Crystal Structure of 5-(4-Methylbenzoyl)-1-(methyl-4-methylphenyl-methylene amino)-4-(4-methylphenyl)-1H-pyrimidine-2-thione

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The title compound, C₂₈H₂₅N₃OS, has been characterized by single-crystal X-ray diffraction. It crystallizes in the triclinic system, space group *P* $\bar{1}$ (No. 2), *a* = 10.058(3), *b* = 10.318(3), *c* = 13.560(3) Å, α = 98.694(19), β = 107.418(19), γ = 107.069(19)°; *V* = 1238.7(5) Å³ and *D*_x = 1.211 Mg m⁻³, *Z* = 2. The structure was refined to an *R*-value of 0.0573 for 1749 observed reflections using three-dimensional X-ray diffraction data. The pyrimidine ring is slightly distorted from planarity, with the maximum deviation from the mean plane of -0.072(4) Å for atom C1. The molecules contain four rings that are not coplanar. The dihedral angles between three benzene rings are 44.6(3), 77.6(2) and 87.4(2)°. The three benzene rings form dihedral angles of 31.4(2), 57.4(2) and 61.2(2)° with the pyrimidine ring. No classic hydrogen bonds were found.

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The 4-aryl-5-aryl-2,3-dihydro-2,3-furandiones are obtained starting from 1,3-dicarbonyl compounds with oxalyl halides. Due to their high reactivity, numerous reports have highlighted their chemistry and use. Reactions of substituted 2,3-furandiones with various nucleophiles in different solvents and at various temperatures have also been studied. Pyrimidines in general have received much interest for biological and medical reasons, and thus their chemistry has been investigated extensively. In particular, various analogues of thiopyrimidines possess effective herbicidal, antibacterial, antifungal, antiviral properties. Some of them are frequently encountered in many drugs used for the treatment of hypothyroidy, hypertension, cancer chemotherapy or HIV infection. In this context, we have synthesized several new compounds, including the title compound.¹⁻³ We have carried out X-ray studies to obtain more information on the structure and geometrical features of this title compound.

An equimolar mixture of the 4-(4-methylbenzoyl)-5-(4-methylphenyl)-2,3-furandione (0.50 g) and 4-methylacetophenonthiosemicarbazone (0.31 g) (molar ratio 1:1) was refluxed in 30 mL of benzene for 5 h. The solvent was

evaporated. Then, the residue was treated with dry diethyl ether and filtered. The so-formed crude product was recrystallized from ethanol and allowed to dry on P₂O₅; yield, 0.38 g (53%); m.p., 489 K. IR (KBr, ν , cm⁻¹): 3028 (aromatic C-H), 2911 (aliphatic C-H), 1650 s (C=O), 1582 - 1450 m (C=C and C=N),

Table 1 Crystal data and structure refinement

Empirical formula	C ₂₈ H ₂₅ N ₃ OS
Formula weight	451.57
Temperature (K)	293(2)
Wavelength	0.71069
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$ (No. 2)
<i>a</i>	10.058(3) Å
<i>b</i>	10.318(3) Å
<i>c</i>	13.560(3) Å
α	98.694(19)°
β	107.418(19)°
γ	107.069(19)°
Volume	1238.7(5) Å ³
<i>Z</i>	2
Calculated density	1.211 Mg m ⁻³
<i>F</i> (0 0 0)	476
θ range for data collection	1.63° - 28.06°
Limiting indices	-11 ≤ <i>h</i> ≤ 13, -13 ≤ <i>k</i> ≤ 13, -17 ≤ <i>l</i> ≤ 17
Reflections collected/unique	18664/5933 <i>R</i> _{int} = 0.12
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1749/0/299
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0573, <i>wR</i> ₂ = 0.0887
Largest diff. peak and hole	0.136 and -0.122 e Å ⁻³
Measurements	Stoe IPDS II diffractometer
Program system	X-AREA (Version 1.18) and X-RED32 (Version 1.04)
Structure determination	direct methods (SIR-97)
Refinement	full-matrix least-squares (SHELXL-97)
CCDC	671997

Fig. 1 Scheme of the title compound.

