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4-{[(1*E*)-(3,5-Dibromo-2-hydroxyphenyl)methylene]-amino}-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.032
wR factor = 0.078
Data-to-parameter ratio = 13.4

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

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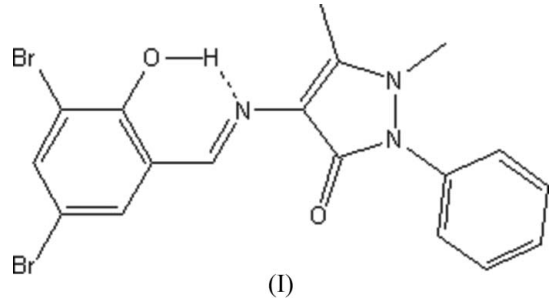
The crystal structure of the title compound, $C_{18}H_{15}Br_2N_3O_2$, shows a strong intramolecular O—H···N hydrogen bond [N···O = 2.609 (4) Å, O—H = 0.90 Å, H···N = 1.80 Å and O—H···N = 148°], which leads to the existence of a phenol–imine tautomer.

Comment

The Schiff bases derived from salicylaldehyde have been much studied because of their properties, such as tautomeric (Salman *et al.*, 1991), fluorescent (Morishige *et al.*, 1980), and thermo- and photochromic properties (Barbara *et al.*, 1980; Cohen *et al.*, 1964). In a search for new analytical reagents, we have synthesized some compounds of substituted salicylaldehyde with 4-aminoantipyrine. We report here the synthesis and crystal structure of the title compound, (I).



(I)

All bond distances and angles are normal and agree with the corresponding values found in a similar compound 4-[(2-hydroxy-3-methoxybenzylidene)amino]-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (Diao *et al.*, 2005). There is an intramolecular O—H···N hydrogen bond (Table 2); the compound is, therefore, in the phenol–imine form, as in 4-{[(1*Z*)-2-hydroxyphenyl)methylene]amino}-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one [N1···O1 = 2.607 (3) Å, O1—H1 = 0.97 (3) Å, H1···N1 = 1.71 (3) Å and O1—H1···N1 = 153 (2)°; Hökelek *et al.*, 2001].

Experimental

3,5-Dibromosalicylaldehyde was synthesized according to the published method (Brewsler, 1924). Ethanol solutions of 3,5-dibromosalicylaldehyde (10 mmol, 2.80 g) and 4-aminoantipyrine (10 mmol, 2.03 g) were mixed and refluxed on a water bath for 5 h. The precipitate was filtered off and recrystallized from methanol (yield 81%, m.p. 501–502 K). IR (KBr, cm^{-1}): ν_{max} 3410.5, 1659.6, 1591.2, 1446.5, 1363.6, 1290.3, 1135.0, 765.7. ^{1}H NMR (200 MHz, $CDCl_3$): δ 14.42 (1H), 9.71 (1H), 7.22–7.72 (7H), 3.21 (3H), 2.42 (3H).

Crystal data

$C_{18}H_{15}Br_2N_3O_2$
M_r = 465.15
Monoclinic, $P2_1/n$
a = 7.092 (5) Å
b = 8.231 (5) Å
c = 30.487 (2) Å
β = 91.725 (12)°
V = 1779 (2) Å^3
Z = 4
D_x = 1.737 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3452 reflections
θ = 2.6–25.3°
μ = 4.57 mm^{-1}
T = 293 (2) K
Block, orange
0.24 × 0.19 × 0.12 mm

Data collection

Siemens SMART CCD area detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker 2002)
T_{min} = 0.367, T_{max} = 0.578
9143 measured reflections
3224 independent reflections
2631 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.3°
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -33 \rightarrow 36$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.078
S = 1.03
3224 reflections
239 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.3014P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0018 (4)

Table 1
Selected geometric parameters (Å, °).

