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4-(4-Chlorobenzylideneamino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one and 4-(2-chlorobenzylideneamino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one

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The two title compounds, both with formula $C_{18}H_{16}ClN_3O$, are structurally similar Schiff bases derived from the condensation of 4-chlorobenzaldehyde or 2-chlorobenzaldehyde with 4-aminoantipyrine in methanol solution. As expected, both compounds adopt *trans* configurations about the central C=N bonds. In the crystal structure of the 4-chloro analogue, molecules are linked through weak C—H···O hydrogen bonds, forming chains running along the *a* axis. In the crystal structure of the 2-chloro analogue, molecules are linked through weak C—H···O and C—H···Cl hydrogen bonds, forming layers parallel to the *ab* plane.

Comment

Antipyrine and its derivatives exhibit a wide range of biological activities and applications (Yadav *et al.*, 2003; Ismail, 2000; Abd El Rehim *et al.*, 2001). A few crystal structures of antipyrine derivatives have been investigated (Liang *et al.*, 2002; Li & Zhang, 2004, 2005; Zhang & Li, 2005). Schiff bases have demonstrated significant biological activity and new examples are being tested for their antitumour, antimicrobial and antiviral activities (Tarafder *et al.*, 2002; Cukurovali *et al.*, 2002; Ali *et al.*, 2002). Recently, the crystal structure of 4-[(2,4-dichlorobenzylidene)amino]-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one, (III), has been reported (Jing *et al.*, 2005). However, the influence of the substituent groups on the crystal structures of antipyrine derivatives has seldom been reported. In this paper, the crystal structures and the substituent effects of the two structurally similar title antipyrine derivatives, *viz.* the *para*-substituted compound (I) and the *ortho*-substituted compound (II), are reported.

The structures of (I) and (II) (Figs. 1 and 2) are analogous to those of *ortho*- and *para*-substituted (III). The bond lengths and angles in (I) and (II) are comparable to one another and to the corresponding values in (III), and all lie within normal ranges (Allen *et al.*, 1987). The main difference between the two structures is the position of the Cl atoms. In (I), atom Cl1 is located at the *para* position, and thus it cannot participate in the formation of intramolecular hydrogen bonds, while in (II), atom Cl1 is located at the *ortho* position, forming an intramolecular C7—H7···Cl1 hydrogen bond (Table 2). In each of the compounds, the C7=N1 bond lengths [1.276 (2) Å in (I) and 1.278 (3) Å in (II)] conform to the value for a double bond. The distance between atoms C8 and N1 [1.392 (2) Å in

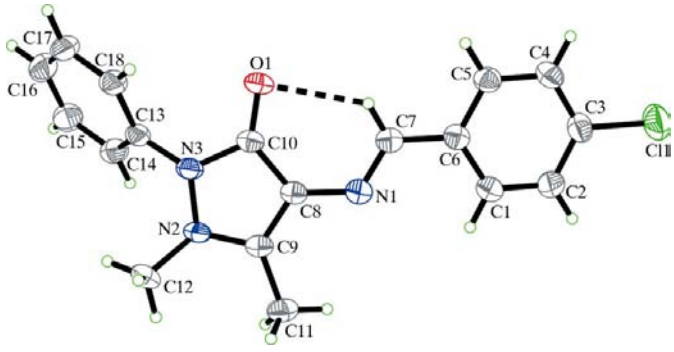

Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The intramolecular hydrogen bond is shown as a dashed line.

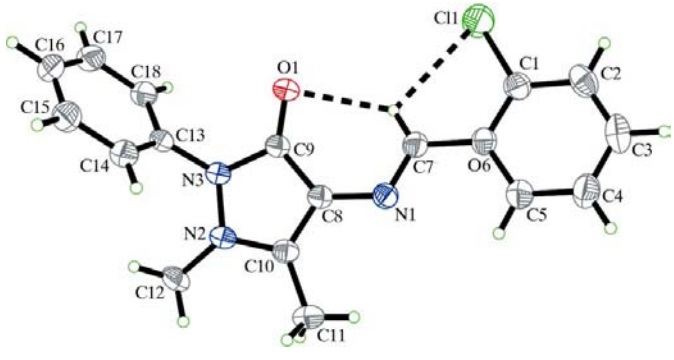

Figure 2
The structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Intramolecular hydrogen bonds are shown as dashed lines.

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both (I) and (II)] is intermediate between a C—N single and a C=N double bond length, because of conjugation effects in each of the molecules. The conjugation effects also cause the pyrazoline and C1–C6 benzene rings to be nearly coplanar, with a mean deviation from the overall plane of 0.0672 Å in (I) and 0.1125 Å in (II). The dihedral angle between the C1–C6 benzene ring and the pyrazoline ring is 8.7 (2)° for (I) and 13.2 (2)° for (II). The dihedral angle between the C13–C18 phenyl ring and the pyrazoline ring is 51.6 (2)° for (I) and 75.5 (2)° for (II). As expected, the molecular structures adopt *trans* configurations about the central C=N bonds, which is also observed in (III).