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Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U_{eq}
C1	0.1663 (4)	0.4292 (3)	0.4748 (2)	0.0515 (10)
C2	0.2656 (4)	0.6058 (3)	0.6400 (3)	0.0541 (10)
C3	0.2686 (4)	0.5087 (3)	0.6973 (2)	0.0446 (9)
C4	0.2342 (3)	0.3699 (3)	0.6372 (3)	0.0430 (9)
C5	0.2566 (4)	0.2593 (3)	0.6899 (2)	0.0433 (9)
C6	0.3683 (4)	0.2889 (3)	0.7872 (3)	0.0571 (10)
C7	0.3808 (4)	0.1856 (4)	0.8398 (3)	0.0654 (11)
C8	0.2833 (4)	0.0500 (4)	0.7958 (3)	0.0556 (10)
C9	0.1756 (4)	0.0172 (3)	0.6959 (3)	0.0623 (11)
C10	0.1617 (4)	0.1206 (3)	0.6434 (3)	0.0539 (10)
C11	0.2927 (4)	-0.0605 (4)	0.8569 (3)	0.0842 (13)
C12	0.3056 (4)	0.5593 (4)	0.8157 (3)	0.0547 (10)
C13	0.2137 (4)	0.4783 (3)	0.8678 (2)	0.0521 (10)
C14	0.2726 (5)	0.4954 (4)	0.9765 (3)	0.0869 (14)
C15	0.1887 (6)	0.4220 (5)	1.0274 (3)	0.0955 (15)
C16	0.0446 (5)	0.3312 (4)	0.9717 (3)	0.0772 (12)
C17	-0.0149 (4)	0.3152 (4)	0.8631 (3)	0.0714 (11)
C18	0.0687 (4)	0.3872 (4)	0.8111 (3)	0.0576 (10)
C19	-0.0489 (5)	0.2508 (4)	1.0271 (3)	0.1129 (17)
C20	0.3266 (4)	0.7240 (3)	0.4478 (2)	0.0488 (9)
C21	0.4414 (4)	0.6592 (4)	0.4472 (3)	0.0775 (12)
C22	0.3283 (4)	0.8434 (3)	0.3989 (3)	0.0500 (9)
C23	0.4123 (4)	0.8803 (4)	0.3377 (3)	0.0650 (11)
C24	0.4055 (4)	0.9870 (4)	0.2876 (3)	0.0759 (12)
C25	0.3151 (4)	1.0605 (4)	0.2992 (3)	0.0677 (12)
C26	0.2357 (4)	1.0273 (4)	0.3633 (3)	0.0719 (12)
C27	0.2404 (4)	0.9199 (3)	0.4124 (3)	0.0640 (11)
C28	0.3055 (5)	1.1755 (4)	0.2416 (3)	0.1030 (16)
N1	0.1824 (3)	0.3341 (3)	0.5315 (2)	0.0501 (8)
N2	0.2255 (3)	0.5705 (3)	0.5332 (2)	0.0494 (8)
N3	0.2219 (3)	0.6829 (3)	0.4838 (2)	0.0561 (8)
O1	0.4099 (3)	0.6690 (2)	0.86567 (18)	0.0797 (9)
S1	0.08267 (13)	0.38582 (10)	0.34231 (7)	0.0713 (4)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j).$$

Fig. 2 ORTEP view of the title molecule, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

1181 (C=S). ^1H NMR (200 MHz, DMSO, ppm): 8.09 – 7.02 (m, 13H, ArH), 2.40, 2.35, 2.33, 2.29 (s, 12H, $4 \times \text{CH}_3$).

Analysis calculated for $\text{C}_{28}\text{H}_{25}\text{N}_3\text{OS}$: C, 74.47; H, 5.58; N, 9.31; S, 7.10%. Found: C, 74.50; H, 5.47; N, 9.52; S, 7.20%.

