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(4*Z*)-3-Methyl-1-phenyl-4-{(phenyl)[4-(trifluoromethoxy)anilino]methylene}-1*H*-pyrazol-5(4*H*)-one

Hai-Zhen Xu,[a]* You-Quan Zhu[b] and Hai-Bin Song[b]

[a]College of Chemistry and Life Science, Tianjin Normal University, Weijin Road No. 241, Tianjin, People's Republic of China, and [b]State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Correspondence e-mail: zyq8165@nankai.edu.cn

Key indicators

Single-crystal X-ray study
T = 113 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.049
wR factor = 0.125
Data-to-parameter ratio = 14.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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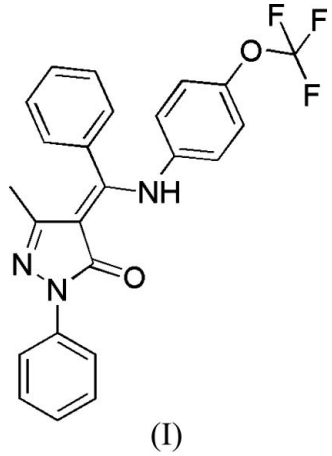
In the title compound, $C_{24}H_{18}F_3N_3O_2$, the dihedral angles formed by the pyrazolone ring with one benzene and two phenyl rings are 26.18 (6), 74.42 (6) and 46.75 (8)°, respectively. The compound is in an enamine–keto form and its structure is stabilized by three intramolecular (N—H···O, C—H···O and C—H···F) and two intermolecular (C—H···O and C—H···F) hydrogen-bond interactions.

Comment

1-Phenyl-3-methyl-4-benzoylpyrazolon-5-one (PMBP), an effective β-diketonate, is widely used and well known for its extractive ability. In recent years, it and its metal complexes have also been found to have good antibacterial and biological properties. Its metal complexes have analgesic activity (Liu *et al.*, 1980; Li *et al.*, 1997; Zhou *et al.*, 1999). Organic fluorine compounds have been receiving significant attention in the materials and pharmaceutical sciences due to their unique physical and biological properties, such as increased membrane permeability, enhanced hydrophobic binding and stability against metabolic oxidation (Kirsch, 2004; Ojima *et al.*, 1996). In order to develop new medicines, we have synthesized the title compound, (I), and its structure is reported here.



(I)

The molecular structure of (I) is shown in Fig. 1. The dihedral angles formed by the pyrazolone ring (C1–C3/N1/N2/O1) with one benzene (C18–C23) and two phenyl rings (C5–C10 and C12–C17) are 46.75 (8), 26.18 (6) and 74.42 (6)°, respectively. Compared with the corresponding angles in compound (II), (4*Z*)-4-[(4-fluorobenzylamino)(phenyl)-methylene]-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (Xu *et al.*, 2006), the first of these dihedral angles is increased and the

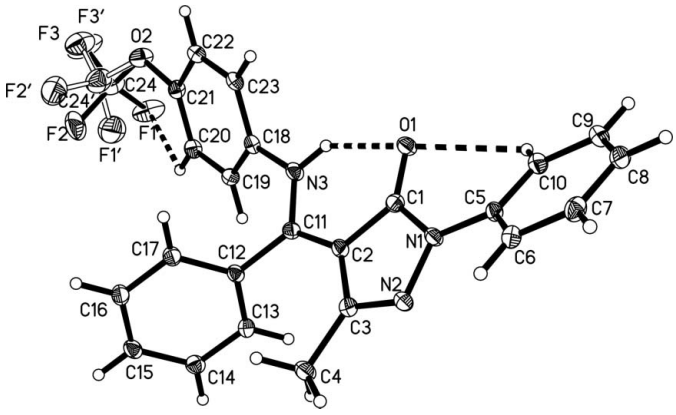


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. Both components of the disorder are shown. Dashed lines indicate intramolecular hydrogen bonds.

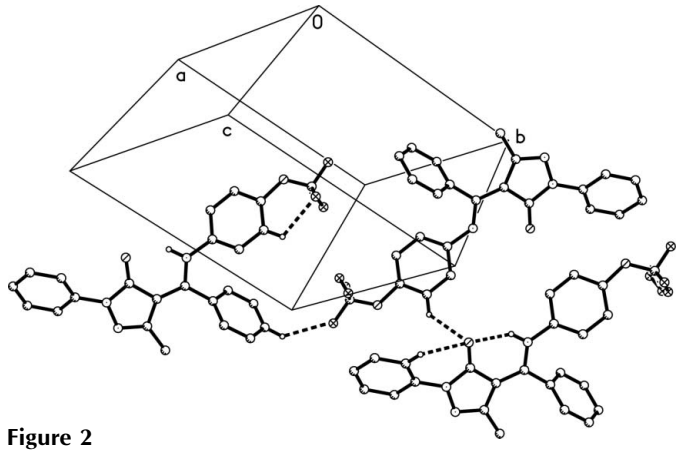


Figure 2
Intermolecular hydrogen-bonding interactions (dashed lines) in the structure of (I). H atoms not involved in hydrogen bonding have been omitted.

