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(*E*)-2-[2-(1-Naphthyl)vinyl]-3-tosyl-2,3-dihydro-1,3-benzothiazole

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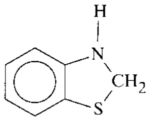
The title compound, $C_{26}H_{21}NO_2S_2$, which consists of a benzothiazole skeleton with α-naphthylvinyl and tosyl groups at positions 2 and 3, respectively, was prepared by palladium–copper-catalyzed heteroannulation. The *E* configuration of the molecule about the vinyl C=C bond is established by the benzothiazole–naphthyl C—C—C—C torsion angle of 177.5 (4)°. The five-membered heterocyclic ring adopts an envelope conformation with the Csp^3 atom 0.380 (6) Å from the C_2NS plane. The two S—C [1.751 (4) and 1.838 (4) Å] and two N—C [1.426 (5) and 1.482 (5) Å] bond lengths in the thiazole ring differ significantly.

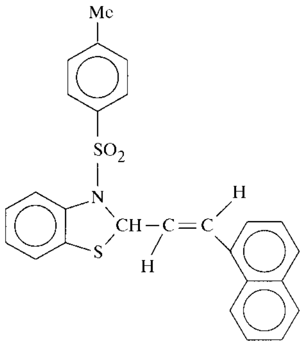
Comment

The benzothiazole system, (I), containing a heterocyclic ring with sulfur and nitrogen as heteroatoms, is often used as an antihypertensive, an anticoagulant and a calcium agonist (Yamamoto *et al.*, 1998). Substituted benzothiazolines find wide-ranging applications as efficient anticonvulsants, vasodilators, blood platelet aggregation inhibitors (Ucar *et al.*, 1998) and antifungal agents (Kanoongo *et al.*, 1990). As part of our ongoing program on the synthesis and characterization of new heterocyclic compounds of biological importance (Kundu *et al.*, 1999; Nandi & Kundu, 2000) and to build up a hierarchy for such systems, the structure determination of (*E*)-2-[2-(1-naphthyl)vinyl]-3-tosyl-2,3-dihydro-1,3-benzothiazole, (II), was undertaken.

The *E* configuration of the molecule of (II), which contains a benzothiazole moiety (*A*) with α-naphthylvinyl (*B*) and tosyl (*C*) substituents at the 2 and 3 positions, respectively, is established by the torsion angle C14—C15—C16—C17 of 177.5 (4)°. The five-membered thiazole ring (atoms N, C8, C13, S2 and C14) displays an envelope conformation, with the C14 atom 0.380 (6) Å from the least-squares plane through the remaining endocyclic atoms (r.m.s deviation 0.006 Å). The dihedral angles between the planar parts of *A* (atoms N, C8–C13 and S2), *B* (atoms C17–C26) and *C* (atoms C1–C7) are *A*/*B* 82 (1), *A*/*C* 112 (1) and *B*/*C* 131.5 (4)°. The maximum deviation for an in-plane atom (C9) from the corresponding least-squares plane is 0.04 (8) Å. The bond lengths and angles observed for the heterocyclic ring in (II) are similar to those reported for related structures (Miler-Srenger, 1973; Yeap *et al.*, 1991). The C13—S2—C14 angle of 91.0 (2)° indicates that the S2 atom uses only the *p* orbital to form bonds with the C13 and C14 atoms, of which C13 is part of an aromatic ring and C14 is sp^3 hybridized. Consequently, the S—C bond distances in the heterocyclic ring [S2—C13 1.751 (4) and S2—C14 1.838 (4) Å] differ significantly. The asymmetric nature of the bonding of the C atoms (C8 and C14) is also reflected in the difference between the two N—C distances [N—C8 1.426 (5) and N—C14 1.482 (5) Å]. The bond distances and angles for the tosyl and α-naphthylvinyl groups are within expected ranges (Chiaroni *et al.*, 1994; Dobson & Gerkin, 1996). A comparison of the geometrical parameters of various heterocyclic derivatives (Table 3) reveals that the conformation of the five-membered C_3NS ring has a profound influence on the molecular dimensions. In compounds with a non-planar C_3NS ring, the S—C and N—C bond distances show greater asymmetry compared with those having a planar C_3NS ring.



(I)



(II)

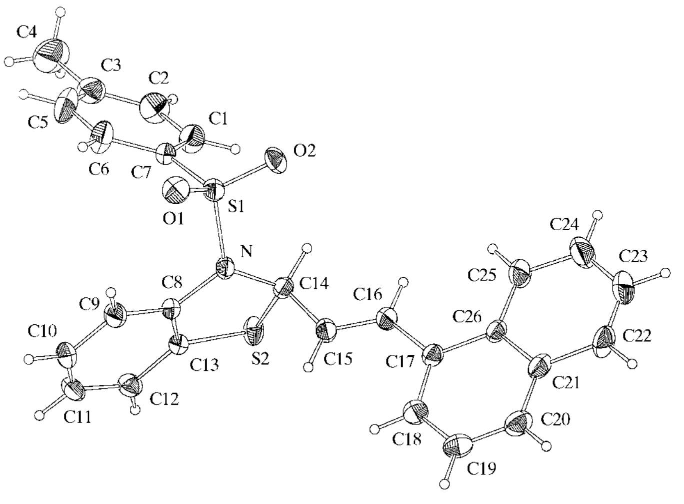


Figure 1
ZORTEP (Zsolnai, 1995) view of (II) with ellipsoids at the 50% probability level.

