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(E)-4-Chloro-N-[(5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-yl)methylene]-aniline

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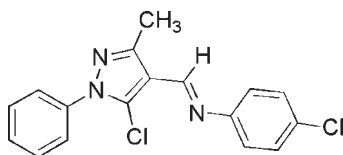
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.032; wR factor = 0.099; data-to-parameter ratio = 17.7.

In the title compound, $\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{N}_3$, the dihedral angle between the pyrazole ring system and 4-chlorophenyl ring is $26.1(2)^\circ$. The $\text{C}=\text{N}$ bond linking the two aromatic rings has an *E* conformation.

Related literature

For the biological properties of pyrazoles, see: Pimerova & Voronina (2001); Selvam *et al.* (2005). For the biological activity of Schiff bases, see: Rajavel *et al.* (2008); Yu *et al.* (2007). For a related structure, see: Sun *et al.* (2007).



Experimental

Crystal data

$\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{N}_3$

$M_r = 330.20$

Orthorhombic, $Pca2_1$

$a = 13.6471(6)$ Å

$b = 15.6315(3)$ Å

$c = 7.3514(6)$ Å

$V = 1568.24(15)$ Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.41$ mm⁻¹

$T = 296$ K

$0.39 \times 0.34 \times 0.10$ mm

Data collection

Rigaku R-Axis RAPID diffractometer

Absorption correction: multi-scan (ABSCOR; Higashi, 1995)

$T_{\min} = 0.839$, $T_{\max} = 0.960$

14704 measured reflections

3558 independent reflections

2533 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.099$

$S = 1.00$

3558 reflections

201 parameters

H-atom parameters constrained

$\Delta\rho_{\max} = 0.21$ e Å⁻³

$\Delta\rho_{\min} = -0.24$ e Å⁻³

Absolute structure: Flack (1983),

1627 Friedel pairs

Flack parameter: $-0.02(6)$

Data collection: *PROCESS-AUTO* (Rigaku, 2006); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2007); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* (Rigaku/MS, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2165).

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supplementary materials

Acta Cryst. (2009). E65, o2424 [doi:10.1107/S1600536809035727]

(*E*)-4-Chloro-*N*-[(5-chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methylene]aniline

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Comment

Pyrazoles continue to attract a great deal of attention due to their extensive utilization in the pharmaceutical and agrochemical fields (Pimerova & Voronina, 2001; Selvam *et al.*, 2005). Schiff base compounds have been used as fine chemicals and medical substrates and they are important ligands in coordination chemistry (Rajavel *et al.*, 2008; Yu *et al.*, 2007). As part of our studies on the synthesis and characterization of pyrazoles containing Schiff base group, we report here the molecular and crystal structure of the title compound (Fig. 1).

Bond lengths and angles of the title molecule agree with those observed in a related compound, such as (*E*)-*N*-[(5-chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl) methylene]aniline (Sun *et al.*, 2007). The dihedral angle between the pyrazole ring (N1/N2/C1–C3) and the substituted phenyl ring (C6–C11) is 26.1 (2)°. The C5=N3 bond linking the two aromatic rings has an *E*-conformation. The angles between the conjugated linkage and the pyrazole ring (C1/C2/C3/N1/N2), and between the linkage and the substituted phenyl ring (C6–C11) are 6.3 (3)° and 38.5 (2)°, respectively.

Experimental

A solution of 5-chloro-3-methyl-1-phenyl-4-formyl-1*H*-pyrazole (5 mmol) and 4-chloroaniline (5 mmol) in ethanol (20 ml) was refluxed for 2 h. After cooling, filtration and drying, the title compound was obtained (yield: 84%, m.p. 434 K). The crystal used for data collection was obtained by slow evaporation from a saturated ethanol solution at room temperature.

Refinement

The H atoms were positioned geometrically with C—H = 0.93 Å for aromatic H and C—H = 0.96 Å for methyl H and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl C})$.

