)	0.0436 (3)
B5	0.4435 (2)	0.64000 (15)	0.4363 (2)	0.0507 (4)
B6	0.5086 (2)	0.6884 (2)	0.3119 (2)	0.0531 (4)
B7	0.3257 (3)	0.7622 (2)	0.2827 (2)	0.0532 (4)
B8	0.1452 (3)	0.75783 (15)	0.3885 (2)	0.0523 (4)
B9	0.2186 (3)	0.6816 (2)	0.48370 (14)	0.0510 (4)
B10	0.4055 (3)	0.79075 (15)	0.4431 (2)	0.0538 (4)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.3723 (15)	B1—B6	1.774 (2)
O1—C8	1.406 (2)	B1—H1B	1.08 (2)
N1—C7	1.140 (2)	B2—B8	1.770 (2)
C1—C2	1.379 (2)	B2—B7	1.771 (2)
C1—C6	1.381 (2)	B2—B3	1.772 (2)
C2—C3	1.400 (2)	B2—H2B	1.06 (2)
C3—C4	1.380 (2)	B3—B4	1.756 (2)
C3—C7	1.440 (2)	B3—B8	1.773 (2)
C4—C5	1.380 (3)	B3—B9	1.776 (2)
C5—C6	1.379 (2)	B4—B9	1.736 (2)
C8—C9	1.521 (2)	B4—B5	1.747 (2)
C9—C10	1.648 (2)	B5—B10	1.765 (2)
C9—B3	1.697 (2)	B5—B6	1.771 (2)
C9—B2	1.706 (2)	B5—B9	1.772 (2)
C9—B4	1.711 (2)	B6—B7	1.771 (2)
C9—B1	1.714 (2)	B6—B10	1.783 (3)
C10—B6	1.703 (2)	B7—B8	1.781 (2)
C10—B4	1.707 (2)	B7—B10	1.781 (2)
C10—B5	1.711 (2)	B8—B10	1.775 (2)
C10—B1	1.728 (2)	B8—B9	1.782 (2)
B1—B2	1.763 (2)	B9—B10	1.773 (2)
B1—B7	1.764 (2)		
C8—C9—C10	119.29 (10)	C8—C9—B4	115.74 (10)
C8—C9—B3	117.88 (10)	C8—C9—B1	119.98 (10)
C8—C9—B2	121.52 (10)		
C8—O1—C1—C2	−13.1 (2)	O1—C8—C9—C10	−33.1 (2)
C8—O1—C1—C6	168.38 (13)	O1—C8—C9—B1	39.4 (2)
C1—O1—C8—C9	−176.12 (11)		

All calcutions were carried out on a VAXstation 4000VLC computer system.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Studies on Condensed Heterocyclic Compounds.† XIII. 6-(4-Methylphenyl)-3-(1-naphthylmethylene)-*s*-triazolo[3,4-*b*]-[1,3,4]thiadiazole

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Abstract

6-(4-Methylphenyl)-3-(1-naphthylmethylene)-*s*-triazolo[3,4-*b*][1,3,4]thiadiazole, $C_{21}H_{16}N_4S$, was prepared by cyclization of 3-(1-naphthylmethylene)-4-amino-5-mercapto-1,2,4-triazole with *p*-methyl benzoic acid in the presence of phosphorus oxychloride. The structure of the compound was determined by elemental analysis, IR and ^{1}H NMR spectroscopy,and X-ray diffraction. The phenyl group and the heteronucleus are almost coplanar. The dihedral angle between the naphthyl group and the heteronucleus is 83.54 (6)°.

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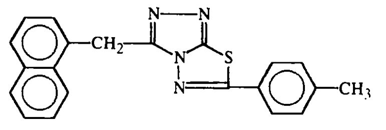
Comment

In recent years the synthesis and characteristics of *s*-triazolo[3,4-*b*]-1,3,4-thiadiazoles have been investigated (Gogoi & Kataky, 1990; Holla, D'Souza & Kalluraya, 1991; Patel, Fernandes & Vyas, 1990). These heterocyclic compounds contain 1,2,4-triazole and 1,3,4-thiadiazole rings condensed through a C—N bond. The substituted groups at the 3 or 6 positions can conjugate with the heterocyclic nucleus giving it new characteristics. In a continuation of our earlier studies, we now report the crystal structure of 6-(4-methylphenyl)-3-(1-naphthylmethylene)-*s*-triazole[3,4-*b*][1,3,4]thiadiazole, (I).



(I)

The central ring system in the present compound does not differ significantly from those in the structures of the two other substituted *s*-triazolo[3,4-*b*]-1,3,4-thiadiazole compounds already determined, the 6-methyl-3-phenyl derivative (Fornies-Marquina, Courseille & Elguero, 1974) and the 3-[2-aminophenyl]-6-tolyl derivative (Molina, Arques, Alias, Llamas Saiz & Foces-Foces, 1989). The atoms in the ten-membered ring, are essentially planar ($\chi^2 = 49.8$) with C8 having maximum deviation from the plane. The bond lengths indicate a degree of delocalization around the ring system with the three C═N bonds averaging 1.304 (5) Å and the N—N bond lengths ranging from 1.377 (5) to 1.406 (4) Å. The phenyl substituent is almost coplanar with the central ring system [dihedral angle 3.0 (1)°] but the bulky naphthyl group is twisted out of this plane, the dihedral angle between it and the central ring system being 83.54 (6)°.