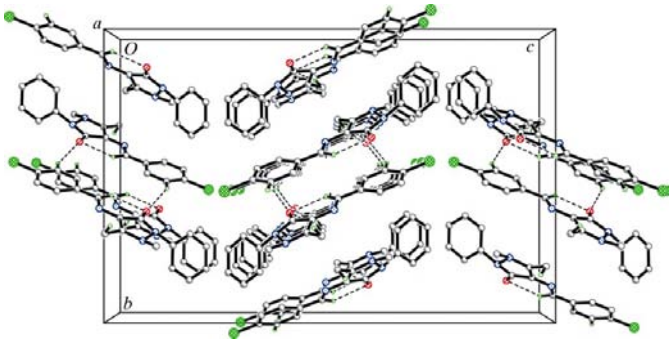

Figure 3
The molecular packing of (I), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in the interactions shown have been omitted.

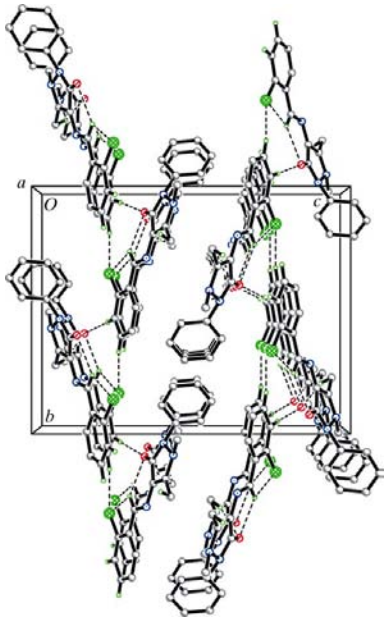

Figure 4
The molecular packing of (II), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in the interactions shown have been omitted.

In the crystal structure of (I), molecules are linked through weak C—H···O hydrogen bonds (Table 1), forming chains running along the *a* axis (Fig. 3). In the crystal structure of (II), molecules are linked through weak C—H···O and C—H···Cl hydrogen bonds, forming layers parallel to the *ab* plane (Fig. 4). The same pattern can be observed in (III), in which the *ortho* Cl1 atom participates in the formation of intermolecular C—H···Cl hydrogen bonds, while the *para* Cl2 atom does not participate in any hydrogen bonds.

In conclusion, in the chloro-substituted antipyrine Schiff bases, the *ortho* Cl atom can participate in the formation of both intra- and intermolecular hydrogen bonds; however, the *para* Cl atom cannot participate in any hydrogen bonds. The positions of substituent groups can significantly influence the final structures.

Experimental

For the preparation of (I), a mixture of 4-chlorobenzaldehyde (0.1 mmol, 14.1 mg) and 4-aminoantipyrine (0.1 mmol, 20.3 mg) were dissolved in methanol (10 ml). The mixture was stirred for about 1 h at room temperature to give a clear yellow solution. After the solution had been kept in air for 3 d, yellow prism-shaped crystals were formed. Compound (II) was prepared by a procedure similar to that described for (I), with 4-chlorobenzaldehyde replaced by 2-chlorobenzaldehyde (0.1 mmol, 14.1 mg). Yellow prism-shaped crystals of (II) were obtained after evaporating the solution in air for 6 d.

Compound (I)

Crystal data

$C_{18}H_{16}ClN_3O$
M_r = 325.79
Orthorhombic, *Pbca*
a = 6.971 (1) Å
b = 17.508 (1) Å
c = 26.905 (2) Å
V = 3283.7 (6) Å^3
Z = 8
D_x = 1.318 Mg m^{-3}
Mo *Kα* radiation
μ = 0.24 mm^{-1}
T = 298 (2) K
Prism, yellow
0.35 × 0.20 × 0.17 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.921, T_{max} = 0.960
24843 measured reflections
3402 independent reflections
2620 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 26.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.126
S = 1.04
3402 reflections
210 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.8176P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	0.93	2.43	3.219 (2)	143
C7—H7···O1	0.93	2.33	3.016 (2)	130
C11—H11*A*···O1^{ii}	0.96	2.47	3.407 (5)	165

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

Compound (II)

Crystal data

$C_{18}H_{16}ClN_3O$
M_r = 325.79
Orthorhombic, $P2_12_12_1$
a = 6.848 (1) Å
b = 13.654 (2) Å
c = 17.567 (2) Å
V = 1642.6 (4) Å^3
Z = 4
D_x = 1.317 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 298 (2) K
Prism, yellow
0.25 × 0.18 × 0.18 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.942, T_{max} = 0.958
11680 measured reflections
3377 independent reflections
2979 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 26.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.107
S = 1.04
3377 reflections
211 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.2996P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.043 (3)
Absolute structure: Flack (1983), 1415 Friedel pairs
Flack parameter: −0.01 (10)

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1^{i}	0.93	2.57	3.491 (3)	172
C3—H3···Cl1^{i}	0.93	2.82	3.713 (3)	161
C7—H7···Cl1	0.93	2.67	3.053 (3)	106
C7—H7···O1	0.93	2.35	3.015 (3)	128
C11—H11*C*···O1^{ii}	0.96	2.50	3.435 (3)	163

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

All H atoms in (I) and (II) were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.96 Å and with U_{iso}(H) values of 1.2 or 1.5 times U_{eq}(C). The Flack (1983) parameter value for (II) is based on the 'hole-in-one' refinement method.

For both compounds, data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT-Plus* (Bruker, 2002); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3029). Services for accessing these data are described at the back of the journal.

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