Figures

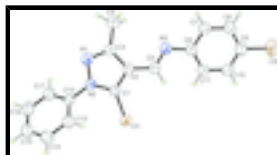


Fig. 1. The molecular structure of title compound with the atom numbering scheme. Displacement ellipsoids are drawn at 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

(*E*)-4-Chloro-*N*-[(5-chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methylene]aniline

Crystal data

C₁₇H₁₃Cl₂N₃

$M_r = 330.20$

$D_x = 1.399 \text{ Mg m}^{-3}$

Melting point: 434 K

supplementary materials

Orthorhombic, $Pca2_1$
Hall symbol: P 2c -2ac
 $a = 13.6471$ (6) Å
 $b = 15.6315$ (3) Å
 $c = 7.3514$ (6) Å
 $V = 1568.24$ (15) Å³
 $Z = 4$
 $F_{000} = 680.00$

Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 10504 reflections
 $\theta = 3.0$ – 27.4°
 $\mu = 0.41$ mm⁻¹
 $T = 296$ K
Plate, colourless
 $0.39 \times 0.34 \times 0.10$ mm

Data collection

Rigaku R-AXIS RAPID
diffractometer
Detector resolution: 10.00 pixels mm⁻¹
 $T = 296$ K
 ω scans
Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)
 $T_{\min} = 0.839$, $T_{\max} = 0.960$
14704 measured reflections

3558 independent reflections
2533 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 27.4^\circ$
 $h = -17 \rightarrow 17$
 $k = -20 \rightarrow 20$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.099$
 $S = 1.00$
3558 reflections
201 parameters
Primary atom site location: Direct
Secondary atom site location: Difmap
Hydrogen site location: Geom

