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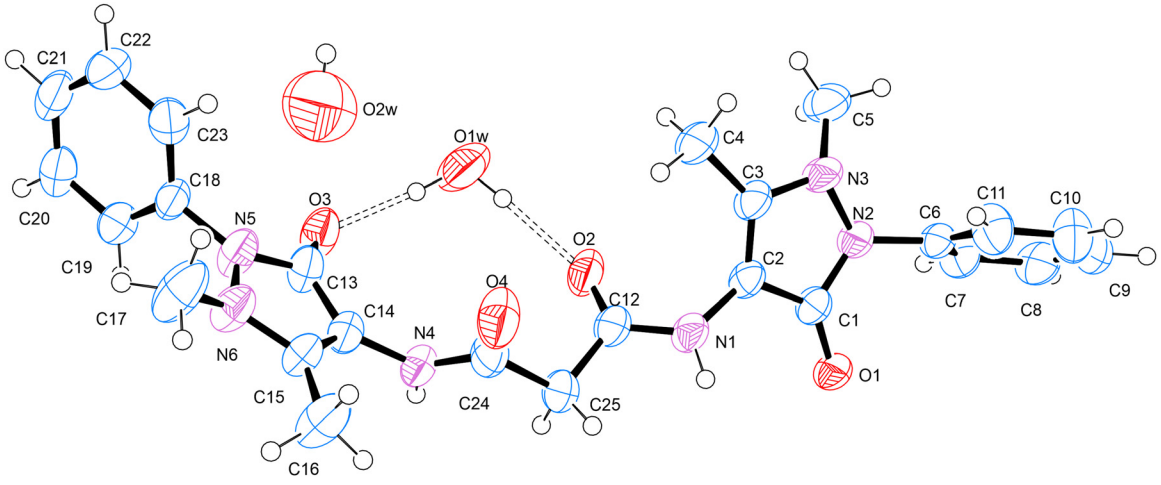
The crystal structure of *N1,N3*-bis(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)\ propanediamide hydrate, $C_{25}H_{26}N_6O_4$, $2(H_2O)$



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Abstract

$C_{25}H_{26}N_6O_4$, $2(H_2O)$, triclinic, $P\bar{1}$ (no. 2), a = 9.8423(6) Å, b = 11.2923(7) Å, c = 13.3810(8) Å, α = 69.053(3)°, β = 73.926(4)°, γ = 68.979(3)°, V = 1277.49(14) Å^3, Z = 2, $R_{gt}(F)$ = 0.0757, $wR_{ref}(F^2)$ = 0.2364, T = 173 K.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.29 × 0.20 × 0.14 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Photon CCD, ω
θ_{max}, completeness:	28.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	22,991, 6140, 0.063
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3310
$N(param)_{refined}$:	348
Programs:	Bruker (*1*), SHELX (*2*, *3*), WinGX/ORTEP-3 (*4*), PLATON (*5*)

1 Source of materials

All reagents used were commercially available and used without further purification. An amount of 0.074 g of 4-aminoantipyrine (0.365 mmol) and 0.039 g of malonic acid (0.376 mmol) were added into a sample vial. The solids were dissolved in 3 mL of a 1:1 mixture of 1,2-dichloroethane:methanol, stirred for 30 min at room temperature, and were left to stand very slightly opened to the atmosphere. The resultant solid was re-dissolved in chloroform and again left to stand very slightly opened to the atmosphere. Colourless blocks were afforded after three days (Tables 1 and 2).

2 Experimental details

C-bound hydrogen atoms were located in the difference map then positioned geometrically and were allowed to ride on their respective parent atoms with thermal displacement parameters 1.2 times of the parent C atom. The coordinates and isotropic displacement parameters of all N-bound and