Three-dimensional intensity data of a yellow crystal were collected on an STOE IPDS II diffractometer with an imaging-plate detector diffractometer using a graphite monochromator equipped with Mo K_α radiation ($\lambda = 0.71069 \text{ \AA}$). A ω scan mode was employed for data collection. A total of 18664 reflections were measured, out of which 5933 were found to be unique ($-11 \leq h \leq 13$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$). The data were reduced for a background correction as well as Lorenz, polarization and decay corrections by using X-RED32. The crystal structure was solved by direct methods using SIR92, and refined by a full-matrix least-square method on F^2 using SHELXL97. Non-hydrogen atoms were refined with anisotropic displacement parameters.

All H atoms were positioned geometrically, with C–H = 0.93 and 0.96 $\text{\AA}$ for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(\text{H}) = 1.2$ or $1.5U_{eq}(\text{C})$. The methyl groups were allowed to rotate, but not to

Table 3 Selected bond lengths ($\text{\AA}$) and angles ($^\circ$)

C1–N1	1.351 (3)	C4–N1	1.320 (3)
C1–N2	1.403 (3)	C12–O1	1.219 (4)
C1–S1	1.664 (3)	C20–N3	1.278 (4)
C2–N2	1.340 (4)	N2–N3	1.428 (3)
N1–C1–N2	116.7 (3)	N3–C20–C22	115.8 (3)
N1–C1–S1	123.3 (3)	N3–C20–C21	125.9 (3)
N2–C1–S1	120.0 (2)	C4–N1–C1	121.7 (3)
N2–C2–C3	121.7 (3)	C2–N2–C1	120.9 (3)
N1–C4–C3	121.8 (3)	C2–N2–N3	115.2 (3)
N1–C4–C5	116.6 (3)	C1–N2–N3	122.9 (3)
O1–C12–C13	121.7 (3)	C20–N3–N2	114.7 (3)
O1–C12–C3	118.6 (3)		

tip. The refinement was continued until max. shift/esd. was zero. The final residue factor, R , was 0.0573.

A summary of the crystallographic information is given in Table 1. The atomic coordinates and equivalent isotropic displacement parameters, along with the estimated standard deviations for the other atoms, except for H, are listed in Table 2, and selected bond lengths and angles are given in Table 3. An ORTEP-3 drawing of the title compound with the atom numbering is shown in Fig. 2.

In the title compound, all of bond lengths and angles show normal values, and are in good agreement with those observed in similar compounds. The C1–S1 [1.664(3) $\text{\AA}$] double-bond length of the pyrimidine ring is the same as the C=S double-bond length [1.664(2) $\text{\AA}$] in 3-acetyl-4-benzoyl-2-methyl-5-phenyl-3,4-dihydropyrazolo[2,3-*c*]-pyrimidine-7(6*H*)-thione.⁴ The three phenyl rings (B (C5–C10), C (C13–C18) and D (C22–C27)) are planar, with maximum deviations of $-0.021(4) \text{ \AA}$ for C5 and $-0.020(4) \text{ \AA}$ for C8 from the least-squares planes. The molecular structure of the title compound is closely related to that of 5-(4-methylbenzoyl)-4-(4-methylphenyl)-1-(methylphenyl-methylenamino)-1*H*-pyrimidin-2-one and 1-[(4-methylbenzylidene)amino]-5-(4-methylbenzoyl)-4-(*p*-tolyl)pyrimidin-2(1*H*)-one.^{5,6} The pyrimidine ring is slightly distorted from planarity with a maximum deviation of $-0.072(4) \text{ \AA}$ for atom C1. The mean planes of rings A, B, C and D make the following dihedral angles with each other: A/B = $31.4(2)$, A/C = $57.4(2)$, A/D = $61.2(2)$, B/C = $44.6(2)$, C/D = $77.6(2)$ and D/B = $87.4(2)^\circ$.

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