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.089P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.21$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ e Å⁻³
Extinction correction: *SHELXL97* (Sheldrick, 2008)
Extinction coefficient: 0.0049 (8)
Absolute structure: Flack (1983), 1627 Friedel pairs
Flack parameter: -0.02 (6)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| C11 | 0.42986 (4) | 0.48323 (3) | 0.33646 (10) | 0.04844 (15) |
| C12 | 0.32167 (6) | -0.08853 (5) | 0.43233 (18) | 0.0893 (3) |
| N1 | 0.71398 (12) | 0.47004 (11) | 0.3343 (3) | 0.0478 (4) |
| N2 | 0.62562 (11) | 0.51191 (10) | 0.3340 (2) | 0.0391 (3) |
| N3 | 0.56891 (12) | 0.22175 (11) | 0.3631 (3) | 0.0480 (5) |
| C1 | 0.55095 (13) | 0.45498 (12) | 0.3464 (3) | 0.0395 (4) |
| C2 | 0.58944 (14) | 0.37384 (12) | 0.3577 (3) | 0.0411 (4) |
| C3 | 0.69251 (14) | 0.38699 (14) | 0.3490 (4) | 0.0452 (5) |
| C4 | 0.77319 (18) | 0.32253 (16) | 0.3538 (5) | 0.0629 (7) |
| C5 | 0.53181 (17) | 0.29634 (13) | 0.3730 (3) | 0.0446 (5) |
| C6 | 0.50557 (16) | 0.14994 (13) | 0.3773 (3) | 0.0436 (5) |
| C7 | 0.5429 (2) | 0.07657 (16) | 0.4568 (4) | 0.0565 (6) |
| C8 | 0.4858 (2) | 0.00375 (17) | 0.4763 (4) | 0.0624 (7) |
| C9 | 0.3916 (2) | 0.00400 (16) | 0.4118 (3) | 0.0539 (6) |
| C10 | 0.35333 (17) | 0.07546 (14) | 0.3280 (5) | 0.0548 (6) |
| C11 | 0.41003 (16) | 0.14831 (14) | 0.3120 (3) | 0.0490 (6) |
| C12 | 0.62388 (16) | 0.60273 (12) | 0.3108 (3) | 0.0393 (5) |
| C13 | 0.55665 (18) | 0.65294 (14) | 0.4025 (3) | 0.0467 (5) |
| C14 | 0.55583 (19) | 0.74051 (14) | 0.3718 (3) | 0.0539 (6) |
| C15 | 0.6222 (2) | 0.77754 (17) | 0.2553 (3) | 0.0558 (7) |
| C16 | 0.6905 (2) | 0.72688 (18) | 0.1672 (3) | 0.0550 (6) |
| C17 | 0.69122 (17) | 0.63883 (17) | 0.1930 (3) | 0.0467 (5) |
| H5 | 0.4646 | 0.3013 | 0.3909 | 0.054* |
| H7 | 0.6073 | 0.0761 | 0.4978 | 0.068* |
| H8 | 0.5111 | -0.0447 | 0.5326 | 0.075* |
| H10 | 0.2898 | 0.0746 | 0.2825 | 0.066* |
| H11 | 0.3840 | 0.1968 | 0.2569 | 0.059* |
| H13 | 0.5126 | 0.6284 | 0.4837 | 0.056* |
| H14 | 0.5098 | 0.7746 | 0.4307 | 0.065* |
| H15 | 0.6213 | 0.8363 | 0.2357 | 0.067* |
| H16 | 0.7363 | 0.7520 | 0.0901 | 0.066* |
| H17 | 0.7363 | 0.6047 | 0.1319 | 0.056* |
| H41 | 0.7578 | 0.2762 | 0.2731 | 0.076* |
| H42 | 0.7803 | 0.3010 | 0.4754 | 0.076* |
| H43 | 0.8333 | 0.3490 | 0.3160 | 0.076* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|-------------|-------------|-------------|--------------|-------------|
| C11 | 0.0317 (2) | 0.0431 (2) | 0.0705 (3) | -0.0001 (2) | 0.0023 (3) | 0.0004 (3) |
| C12 | 0.0752 (5) | 0.0612 (4) | 0.1317 (7) | -0.0261 (3) | 0.0065 (5) | 0.0141 (5) |
| N1 | 0.0334 (8) | 0.0459 (10) | 0.0642 (12) | -0.0012 (7) | -0.0001 (12) | 0.0000 (13) |
| N2 | 0.0288 (8) | 0.0372 (8) | 0.0513 (9) | -0.0004 (6) | 0.0006 (11) | 0.0029 (10) |
| N3 | 0.0417 (9) | 0.0363 (9) | 0.0659 (14) | -0.0003 (7) | -0.0003 (10) | 0.0005 (10) |

