Crystal Structure of 3-*para*-tolyl-6-(4'-methyl-biphenyl-2-yl)-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole

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The title compound, C₂₃H₁₈N₄S, was synthesized and the structure was investigated by X-ray crystallography. The compound crystallizes in the monoclinic crystal class in the space group *P*2₁/*c* with cell parameters *a* = 16.378(2) Å, *b* = 5.9050(4) Å, *c* = 25.026(3) Å, β = 127.981(3)°, *Z* = 4 and *V* = 1907.7(4) Å³. The condensed 1,2,4-triazolo thiadiazole ring is planar. The bond lengths indicate electron delocalization in the triazole ring system.

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The chemistry of condensed heterocycles, such as the 1,2,4-triazolo thiadiazole ring, occupies an extremely important niche within the family of 5 and 6 membered ring heteroaromatics. They play a central role in numerous molecules of established bioactivities, which includes fungicidal, insecticidal, bactericidal,¹ herbicidal, anti-tumor, anti-inflammatory, CNS stimulant² properties. They also find applications as dyes, lubricants and analytical reagents. A triazolo-thiadiazole system may be viewed as a cyclic analog of two very important components—thiosemicarbazide and biguanide, which often display diverse biological activities. Therefore, it is worthwhile to investigate the system of combining these three biologically active components in a compact system for screening of their biological activities. In view of the above, we herein report on the synthesis and crystal structure of the title compound.

We synthesized the compound, 4-amino-3-(*p*-tolyl)-5-mercapto-[1,2,4]-triazole using one of the reported procedures.³ The second set of syntheses involves an efficient one-pot method, where the condensation of 4-amino-3-(*p*-tolyl)-5-mercapto-[1,2,4]-triazole with 4'-methyl-biphenyl carboxylic acid under different conditions including microwave irradiation in the DMF solvent and 3-substituted-6-(4'-methyl-biphenyl-2-yl)-[1,2,4]triazolo[3,4-*b*] [1,3,4]thiadiazoles. The condensation was carried out as shown in either POCl₃ at reflux temperature for overnight or with *para*-toulene sulfonyl chloride in toulene for 12 h at 65 – 70°, or microwave irradiation (Kenstar) in DMF as a solvent for about 30 – 40 s at 60% power. A schematic

diagram of the molecule is shown in Fig. 1. The crystal and experimental details are given in Table 1.

A single crystal of the title compound with dimensions of 0.3 × 0.27 × 0.25 mm was chosen for an X-ray diffraction study. The data were collected on a DIPLabo Image Plate system with graphite monochromated Mo *K*_α radiation. Thirty six frames of data were collected in oscillation mode with an oscillation range of 5°, and processed using Denzo.⁴ The reflections were merged with Scalepack. Table 2 gives selected bond lengths and bond angles of the non-hydrogen atoms.

The structure was solved by direct methods using SHELXS-97. The structure was refined by a fullmatrix least-squares method with anisotropic temperature factors for non-hydrogen

Fig. 1 Schematic diagram.

Table 1 Crystal data and structure refinement table

Empirical formula	C ₂₃ H ₁₈ N ₄ S
Formula weight	382.47
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> <i>Z</i> = 4
Cell dimensions	<i>a</i> = 16.378(2) Å <i>b</i> = 5.9050(4) Å <i>c</i> = 25.026(3) Å β = 127.981(3)°
Volume	1907.7(4) Å ³
<i>D</i> _c	1.332 Mg/m ³
θ _{max}	25.0°
Reflections collected	5166
<i>R</i> ₁	0.0925
(Δ/ <i>σ</i>) _{max}	0.001
(Δρ) _{max}	1.310 e Å ⁻³
(Δρ) _{min}	-0.724 e Å ⁻³
Refinement method	full-matrix least-squares on <i>F</i> ²
Measurement	DIPLabo Kappa
Structure determination	SHELXS-97
Refinement	full-matrix: SHELXL-97
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Fig. 2 ORTEP drawing of the molecule at 50% probability.

atoms using SHELXL-97. The hydrogen atoms were placed at idealized positions, and were allowed to ride with isotropic temperature factors. An ORTEP drawing of the molecule at 50% probability is shown in Fig. 2.

The 1,2,4-triazolo thiadiazole ring is planar. The dihedral angle between the fused triazolo thiadiazole ring plane and the methylphenyl ring plane (A) is $10.79(26)^\circ$, while that between the triazolo thiadiazole ring plane and the phenyl ring plane (B) is $16.49(25)^\circ$. The torsion angle of $78.0(6)^\circ$ for C16–C21–C22–C23 indicates that the methylphenyl ring plane (C) is twisted along the phenyl ring plane (B). The C–N bond lengths in the five-membered triazole ring system C2–N1 = $1.322(5)\text{\AA}$, C2–N6 = $1.362(5)\text{\AA}$ and C7–N8 = $1.324(5)\text{\AA}$ are longer than a typical C=N bond, but shorter than the C–N bond, indicating electron delocalization in the ring. The thiadiazole moiety displays differences in the pairs of bonds S3–C2/S3–C4 and C2–N6/C4–N5, due to the fused 1,2,4-triazole ring and the two different groups attached to either side of the triazolo thiadiazole system. The difference between the S3–C2 [$1.726(4)\text{\AA}$] and S3–C4 [$1.753(4)\text{\AA}$] indicates that the resonance effect caused by the triazole ring is stronger than that caused by the thiadiazole ring. The molecule exhibits weak intramolecular hydrogen bonds of type C–H $\cdots$ N. The C $\cdots$ N

Table 2 Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$)

Atoms	Length	Atoms	Length
N1–C2	1.322(5)	C4–N5	1.305(5)
C2–N6	1.362(5)	N5–N6	1.382(4)
N1–N8	1.399(5)	N6–C7	1.379(5)
C2–S3	1.726(4)	C7–N8	1.324(5)
S3–C4	1.753(4)	C21–C22	1.482(6)
C2–N1–N8	105.2(3)	N5–C4–C16	117.2(4)
N1–C2–N6	110.8(4)	N5–C4–S3	117.3(3)
N1–C2–S3	139.4(4)	C16–C4–S3	125.4(3)
N6–C2–S3	109.7(3)	C4–N5–N6	107.3(3)
C2–S3–C4	87.7(2)	N8–C7–C9	125.8(4)

distance of $3.146(9)\text{\AA}$ about C14–H14 $\cdots$ N5 is slightly greater than those reported in the literature.⁵

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