

3-Benzyl-4-(4-methylphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thioneSema Öztürk Yıldırım,^{a*} Mehmet Akkurt,^a Metin Koparrı,^b Ahmet Cansız,^b Memet Şekerci^b and Frank W. Heinemann^c^aDepartment of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey, ^bDepartment of Chemistry, Faculty of Arts and Sciences, Firat University, 23119 Elazığ, Turkey, and ^cInstitut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstraße 1, D-91058 Erlangen, Germany

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.038
wR factor = 0.083
Data-to-parameter ratio = 20.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The title compound, $\text{C}_{16}\text{H}_{15}\text{N}_3\text{S}$, displays the usual geometrical parameters of 1,2,4-triazole derivatives. The occurrence of $\text{N}-\text{H}\cdots\text{S}$ hydrogen-bonding interactions results in the formation of dimers.

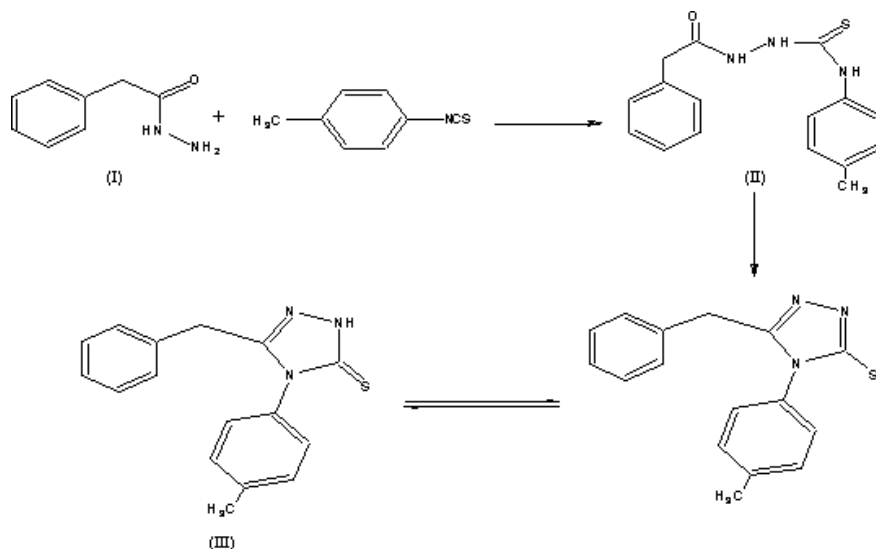
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Comment

Derivatives of 1,2,4-triazole are known to exhibit anti-inflammatory (Unangst *et al.*, 1992; Mullican *et al.*, 1993), antiviral, analgesic (Sughen & Yoloye, 1978), antimicrobial (Shams El-Dine & Hazzaa, 1974; Misato *et al.*, 1977; Cansız *et al.*, 2001), anticonvulsant (Stillings *et al.*, 1986) and anti-depressant activity (Kane *et al.*, 1988), the latter being usually explored by the forced swim test (Porsolt *et al.*, 1977; Vamvakides, 1990). Among the pharmacological profiles of 1,2,4-triazoles, their antimicrobial, anticonvulsant and anti-depressant properties seem to be the best documented. Derivatives of 4,5-disubstituted 1,2,4-triazole are known to be synthesized by intramolecular cyclization of 1,4-disubstituted thiosemicarbazides (Zamani *et al.*, 2003; Cansız *et al.*, 2004; Koparrı *et al.*, 2004). In addition, there are some studies on the electronic structures and thiol–thione tautomeric equilibrium of heterocyclic thione derivatives (Aydoğan *et al.*, 2002; Charistos *et al.*, 1994). In the present study, the synthesis and structural characterization of 3-benzyl-4-(4-methylphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione, (III), are reported.



The 1,2,4-triazole ring is planar, the maximum deviation from planarity being 0.002 (1) Å for atom N2 (Fig. 1). The tolyl ring is twisted by 67.38 (5)° around the N1–C10 bond with respect to the triazole ring, whereas the phenyl and triazole rings make a dihedral angle of 68.38 (5)°.