supplementary materials

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C1 | 0.0321 (9) | 0.0388 (9) | 0.0476 (11) | -0.0005 (8) | 0.0036 (12) | -0.0007 (12) |
| C2 | 0.0373 (10) | 0.0387 (10) | 0.0473 (12) | -0.0003 (8) | 0.0025 (11) | 0.0031 (11) |
| C3 | 0.0367 (10) | 0.0467 (11) | 0.0522 (12) | 0.0019 (8) | -0.0021 (12) | 0.0010 (12) |
| C4 | 0.0469 (13) | 0.0501 (13) | 0.092 (2) | 0.0085 (11) | -0.0008 (16) | 0.0068 (17) |
| C5 | 0.0400 (11) | 0.0424 (10) | 0.0515 (15) | -0.0033 (9) | 0.0034 (10) | 0.0036 (11) |
| C6 | 0.0409 (11) | 0.0384 (10) | 0.0515 (14) | 0.0015 (8) | 0.0012 (10) | 0.0010 (10) |
| C7 | 0.0449 (13) | 0.0452 (13) | 0.0795 (18) | -0.0018 (10) | -0.0114 (14) | 0.0083 (13) |
| C8 | 0.0650 (19) | 0.0426 (13) | 0.0795 (18) | -0.0026 (11) | -0.0083 (15) | 0.0170 (13) |
| C9 | 0.0514 (14) | 0.0456 (12) | 0.0647 (15) | -0.0067 (11) | 0.0055 (13) | 0.0008 (12) |
| C10 | 0.0360 (10) | 0.0501 (12) | 0.0782 (16) | 0.0023 (10) | -0.0013 (15) | -0.0023 (14) |
| C11 | 0.0445 (13) | 0.0371 (11) | 0.0656 (16) | 0.0045 (8) | -0.0004 (13) | 0.0010 (12) |
| C12 | 0.0353 (11) | 0.0362 (10) | 0.0463 (13) | -0.0054 (8) | -0.0049 (10) | -0.0002 (10) |
| C13 | 0.0462 (13) | 0.0439 (11) | 0.0501 (13) | -0.0043 (10) | 0.0019 (11) | -0.0011 (10) |
| C14 | 0.0535 (14) | 0.0424 (11) | 0.0658 (18) | 0.0032 (10) | -0.0061 (13) | -0.0073 (13) |
| C15 | 0.0620 (18) | 0.0413 (13) | 0.0642 (15) | -0.0111 (12) | -0.0165 (14) | 0.0050 (12) |
| C16 | 0.0493 (14) | 0.0580 (16) | 0.0578 (14) | -0.0171 (12) | -0.0065 (12) | 0.0147 (13) |
| C17 | 0.0377 (12) | 0.0513 (13) | 0.0510 (13) | -0.0063 (10) | -0.0009 (10) | 0.0039 (11) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|-----------|-------------|-------------|-----------|
| C11—C1 | 1.7121 (19) | C12—C17 | 1.383 (3) |
| C12—C9 | 1.740 (2) | C13—C14 | 1.387 (3) |
| N1—N2 | 1.372 (2) | C14—C15 | 1.375 (3) |
| N1—C3 | 1.335 (2) | C15—C16 | 1.384 (3) |
| N2—C1 | 1.356 (2) | C16—C17 | 1.389 (3) |
| N2—C12 | 1.430 (2) | C4—H41 | 0.960 |
| N3—C5 | 1.273 (2) | C4—H42 | 0.960 |
| N3—C6 | 1.421 (2) | C4—H43 | 0.960 |
| C1—C2 | 1.375 (2) | C5—H5 | 0.930 |
| C2—C3 | 1.423 (2) | C7—H7 | 0.930 |
| C2—C5 | 1.449 (3) | C8—H8 | 0.930 |
| C3—C4 | 1.493 (3) | C10—H10 | 0.930 |
| C6—C7 | 1.384 (3) | C11—H11 | 0.930 |
| C6—C11 | 1.390 (3) | C13—H13 | 0.930 |
| C7—C8 | 1.387 (3) | C14—H14 | 0.930 |
| C8—C9 | 1.370 (4) | C15—H15 | 0.930 |
| C9—C10 | 1.379 (3) | C16—H16 | 0.930 |
| C10—C11 | 1.382 (3) | C17—H17 | 0.930 |
| C12—C13 | 1.383 (3) | | |
| N2—N1—C3 | 105.73 (16) | C14—C15—C16 | 119.6 (2) |
| N1—N2—C1 | 110.32 (15) | C15—C16—C17 | 120.5 (2) |
| N1—N2—C12 | 119.23 (15) | C12—C17—C16 | 119.0 (2) |
| C1—N2—C12 | 130.32 (16) | C3—C4—H41 | 109.5 |
| C5—N3—C6 | 118.52 (18) | C3—C4—H42 | 109.5 |
| C11—C1—N2 | 123.59 (15) | C3—C4—H43 | 109.5 |
| C11—C1—C2 | 127.52 (15) | H41—C4—H42 | 109.5 |
| N2—C1—C2 | 108.80 (16) | H41—C4—H43 | 109.5 |
| C1—C2—C3 | 103.98 (18) | H42—C4—H43 | 109.5 |
| C1—C2—C5 | 124.65 (19) | N3—C5—H5 | 118.5 |