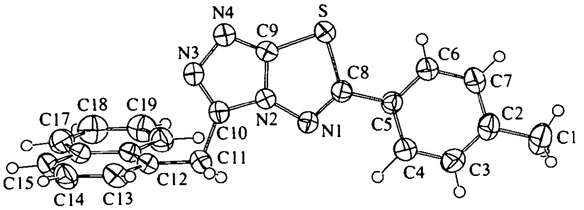


Fig. 1. View of the molecular structure (Johnson, 1976) showing 50% probability displacement ellipsoids.

Experimental

A mixture of 3-(1-naphthylmethylene)-4-amino-5-mercapto-1,2,4-triazole (0.384 g/1.5 mmol) and *p*-methyl benzoic acid (0.272 g/2 mmol) in phosphorus oxychloride (6 ml) was refluxed for 6 h. The excess phosphorus oxychloride was then removed under reduced pressure. The mixture was cooled and poured into ice-cold water (50 ml). The precipitate was filtered, washed with aqueous sodium carbonate (2.5 N, 15 ml) followed by water (20 ml) and dried. The crude product was separated by column chromatography. Yield 46%, m.p. 452–453 K, ν_{max}: 3026 (*w*, Ar—H), 2904 (*w*, CH_2 or CH_3), 1591, 1568, 1456 (*s*, Ar), 1591 (*m*, C═N), 1231 (*w*, N—N═C), 711 (*w*, C—S—C) cm^{-1}. δ_H: 8.32 (*m*, 1H, ArH), 7.36–7.98 (*m*, 10H, ArH), 4.96 (*s*, 2H, CH_2), 2.28 (*s*, 3H, CH_3) p.p.m. Analysis for $C_{21}H_{16}N_4S$: calculated C 70.79, H 4.49, N 15.73; found C 70.38, H 4.33, N 15.76. The purified product was dissolved in ethyl acetate–petroleum ether solution. The crystal was obtained after 6 d by evaporation of the solution.

Crystal data

$C_{21}H_{16}N_4S$
$M_r = 356$
Triclinic
$P\bar{1}$
$a = 9.430(1)$ Å
$b = 10.007(1)$ Å
$c = 10.023(2)$ Å
$\alpha = 90.29(1)°$
$\beta = 109.01(1)°$
$\gamma = 104.1(1)°$
$V = 863.6$ Å^3
$Z = 2$
$D_x = 1.371$ Mg m^{-3}

Cu *Kα* radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 15–35°$
$\mu = 1.706$ mm^{-1}
$T = 293$ K
Prism
0.18 × 0.10 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical, ψ scans (*SDP/PDP*; Enraf–Nonius, 1985)
$T_{min} = 0.53$, $T_{max} = 0.92$
3131 measured reflections
2753 independent reflections

2559 observed reflections [$I \geq 3\sigma(I)$]
$R_{int} = 0.016$
$\theta_{max} = 60°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 11$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on *F*
$R = 0.069$
$wR = 0.072$
$S = 0.91$
2559 reflections
299 parameters
Only coordinates of H atoms refined

Unit weights applied
$(\Delta/\sigma)_{max} = 0.5$
$\Delta\rho_{max} = 0.379$ e Å^{-3}
$\Delta\rho_{min} = -0.670$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SDP/PDP*

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S	0.6115 (1)	0.49991 (9)	0.3069 (1)	3.59 (2)
N1	0.5179 (3)	0.2522 (3)	0.1722 (3)	3.06 (6)
N2	0.4680 (3)	0.2482 (3)	0.2872 (3)	2.91 (6)
N3	0.3760 (4)	0.2047 (3)	0.4590 (3)	3.79 (7)
N4	0.4535 (4)	0.3461 (3)	0.4774 (3)	3.88 (7)

C1	0.8796 (5)	0.5466 (5)	−0.2532 (5)	5.3 (1)
C2	0.8067 (4)	0.5017 (4)	−0.1422 (4)	3.80 (9)
C3	0.7181 (5)	0.3680 (4)	−0.1477 (4)	4.4 (1)
C4	0.6481 (5)	0.3268 (4)	−0.0476 (4)	3.91 (9)
C5	0.6664 (4)	0.4216 (4)	0.0633 (4)	3.10 (8)
C6	0.7526 (5)	0.5554 (4)	0.0680 (4)	4.2 (1)
C7	0.8216 (5)	0.5955 (4)	−0.0329 (4)	4.4 (1)
C8	0.5959 (4)	0.3776 (4)	0.1714 (4)	2.99 (8)
C9	0.5056 (4)	0.3678 (4)	0.3719 (4)	3.23 (8)
C10	0.3871 (4)	0.1478 (4)	0.3451 (4)	3.20 (8)
C11	0.3266 (4)	−0.0018 (4)	0.2906 (4)	3.80 (9)
C12	0.1928 (4)	−0.0738 (4)	0.3377 (4)	3.34 (8)
C13	0.2165 (5)	−0.1661 (4)	0.4398 (4)	4.0 (1)
C14	0.0961 (5)	−0.2314 (4)	0.4901 (4)	4.4 (1)
C15	−0.0449 (5)	−0.2056 (4)	0.4413 (4)	3.95 (9)
C16	−0.0742 (4)	−0.1137 (4)	0.3344 (4)	3.38 (8)
C17	−0.2225 (5)	−0.0866 (5)	0.2802 (5)	4.5 (1)
C18	−0.2501 (5)	0.0037 (5)	0.1770 (5)	5.2 (1)
C19	−0.1317 (6)	0.0698 (5)	0.1273 (5)	4.9 (1)
C20	0.0130 (5)	0.0461 (4)	0.1770 (4)	4.1 (1)
C21	0.0459 (4)	−0.0471 (4)	0.2836 (4)	3.10 (8)