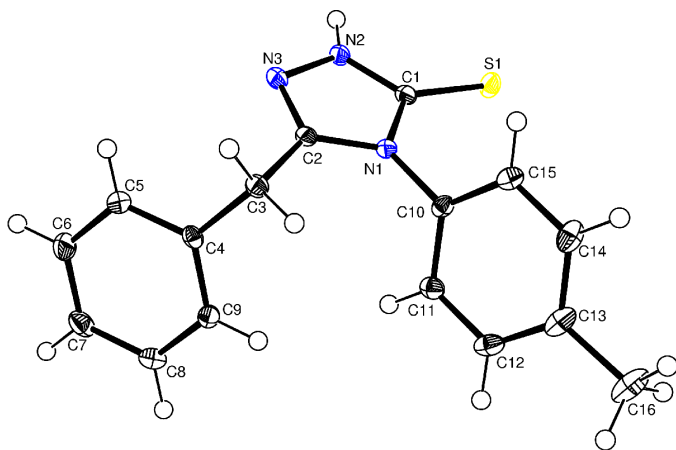


Figure 1
ORTEP-3 view (Farrugia, 1997) of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

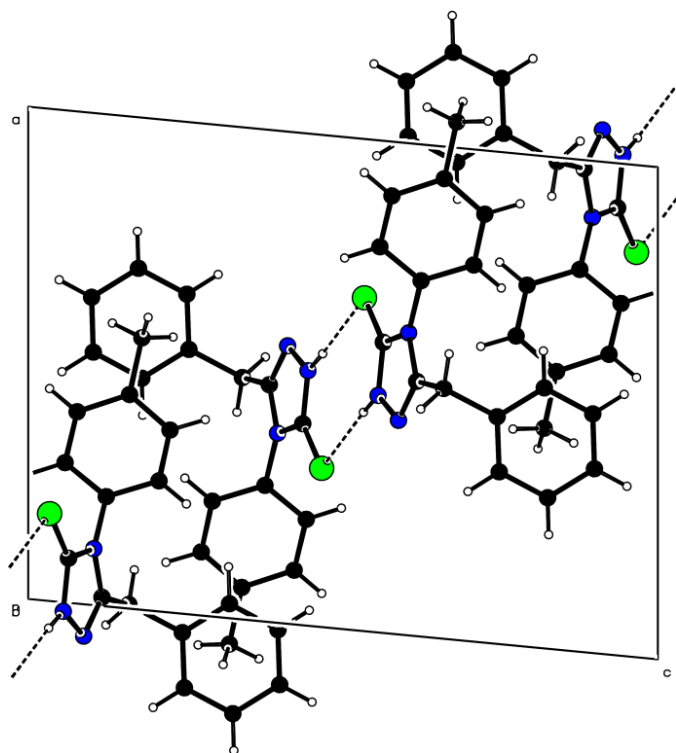


Figure 2
A packing diagram of (III), illustrating the formation of dimers through N—H...S hydrogen bonding (dashed lines).

All bond lengths and angles have values comparable with those reported in the literature for related structures (Öztürk *et al.*, 2004; Akkurt *et al.*, 2004).

In the crystal structure, the occurrence of intermolecular N—H...S hydrogen bonding (Table 2) results in the formation of dimers (Fig. 2).

Experimental

The title compound, (III), was synthesized by the reaction of 1-isothiocyanato-4-methylbenzene and 2-phenylaceto-hydrazide, (I),