other two are decreased. The O atom of the 3-methyl-1-phenylpyrazol-5-one unit and the N atom of the 4-trifluoromethoxyphenylamino group are available for coordination with metals. The pyrazole ring is planar and atoms O1, C1, C2, C11 and N3 are coplanar, the largest deviation being 0.0151 (12) Å for atom C1. The dihedral angle between this mean plane and the pyrazoline ring of PMBP is 5.35 (10)°, close to the value of 4.01 (12)° found in (II). The bond lengths within this part of the molecule (Table 1) lie between classical single and double bond lengths, indicating extensive conjugation.

A strong intramolecular N3—H3···O1 hydrogen bond (Table 2) is observed, leading to an enamine–keto form. This is similar to what is observed in (II) [N···O = 2.695 (3) Å and N—H···O = 141°]. The structure is further stabilized by C—H···O and C—H···F intramolecular and C—H···O and C—H···F intermolecular hydrogen-bonding interactions (Table 2). Part of the crystal structure is shown in Fig. 2.

Experimental

Compound (I) was synthesized by refluxing a mixture of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (10 mmol) and 4-(trifluoromethoxy)benzenamine (10 mmol) in ethanol (80 ml) over a steam bath for about 4 h. Excess solvent was removed by evaporation and the solution was cooled to room temperature. After 2 d, a yellow solid was obtained and this was dried in air. The product was recrystallized from ethanol, to afford yellow crystals of (I) suitable for X-ray analysis.

Crystal data

$C_{24}H_{18}F_3N_3O_2$
M_r = 437.41
Triclinic, $P\overline{1}$
a = 8.0696 (9) Å
b = 11.0945 (12) Å
c = 13.1253 (14) Å
α = 106.698 (4)°
β = 99.688 (5)°
γ = 108.459 (9)°
V = 1023.2 (2) Å^3
Z = 2
D_x = 1.420 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 113 (2) K
Platelet, yellow
0.32 × 0.20 × 0.10 mm

Data collection

Rigaku Saturn diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.966, T_{max} = 0.989
9409 measured reflections
4770 independent reflections
2854 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 27.9°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.125
S = 0.94
4770 reflections
332 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.028 (4)

Table 1
Selected bond lengths (Å).

O1—C1	1.251 (2)	C1—C2	1.448 (2)
N3—C11	1.344 (2)	C2—C11	1.394 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O1	0.90 (2)	1.92 (2)	2.6938 (19)	143 (2)
C20—H20···F1	0.95	2.38	2.906 (2)	114
C10—H10···O1	0.95	2.43	2.965 (2)	115
C15—H15···F3^{i}	0.95	2.53	3.178 (2)	126
C22—H22···O1^{ii}	0.95	2.58	3.306 (2)	133

Symmetry codes: (i) $-x, -y+2, -z+1$; (ii) $-x+1, -y+1, -z+1$.

The trifluoromethyl group shows positional disorder. The site occupancy factors for C24/F1/F2/F3 and C24′/F1′/F2′/F3′ refined to 0.921 (3) and 0.079 (3), respectively. All H atoms were positioned geometrically, with C—H = 0.95–0.98 Å and N—H = 0.90 Å, and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2U_{eq}(C,N), or 1.5U_{eq}(C) for methyl H.

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalStructure* (Rigaku/MSC, 2004); software used to prepare material for publication: *CrystalStructure*.

References

Kirsch, P. (2004). *Modern Fluoroorganic Chemistry: Synthesis, Reactivity and Applications*, pp. 203–271. New York, Heidelberg: Wiley–VCH.

Li, J.-Z., Yu, W.-J. & Du, X.-Y. (1997). *Chin. J. Appl. Chem.* **14**, 98–100.

Liu, J.-M., Yang, R.-D. & Ma, T.-R. (1980). *Chem. J. Chin. Univ.* **1**, 23–29.

Ojima, I., McCarthy, J. R. & Welch, J. T. (1996). *Biomedical Frontiers of Fluorine Chemistry*, pp. 3–41. Washington, DC: American Chemical Society.

Rigaku/MSC (2004). *CrystalStructure*. Version 3.7.0. Rigaku/MSC, The Woodlands, Texas, USA.

Rigaku/MSC (2005). *CrystalClear*. Rigaku/MSC, The Woodlands, Texas, USA.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1996). *SADABS*. Version 4.202. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Xu, H.-Z., Si, X.-K., Zhu, Y.-Q. & Song, H.-B. (2006). *Acta Cryst.* E**62**, o3266–o3268.

Zhou, Y.-P., Yang, Zh.-Y., Yu, H.-J. & Yang, R.-D. (1999). *Chin. J. Appl. Chem.* **16**, 37–41.