Br1—C3	1.900 (3)	N1—C7	1.292 (4)
Br2—C5	1.889 (3)	N1—C8	1.393 (4)
O1—C6	1.344 (3)	N2—N3	1.414 (3)
O2—C10	1.228 (3)	N3—C10	1.409 (3)
C7—N1—C8	120.4 (3)	O1—C6—C5	120.3 (3)
C2—C1—C7	118.9 (3)	O1—C6—C1	121.9 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···N1	0.90	1.80	2.609 (4)	148
C7—H7A···O2	0.93	2.26	2.958 (4)	131
C18—H18A···O2	0.93	2.46	2.882 (4)	108

The hydroxy H atom (H1A) was positioned from a difference map, refined for several cycles and then fixed at a distance of 0.90 Å; the methyl H atoms on C11 were located in a Fourier synthesis and refined freely. The remaining H atoms were positioned geometrically and treated as riding, at distances of 0.93 (CH) and 0.96 Å (CH_3) [U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C_{methyl},O)].

Data collection: *SMART* (Bruker 2002); cell refinement: *SAINT* (Bruker 2002); data reduction: *SAINT* and *SHELXTL* (Bruker 2002); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

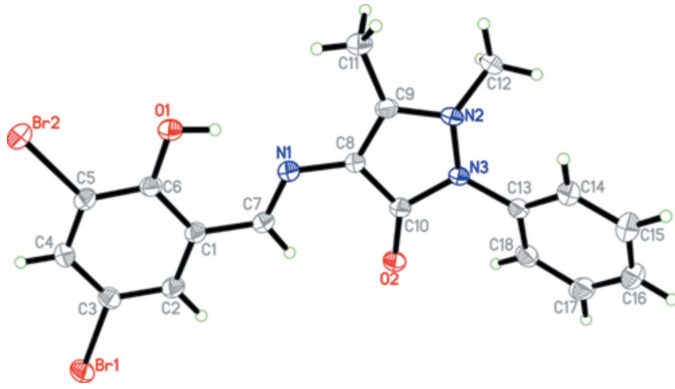


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

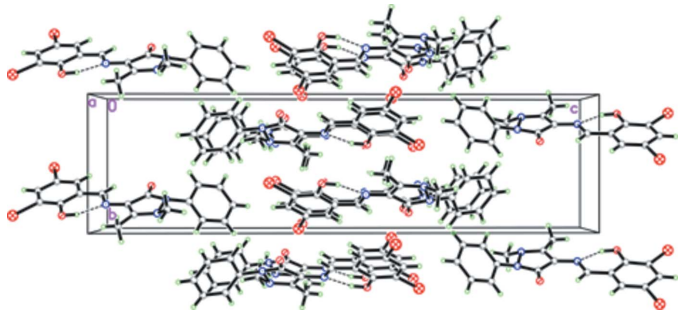


Figure 2
The packing of (I), viewed down the a axis. Dashed lines indicate hydrogen bonds.

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References

Barbara, P. F., Rentzepis, P. M. & Brus, L. E. (1980). *J. Am. Chem. Soc.* **102**, 2786–2791.
Brewsler, C. M. (1924). *J. Am. Chem. Soc.* **46**, 2464–2468.
Bruker (2002). *SMART* (Version 5.62), *SAINT* (Version 6.02), *SADABS* (Version 2.03) and *SHELXTL*. Bruker AXS Inc., Madison, Winsonsin, USA.
Cohen, M. D., Schmidt, G. M. J. & Flavin, S. (1964). *J. Chem. Soc.* pp. 2041–2051.
Diao, C.-H., Fan, Z. & Yu, M. (2005). *Acta Cryst.* E**61**, o3271–o3272.
Hökelek, T., Işiklan, M. & Kılıç, Z. (2001). *Acta Cryst.* C**57**, 117–119.
Morishige, K. (1980). *Anal. Chim. Acta*, **121**, 301–308.
Salman, S. R., Farrant, R. D. & Lindon, J. C. (1991). *Spectrosc. Lett.* **24**, 1071–1078.