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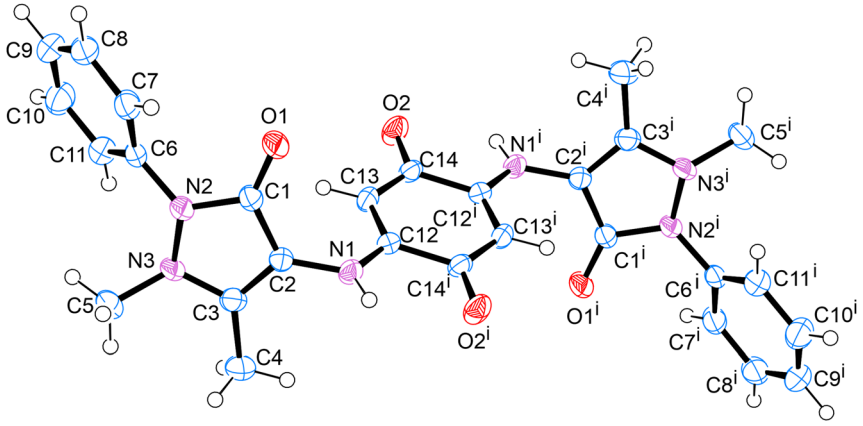
The crystal structure of 2,5-bis[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]cyclohexa-2,5-diene-1,4-dione, $C_{28}H_{26}N_6O_4$



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Abstract

$C_{28}H_{26}N_6O_4$, monoclinic, $P2_1/n$ (no. 14), a = 13.0398(4) Å, b = 7.1786(2) Å, c = 14.9824(5) Å, β = 112.642(2)°, V = 1294.37(7) Å^3, Z = 2, $R_{gt}(F)$ = 0.0458, w$R_{ref}(F^2)$ = 0.1133, T = 173 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.

Table 1: Data collection and handling.

Crystal:	Red plate
Size:	0.27 × 0.22 × 0.05 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Photon, ω
θ_{max}, completeness:	28.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13992, 3129, 0.055
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2084
$N(param)_{refined}$:	174
Programs:	Bruker [1], SHELX [2, 3], ORTEP-3 [4], WinGX [5], PLATON [6]

1 Source of materials

All reagents used were commercially available and used without further purification. An amount of 0.0832 g of 4-aminoantipyrine (0.409 mmol) and 0.0611 g of 2,5-dihydroxy-1,4-benzoquinone (0.408 mmol) were added into a sample vial. The solids were dissolved in 20 mL of a mixture of equal parts of 1,2-dichloroethane, methanol, chloroform, and toluene, and stirred for 120 min. Six drops of dimethylformamide were added to ensure that the solid was fully dissolved. The solution was left to stand very slightly opened to the atmosphere. Red plates were afforded after 14 days. The unusual mixture of solvents is due to the fact that initially the reagents would not dissolve in 5 mL of 1,2-dichloroethane. Therefore, 5 mL of each of the other solvents were added one by one until the reagents started dissolving.

2 Experimental details

C-bound hydrogen atoms were located in the difference map then were allowed to ride on their respective parent atoms

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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	0.84918 (13)	0.1380 (2)	0.18497 (12)	0.0270 (4)
C2	0.75806 (12)	0.2663 (2)	0.14884 (12)	0.0261 (4)
C3	0.79275 (13)	0.4234 (2)	0.11951 (12)	0.0298 (4)
C4	0.72905 (15)	0.5966 (3)	0.08058 (16)	0.0442 (5)
H4A	0.652278	0.580644	0.075273	0.066*
H4B	0.729433	0.622967	0.016525	0.066*
H4C	0.76339	0.700644	0.124236	0.066*
C5	0.98011 (15)	0.5597 (2)	0.15612 (15)	0.0378 (4)
H5A	0.943209	0.672252	0.121597	0.057*
H5B	1.042865	0.528893	0.138161	0.057*
H5C	1.007221	0.581582	0.225979	0.057*
C6	1.03204 (12)	0.1451 (2)	0.16911 (13)	0.0284 (4)
C7	1.09452 (13)	0.0243 (3)	0.24133 (14)	0.0376 (5)
H7	1.077947	0.006366	0.297181	0.045*
C8	1.18207 (15)	−0.0706 (3)	0.23076 (17)	0.0470 (5)
H8	1.224428	−0.156435	0.279199	0.056*
C9	1.20830 (15)	−0.0423 (3)	0.15143 (17)	0.0482 (5)
H9	1.269145	−0.106364	0.145522	0.058*
C10	1.14578 (15)	0.0794 (3)	0.08065 (16)	0.0447 (5)
H10	1.163957	0.099844	0.025822	0.054*
C11	1.05667 (14)	0.1724 (3)	0.08834 (14)	0.0350 (4)
H11	1.012794	0.25432	0.03847	0.042*
C12	0.58126 (12)	0.1152 (2)	0.06900 (12)	0.0245 (4)
C13	0.61111 (12)	0.0224 (2)	0.00389 (12)	0.0279 (4)
H13	0.683835	0.039001	0.004929	0.033*
C14	0.53623 (13)	−0.0990 (2)	−0.06586 (12)	0.0263 (4)
N1	0.64785 (10)	0.22716 (19)	0.13868 (10)	0.0279 (3)
H1	0.62223	0.277971	0.179431	0.033*
N2	0.93877 (10)	0.23537 (18)	0.17834 (10)	0.0281 (3)
N3	0.90109 (11)	0.40502 (18)	0.13017 (11)	0.0299 (3)
O1	0.85424 (9)	−0.02470 (16)	0.21230 (9)	0.0372 (3)
O2	0.56117 (9)	−0.19396 (17)	−0.12277 (9)	0.0378 (3)

with thermal displacement parameters 1.2 times of the parent C atom. Diagrams and publication material were generated using ORTEP-3 [4], WinGX [5] and PLATON [6].

3 Comment

4-Aminoantipyrine (4AAP) was traditionally employed as a preventative measure against oxidative stress [7] and as an antipyretic medicinal medicine [8]. Li et al. [9], as well as Mnguni et al. [10] have both published the crystal structure of 4AAP. Furthermore, a co-crystal of 4AAP has been reported by Smith and Lemmerer [11]. Two derivatives of 4AAP, namely aminoantipyrine and 4-(N,N-dimethyl)-aminoantipyrine have been used medicinally since the 19th century, and the modification of 4AAP therefore presents potential for the creation of new pharmaceutical drugs. This paper presents the crystal structure of a modification of 4AAP.

The structure crystallizes in the $P2_1/n$ space group and the asymmetric unit contains one molecule. As shown in the figure, the molecule has a center of inversion and one half of the molecule is generated by symmetry. The reaction of the two hydroxy groups of 2,5-dihydroxy-1,4-benzoquinone with the amine groups of two 4AAP molecules produced the enamine structure presented in this paper. The two amine groups provide hydrogen bond donors to the antipyrine carbonyl acceptor of two different molecules to form two N–H···O heterosynthons. These hydrogen bonds form a C(10) chain with a screw axis down the b-axis, resulting in 1D ribbons along that axis.

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