Table 2. *Geometric parameters (Å, °)*

S—C8	1.769 (4)	C5—C8	1.463 (6)
S—C9	1.720 (4)	C6—C7	1.382 (7)
N1—N2	1.377 (5)	C10—C11	1.495 (5)
N1—C8	1.292 (4)	C11—C12	1.510 (6)
N2—C9	1.365 (5)	C12—C13	1.383 (6)
N2—C10	1.361 (5)	C12—C21	1.406 (5)
N3—N4	1.406 (4)	C13—C14	1.408 (7)
N3—C10	1.318 (6)	C14—C15	1.349 (7)
N4—C9	1.302 (6)	C15—C16	1.419 (6)
C1—C2	1.506 (7)	C16—C17	1.419 (6)
C2—C3	1.384 (6)	C16—C21	1.413 (6)
C2—C7	1.387 (6)	C17—C18	1.380 (7)
C3—C4	1.384 (7)	C18—C19	1.391 (7)
C4—C5	1.397 (6)	C19—C20	1.372 (7)
C5—C6	1.379 (5)	C20—C21	1.430 (6)
C8—S—C9	87.7 (2)	N2—C9—N4	110.0 (3)
N2—N1—C8	107.6 (3)	N2—C10—N3	108.2 (4)
N1—N2—C9	118.5 (3)	N2—C10—C11	125.4 (4)
N1—N2—C10	135.2 (3)	N3—C10—C11	126.4 (4)
C9—N2—C10	106.5 (3)	C10—C11—C12	112.0 (4)
N4—N3—C10	108.9 (3)	C11—C12—C13	119.1 (4)
N3—N4—C9	105.6 (3)	C11—C12—C21	122.0 (3)
C1—C2—C3	121.7 (4)	C13—C12—C21	118.9 (4)
C1—C2—C7	120.6 (4)	C12—C13—C14	120.7 (4)
C3—C2—C7	117.6 (4)	C13—C14—C15	121.5 (5)
C2—C3—C4	122.1 (5)	C14—C15—C16	119.4 (4)
C3—C4—C5	119.9 (3)	C15—C16—C17	120.3 (4)
C4—C5—C6	118.3 (4)	C15—C16—C21	119.6 (4)
C4—C5—C8	120.0 (3)	C17—C16—C21	120.1 (4)
C6—C5—C8	121.7 (4)	C16—C17—C18	120.1 (4)
C5—C6—C7	121.3 (4)	C17—C18—C19	119.9 (4)
C2—C7—C6	120.9 (4)	C18—C19—C20	121.6 (4)
S—C8—N1	116.9 (4)	C19—C20—C21	120.1 (4)
S—C8—C5	119.9 (2)	C12—C21—C16	119.9 (3)
N1—C8—C5	123.2 (3)	C12—C21—C20	121.9 (4)
S—C9—N2	109.3 (3)	C16—C21—C20	118.2 (4)
S—C9—N4	139.8 (3)		

The structure was determined by direct methods and refined by least-squares techniques. The melting point was determined on an X-4 microscopic melting apparatus and is uncorrected. Elemental analysis was performed on an Italian 1106 analyser, IR spectra on a Nicolet FT-5DX (KBr), ^{1}H NMR spectra on a Varian FT-80A using tetramethylsilane as the internal standard and deuterated dimethyl sulfoxide as the solvent.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1985). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SDP/PDP*. Program(s) used to refine structure: *SDP/PDP*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(2,4-Dinitrophenyl)(10-methyl-3-phenothiazinyl)diazene Hemimethanol Solvate

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Abstract

In the title compound, $C_{19}H_{13}N_5O_4S.0.5CH_3OH$, the phenylazo group and the substituted benzene ring of the phenothiazine system are almost in the same plane, resulting in the formation of a conjugated system.

Comment

Phenothiazine and its substituted derivatives are highly reactive compounds. Because of this, they have aroused the curiosity of chemists and an increasing number of new derivatives have been synthesized. We have prepared recently a series of new phenothiazineazo derivatives by the reaction of 10-alkyl phenothiazine radical cations with 2,4-dinitrophenylhydrazine (Liu, Liu & Guo, 1994). In order to confirm their structures,