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6786 (3)	0.8612 (3)	0.0977 (2)	0.0414 (7)
C2	0.5624 (3)	0.8049 (3)	0.1647 (2)	0.0420 (7)
C3	0.6230 (3)	0.6766 (3)	0.2158 (2)	0.0474 (7)
C4	0.5496 (4)	0.5765 (3)	0.2956 (3)	0.0651 (10)
H4A	0.558727	0.567145	0.369294	0.098*
H4B	0.597096	0.490897	0.280079	0.098*
H4C	0.444858	0.605704	0.289645	0.098*
C5	0.8775 (4)	0.5583 (4)	0.2582 (3)	0.0667 (10)
H5A	0.884783	0.60918	0.301475	0.1*
H5B	0.975068	0.525856	0.216878	0.1*
H5C	0.841992	0.482882	0.306602	0.1*
C6	0.9409 (3)	0.7538 (3)	0.0372 (2)	0.0428 (7)
C7	1.0329 (4)	0.8229 (3)	0.0335 (3)	0.0525 (8)
H7	1.012101	0.869197	0.085456	0.063*
C8	1.1572 (4)	0.8239 (3)	−0.0476 (3)	0.0616 (10)
H8	1.220165	0.873064	−0.051666	0.074*
C9	1.1899 (4)	0.7558 (3)	−0.1208 (3)	0.0622 (10)
H9	1.276178	0.75576	−0.174718	0.075*
C10	1.0966 (4)	0.6866 (4)	−0.1161 (3)	0.0702 (11)
H10	1.117933	0.639908	−0.167841	0.084*
C11	0.9720 (4)	0.6849 (4)	−0.0363 (3)	0.0622 (9)
H11	0.908576	0.636355	−0.032658	0.075*
C12	0.3135 (3)	0.8914 (3)	0.2536 (3)	0.0503 (8)
C13	−0.1345 (4)	0.8295 (3)	0.5725 (3)	0.0530 (8)
C14	−0.1459 (3)	0.8915 (3)	0.4621 (2)	0.0473 (7)
C15	−0.2694 (4)	0.8813 (3)	0.4435 (2)	0.0505 (8)
C16	−0.3248 (5)	0.9282 (5)	0.3396 (3)	0.0764 (12)
H16A	−0.297669	0.853862	0.309515	0.115*
H16B	−0.280774	0.997086	0.288141	0.115*
H16C	−0.432541	0.96473	0.352554	0.115*
C17	−0.4481 (5)	0.7503 (5)	0.5507 (3)	0.0824 (14)
H17A	−0.500776	0.791958	0.488768	0.124*
H17B	−0.518859	0.755633	0.617904	0.124*
H17C	−0.396535	0.657149	0.554231	0.124*
C18	−0.3041 (3)	0.7218 (3)	0.7287 (2)	0.0478 (8)
C19	−0.3756 (4)	0.7997 (3)	0.7966 (3)	0.0531 (8)
H19	−0.397697	0.893311	0.768403	0.064*
C20	−0.4161 (4)	0.7421 (4)	0.9071 (3)	0.0599 (9)
H20	−0.466745	0.795948	0.954429	0.072*
C21	−0.3824 (4)	0.6075 (4)	0.9467 (3)	0.0643 (10)
H21	−0.407897	0.567692	1.022257	0.077*
C22	−0.3118 (4)	0.5283 (4)	0.8783 (3)	0.0674 (10)
H22	−0.290186	0.434731	0.906954	0.081*
C23	−0.2720 (4)	0.5847 (4)	0.7678 (3)	0.0597 (9)
H23	−0.22411	0.530873	0.720141	0.072*
C24	0.0495 (4)	0.8999 (3)	0.3074 (3)	0.0521 (8)
C25	0.1585 (3)	0.9734 (3)	0.2339 (3)	0.0554 (9)
H25A	0.134587	1.059287	0.248471	0.066*
H25B	0.1518	0.99138	0.157149	0.066*
N1	0.4117 (3)	0.8761 (3)	0.1641 (2)	0.0466 (6)
N2	0.8071 (3)	0.7606 (2)	0.1156 (2)	0.0452 (6)
N3	0.7740 (3)	0.6434 (2)	0.1831 (2)	0.0499 (7)
N4	−0.0416 (3)	0.9523 (3)	0.3850 (2)	0.0475 (6)
N5	−0.2559 (3)	0.7810 (3)	0.6160 (2)	0.0584 (8)
N6	−0.3422 (3)	0.8181 (3)	0.5375 (2)	0.0565 (7)
O1	0.6732 (2)	0.97313 (19)	0.03454 (16)	0.0473 (5)
O2	0.3462 (3)	0.8437 (3)	0.34494 (18)	0.0646 (7)
O3	−0.0431 (3)	0.8175 (3)	0.62809 (18)	0.0643 (7)
O4	0.0457 (3)	0.8000 (3)	0.2921 (2)	0.0774 (8)
H1	0.380 (4)	0.927 (3)	0.101 (3)	0.049 (9)*
H4	−0.033 (5)	1.033 (4)	0.394 (3)	0.093 (14)*
O1W	0.2422 (4)	0.7038 (4)	0.5518 (3)	0.162 (2)
H1W	0.269598	0.73732	0.480884	0.242*
H2W	0.150396	0.749045	0.578267	0.242*
O2W	−0.1295 (6)	0.4583 (5)	0.5498 (3)	0.1467 (18)
H3W	−0.077112	0.388863	0.589105	0.17 (3)*

O-bound H atoms were allowed to refine freely. Diagrams and publication material were generated using ORTEP-3 (*4*), WinGX (*6*) and PLATON (*5*).

3 Discussion

4–Aminoantipyrine (4AAP) was historically used as an antipyretic pharmaceutical drug (Acheson (*7*)), and as a prophylactic against oxidative stress (Teng et al. (*8*)). The crystal structure of 4AAP has been reported by Li et al. (*9*) and by Mnguni and Lemmerer (*10*) and a co-crystal of 4AAP has been reported by Smith and Lemmerer (*11*). Derivatives of 4AAP account for at least two pharmaceutical drugs, aminoantipyrine and 4-(N,N-dimethyl)-aminoantipyrine, both which have been used as analgesics for over 100 years. This paper presents the crystal structure a new derivative of 4AAP.

As shown in the figure, the asymmetric unit contains one molecule of *N1,N3*-bis(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) propanediamide and two molecules of water. Although the stoichiometry of the reactants was 1:1, both carboxylic acid groups of the malonic acid reacted with the amine groups of two separate 4AAP molecules. One of the water molecules forms a bridge via hydrogen bonding through its two H-atoms to the carbonyl oxygen atoms of O2 and O3 respectively. This bridge creates an *R*(11) hydrogen bonded ring. There is a second water molecule in the asymmetric unit, but it was not possible to determine the position of the second hydrogen atom, and hence it is shown in the diagram as having only one hydrogen atom, resulting in a larger ellipsoid. In the packing, two *N1,N3*-bis(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) propanediamide molecules are joined to each other via two N–H···O heterosynthons, formed between the amine hydrogen atoms and the antipyrine carbonyl oxygen atoms. This reults in an *R*(10) hydrogen bonded ring between the two molecules. The extensive hydrogen bonding results in a 3D packing network.

Author contributions: The author has accepted responsibility for the entire content of this submitted manuscript and approved submission.

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Conflict of interest statement: The author declares no conflict of interest regarding this article.

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