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The crystal structure of (Z)-2-(4-(4-bromophenyl)thiazol-2-yl)-4-(3-hydroxybut-2-enoyl)-5-methyl-1,2-dihydro-3H-pyrazol-3-one – methanol (1/1), $C_{18}H_{18}N_3O_4S$

Table 1: Data collection and handling.

Crystal:	Brown needle
Size:	0.20 × 0.15 × 0.12 mm
Wavelength:	MoK α radiation (0.71073 Å)
μ :	2.27 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	18136, 4529, 0.041
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3051
$N(\text{param})_{\text{refined}}$:	250
Programs:	Bruker [1], SHELX [2, 3]

Source of material

The title compound was obtained according to the following procedure: to a round-bottom flask (25 mL) was added thiosemicarbazone of dehydroacetic acid (0.5 mmol), 2,4'-dibromoacetophenone (0.5 mmol) and anhydrous EtOH (5 mL). The mixture was then stirred at 80 °C for 20 h, until the starting material was completely consumed monitored by TLC. The solvent was removed under reduced pressure to obtain a residue, which was redissolved in hot methanol for recrystallization. The title compound was obtained as pale brown needles in low yield (22%). The structure was further confirmed by spectroscopical analysis.

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Abstract

$C_{18}H_{18}N_3O_4S$, monoclinic, Cc (no. 9), $a = 10.8839(14)$ Å, $b = 14.2825(18)$ Å, $c = 13.0717(16)$ Å, $\beta = 108.618(3)^\circ$, $V = 1925.6(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0359$, $wR_{\text{ref}}(F^2) = 0.0812$, Flack parameter = 0.009(6), $T = 298(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Experimental details

A Bruker APEX-II CCD diffractometer was employed to perform the diffraction experiment of a single crystal selected carefully. The data was collected using APEX 2 [1] data collection software at 298 K. The structure was solved and refined using the Bruker SHELXTL Software Package [2, 3].

Comment

The pyrazolone structural motif has been a critical pharmacophore in novel drug discovery, which exhibit various biological effects including antimicrobial, anti-tumor,

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Br1	0.09384 (6)	0.45487 (4)	−0.12543 (5)	0.0794 (2)
C1	0.4904 (5)	0.4359 (3)	0.5197 (3)	0.0466 (10)
C2	0.3825 (4)	0.3898 (3)	0.3551 (4)	0.0479 (10)
C3	0.3903 (5)	0.3081 (3)	0.4074 (4)	0.0645 (13)
H3	0.355564	0.252141	0.374204	0.077*
C4	0.3174 (4)	0.4065 (3)	0.2391 (4)	0.0481 (10)
C5	0.2806 (5)	0.3319 (3)	0.1684 (4)	0.0614 (12)
H5A	0.298796	0.271106	0.194387	0.074*
C6	0.2169 (5)	0.3464 (4)	0.0593 (4)	0.0643 (13)
H6B	0.193890	0.295907	0.012154	0.077*
C7	0.1883 (5)	0.4359 (4)	0.0218 (4)	0.0553 (12)
C8	0.2264 (5)	0.5116 (4)	0.0913 (4)	0.0585 (12)
H8	0.208693	0.572432	0.065437	0.070*
C9	0.2902 (5)	0.4959 (4)	0.1981 (4)	0.0564 (12)
H9	0.316056	0.546708	0.244487	0.068*
C10	0.6139 (5)	0.6310 (3)	0.6838 (4)	0.0519 (11)
C11	0.6525 (5)	0.5618 (3)	0.7647 (4)	0.0489 (11)
C12	0.6109 (5)	0.4736 (3)	0.7123 (3)	0.0507 (11)
C13	0.6322 (6)	0.7340 (3)	0.6910 (5)	0.0784 (16)
H00I	0.723092	0.748190	0.711934	0.118*
H00J	0.596601	0.758662	0.743810	0.118*
H00N	0.588819	0.761683	0.622015	0.118*
C14	0.7196 (5)	0.5757 (3)	0.8768 (4)	0.0522 (11)
C15	0.7757 (5)	0.4988 (3)	0.9463 (4)	0.0542 (11)
H15	0.764093	0.438564	0.917895	0.065*
C16	0.8445 (5)	0.5105 (4)	1.0511 (4)	0.0581 (13)
C17	0.9056 (6)	0.4324 (4)	1.1251 (5)	0.0744 (15)
H00A	0.879218	0.373740	1.088917	0.112*
H00C	0.878845	0.435130	1.188234	0.112*
H00E	0.998250	0.437953	1.145836	0.112*
C18	0.5241 (8)	0.2284 (4)	0.8762 (6)	0.103 (2)
H00B	0.493715	0.223414	0.798947	0.155*
H00D	0.463169	0.198916	0.905219	0.155*
H00Y	0.606785	0.197929	0.904154	0.155*
N1	0.4413 (4)	0.4648 (2)	0.4212 (3)	0.0469 (8)
N2	0.5544 (3)	0.4956 (3)	0.6036 (3)	0.0499 (9)
N3	0.5563 (4)	0.5906 (2)	0.5886 (3)	0.0509 (9)
H3C	0.525497	0.619240	0.527964	0.061*
O1	0.6144 (4)	0.3918 (2)	0.7440 (3)	0.0649 (9)
O2	0.7329 (4)	0.6581 (2)	0.9160 (3)	0.0739 (10)
O3	0.8616 (5)	0.5934 (3)	1.0968 (3)	0.0843 (11)
H3A	0.820199	0.632460	1.053497	0.14 (3)*
O4	0.5361 (8)	0.3165 (3)	0.9039 (4)	0.138 (3)
H00W	0.564160	0.345837	0.862213	0.208*
S1	0.47262 (14)	0.31900 (8)	0.54377 (10)	0.0660 (3)

anti-inflammatory activities and so on [4, 5]. Thus, a lot of methods have been developed to synthesize pyrazolone derivatives with structural diversity [6]. Dehydroacetic acid has also been employed as the starting material to obtain pyrazolone derivatives containing a β -diketone moiety [7, 8].

There is one crystallographically independent target molecule and one additional methanol molecule in the asymmetric unit. The geometric parameters in the crystal structure of the title compound are all in normal ranges. In addition to the basic pyrazolone skeleton, the title compound contains a β -diketone moiety, and a 4-(4-bromophenyl)thiazol-2-yl group. After careful analysis of the crystallographic data, the β -diketone moiety was identified to be present in its enol form, while NMR analysis indicated the presence of ketone/enol (4:5) mixed forms in deuterated DMSO. The observed phenomenon was in accordance with the literature [9, 10]. Based on the following characteristic bond length: $d(\text{O1}–\text{C12}) = 1.235(5) \text{ \AA}$, $d(\text{C11}–\text{C12}) = 1.437(6) \text{ \AA}$, $d(\text{C10}–\text{C11}) = 1.410(6) \text{ \AA}$, $d(\text{N3}–\text{C10}) = 1.332(5) \text{ \AA}$, $d(\text{N2}–\text{N3}) = 1.371(5) \text{ \AA}$, $d(\text{N2}–\text{C12}) = 1.392(6) \text{ \AA}$, the pyrazolone motif was then identified to be present in its NH tautomer, rather than in CH or OH tautomer in the literature [10]. The thiazol-2-yl group at N-2 seems to exhibit effects on the tautomeric forms of the pyrazolone, which deserves further studies in detail.

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