through the intermediate *N*-(4-methylphenyl)-2-(phenylacetyl)-hydrazinecarbothioamide, (II). Base-catalysed intramolecular dehydrative cyclization of this intermediate furnished the thione in good yield. For the synthesis of (II), a mixture of (I) (0.01 mol) and the appropriate 1-isothiocyanato-4-methylbenzene (0.01 mol) in absolute ethanol (100 ml) were refluxed for 7 h. The solid material obtained on cooling was filtered off, washed with diethyl ether, dried and crystallized from methanol (yield 88%; m.p. 433–434 K). IR ν (cm^{-1}): 3450–3329 (N—H), 1678 (C=O), 1250 (C=S). ^1H NMR: δ 2.28 (*s*, 3H, CH₃), 3.53 (*s*, 2H, CH₂), 7.30–7.45 (*m*, 9H, Ar. H), 8.17–8.24 (*br*, 1H, —NH—Ar); 10.13–10.15 (*br*, 2H, 2 × NH); analysis calculated for C₁₆H₁₇N₃OS (299): C 64.19, H 5.72, N 14.03, S 10.71%; found C 64.11, H 5.69, N 14.01, S 10.59%.

For the synthesis of (III), a stirred mixture of (II) (1 mmol) and sodium hydroxide (40 mg, 1 mmol, as a 2 *N* solution) was refluxed for 4 h. After cooling, the solution was acidified with hydrochloric acid and the precipitate was filtered off. The precipitate was then crystallized from a mixture of methanol–dioxane (yield: 71%; m.p.: 455–456 K). IR ν (cm^{-1}): 3358–3290 (NH), 2550 (SH), 1605 (C=N), 1538, 1262, 1050, 950 (N—C=S, amide I, II, III and IV bands); ^1H NMR δ : 2.42 (*s*, 3H, CH₃), 3.81 (*s*, 2H, CH₂), 6.97–7.29 (*m*, 9H, Ar. H), 12.91 (*s*, 1H, SH/NH); analysis calculated for C₁₆H₁₅N₃S (312): C 68.30, H 5.37, N 14.93, S 11.40%; found C 63.38, H 5.37, N 15.00, S 11.47%.

Crystal data

| | |
|--|---|
| C ₁₆ H ₁₅ N ₃ S | $D_x = 1.320 \text{ Mg m}^{-3}$ |
| $M_r = 281.38$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 119 reflections |
| $a = 12.3833$ (12) Å | $\theta = 6\text{--}20^\circ$ |
| $b = 7.2297$ (5) Å | $\mu = 0.22 \text{ mm}^{-1}$ |
| $c = 15.8926$ (15) Å | $T = 100 \text{ K}$ |
| $\beta = 95.488$ (7)° | Prism, colorless |
| $V = 1416.3$ (2) Å ³ | $0.27 \times 0.23 \times 0.18 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|---|--|
| Bruker–Nonius KappaCCD diffractometer | 3712 independent reflections |
| ω – φ scans | 2826 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2002) | $R_{\text{int}} = 0.047$ |
| $T_{\text{min}} = 0.929$, $T_{\text{max}} = 0.962$ | $\theta_{\text{max}} = 29.0^\circ$ |
| 21959 measured reflections | $h = -16 \rightarrow 16$ |
| | $k = -9 \rightarrow 9$ |
| | $l = -21 \rightarrow 21$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | $w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 0.5394P]$ |
| $wR(F^2) = 0.084$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.02$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 3712 reflections | $\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$ |
| 182 parameters | $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$ |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------|-------------|----------|-------------|
| S1—C1 | 1.6853 (13) | N1—C10 | 1.4421 (16) |
| N1—C1 | 1.3750 (17) | N2—C1 | 1.3417 (16) |
| N1—C2 | 1.3850 (16) | N2—N3 | 1.3805 (15) |
| C1—N1—C2 | 107.80 (10) | C1—N2—N3 | 113.44 (11) |
| C1—N1—C10 | 124.41 (11) | C2—N3—N2 | 104.03 (10) |
| C2—N1—C10 | 127.72 (11) | | |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------|-------|-------------|-------------|---------------|
| $N2-H2\cdots S1^i$ | 0.86 | 2.42 | 3.2772 (12) | 174 |

Symmetry code: (i) $1-x, -y, 1-z$.

All the H atoms were located in difference maps, but they were idealized and treated as riding on their parent C or N atoms [N–H = 0.86, C–H = 0.93–0.97 Å; $U_{iso}(H) = 1.2$ or 1.5 times $U_{eq}(\text{parent atom})$].

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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