Both sulfonyl-O atoms are involved in weak (C—H···O) intermolecular hydrogen bonds with benzothiazole and naphthyl C atoms (Table 2). In the solid state, the crystal packing is stabilized by van der Waals interactions and a weak intermolecular hydrogen bond.

Experimental

A mixture of 3-(2-aminophenylthio)prop-1-yne (3.67 mmol) and 1-iodonaphthalene (4.4 mmol) in acetonitrile (5 ml) was stirred at room temperature for 24 h under a nitrogen atmosphere in the presence of $(PPh_3)_2PdCl_2$ (0.11 mmol), CuI (0.22 mmol) and triethylamine (14.68 mmol). The resultant product after tosylation with *p*-TsCl (1.2 equivalents) in the presence of pyridine (2.0 equivalents) in dichloromethane was cyclized with CuI (40 mole%) in triethylamine (4.0 equivalents) by refluxing in tetrahydrofuran (10 ml) for 36 h under an argon atmosphere to afford (II), which was purified by column chromatography on silica gel (60–120 mesh) using 5% ethyl acetate as eluant in light petroleum (333–353 K) (yield 63%, m.p. 452–453 K). Single crystals suitable for X-ray analysis were obtained by slow crystallization from a solution of (II) in a mixture of light petroleum (333–353 K) and ether (3:1).

Crystal data

$C_{26}H_{21}NO_2S_2$
$M_r = 443.56$
Monoclinic, $P2_1/n$
$a = 10.006 (4)$ Å
$b = 8.543 (3)$ Å
$c = 26.09 (1)$ Å
$\beta = 98.52 (4)°$
$V = 2205 (1)$ Å^3
$Z = 4$
$D_x = 1.336$ Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 20 reflections
$\theta = 14.4–16.4°$
$\mu = 2.371$ mm^{-1}
$T = 296.2$ K
Prismatic, colourless
0.30 × 0.30 × 0.20 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2*θ* scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{min} = 0.5365$, $T_{max} = 0.6485$
4742 measured reflections
4476 independent reflections
2609 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 78.26°$
$h = -12 \rightarrow 11$
$k = -8 \rightarrow 10$
$l = -33 \rightarrow 32$
3 standard reflections every 150 reflections intensity decay: 4.20%

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.423 (3)	N—C8	1.426 (5)
S1—O1	1.426 (3)	N—C14	1.482 (5)
S1—N	1.649 (4)	C14—C15	1.492 (6)
S1—C7	1.750 (5)	C15—C16	1.297 (6)
S2—C13	1.751 (4)	C16—C17	1.465 (6)
S2—C14	1.838 (4)		
O2—S1—O1	119.7 (2)	C13—C8—N	113.4 (3)
O2—S1—N	106.2 (2)	C8—C13—S2	113.0 (3)
O1—S1—N	106.1 (2)	N—C14—C15	110.5 (4)
O2—S1—C7	109.4 (2)	N—C14—S2	105.5 (3)
O1—S1—C7	107.1 (2)	C15—C14—S2	112.2 (3)
N—S1—C7	107.9 (2)	C16—C15—C14	123.6 (4)
C13—S2—C14	91.0 (2)	C15—C16—C17	128.6 (4)
C8—N—C14	111.8 (3)		
C14—C15—C16—C17	177.5 (4)		

Table 2
Hydrogen-bonding and short-contact geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···O1^{i}	0.93	2.53	3.411 (6)	159
C12—H12···O1^{ii}	0.93	2.69	3.346 (6)	128
C20—H20···O2^{iii}	0.93	2.71	3.399 (6)	132

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x, y - 1, z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Table 3
Geometric parameters (Å) of heterocyclic compounds containing the C_3NS ring.

Compound	C_3NS ring conformation	D†	S—C	N—C
$C_{15}H_9Cl_2NS_2$^{a}	planar		1.739 (4) 1.760 (4)	1.297 (5) 1.384 (5)
$C_{13}H_9NOS$^{b}	planar		1.732 (2) 1.747 (2)	1.397 (2) 1.297 (2)
$C_{11}H_8N_2S$^{c}	planar		1.739 (3) 1.754 (3)	1.398 (3) 1.299 (3)
$C_{18}H_{18}N_2S_2$^{d}	envelope	0.409 (12)	1.751 (8) 1.861 (9)	1.370 (9) 1.490 (9)
$C_{18}H_{20}N_2S_2$^{e}	envelope	0.288 (1)	1.751 (8) 1.861 (9)	1.370 (3) 1.464 (4)
$C_{11}H_{13}NOS$^{f}	envelope	0.322 (2)	1.748 (2) 1.846 (2)	1.388 (3) 1.463 (3)
$C_{26}H_{21}NO_2S_2$^{g}	envelope	0.380 (6)	1.751 (4) 1.838 (4)	1.426 (5) 1.482 (5)

† Deviation of C atom bonded to S and N atoms from C_2NS plane. References: (*a*) Yang *et al.* (1995); (*b*) Teo *et al.* (1995); (*c*) Davidović *et al.* (1999); (*d*) Miler-Srenger (1969); (*e*) Miler-Srenger (1973); (*f*) Yeap *et al.* (1991); (*g*) present work.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.225$
$S = 1.012$
4476 reflections
282 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1300P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.021$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}

The H atoms were refined using a riding model and their isotropic displacement parameters were set to 1.2 times (1.5 times for CH_3 groups) the equivalent displacement parameters of their parent atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1385). Services for accessing these data are described at the back of the journal.

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