| | | | |
|---------------|-------------|-----------------|------------|
| C3—C2—C5 | 131.37 (19) | C2—C5—H5 | 118.5 |
| N1—C3—C2 | 111.16 (18) | C6—C7—H7 | 119.4 |
| N1—C3—C4 | 119.75 (19) | C8—C7—H7 | 119.4 |
| C2—C3—C4 | 129.1 (2) | C7—C8—H8 | 120.4 |
| N3—C5—C2 | 123.1 (2) | C9—C8—H8 | 120.4 |
| N3—C6—C7 | 117.5 (2) | C9—C10—H10 | 120.2 |
| N3—C6—C11 | 124.1 (2) | C11—C10—H10 | 120.2 |
| C7—C6—C11 | 118.4 (2) | C6—C11—H11 | 119.6 |
| C6—C7—C8 | 121.1 (2) | C10—C11—H11 | 119.6 |
| C7—C8—C9 | 119.3 (2) | C12—C13—H13 | 120.5 |
| C12—C9—C8 | 118.8 (2) | C14—C13—H13 | 120.5 |
| C12—C9—C10 | 120.3 (2) | C13—C14—H14 | 119.6 |
| C8—C9—C10 | 120.8 (2) | C15—C14—H14 | 119.6 |
| C9—C10—C11 | 119.6 (2) | C14—C15—H15 | 120.2 |
| C6—C11—C10 | 120.7 (2) | C16—C15—H15 | 120.2 |
| N2—C12—C13 | 121.07 (19) | C15—C16—H16 | 119.7 |
| N2—C12—C17 | 117.95 (19) | C17—C16—H16 | 119.7 |
| C13—C12—C17 | 121.0 (2) | C12—C17—H17 | 120.5 |
| C12—C13—C14 | 119.1 (2) | C16—C17—H17 | 120.5 |
| C13—C14—C15 | 120.8 (2) | | |
| N2—N1—C3—C2 | 0.2 (3) | C3—C2—C5—N3 | -7.3 (4) |
| N2—N1—C3—C4 | -179.9 (2) | C5—C2—C3—N1 | 179.7 (2) |
| C3—N1—N2—C1 | -0.7 (3) | C5—C2—C3—C4 | -0.2 (4) |
| C3—N1—N2—C12 | -177.0 (2) | N3—C6—C7—C8 | 179.8 (2) |
| N1—N2—C1—C11 | -176.0 (2) | N3—C6—C11—C10 | 178.9 (2) |
| N1—N2—C1—C2 | 0.8 (3) | C7—C6—C11—C10 | 0.7 (4) |
| N1—N2—C12—C13 | -143.5 (2) | C11—C6—C7—C8 | -1.9 (4) |
| N1—N2—C12—C17 | 36.8 (3) | C6—C7—C8—C9 | 1.6 (4) |
| C1—N2—C12—C13 | 41.0 (3) | C7—C8—C9—C12 | 178.5 (2) |
| C1—N2—C12—C17 | -138.7 (2) | C7—C8—C9—C10 | 0.1 (3) |
| C12—N2—C1—C11 | -0.2 (3) | C12—C9—C10—C11 | -179.7 (2) |
| C12—N2—C1—C2 | 176.6 (2) | C8—C9—C10—C11 | -1.3 (4) |
| C5—N3—C6—C7 | -147.9 (2) | C9—C10—C11—C6 | 0.9 (4) |
| C5—N3—C6—C11 | 33.9 (3) | N2—C12—C13—C14 | -178.2 (2) |
| C6—N3—C5—C2 | -179.1 (2) | N2—C12—C17—C16 | 179.6 (2) |
| C11—C1—C2—C3 | 176.1 (2) | C13—C12—C17—C16 | -0.1 (3) |
| C11—C1—C2—C5 | -3.4 (4) | C17—C12—C13—C14 | 1.5 (3) |
| N2—C1—C2—C3 | -0.6 (3) | C12—C13—C14—C15 | -1.6 (3) |
| N2—C1—C2—C5 | 179.87 (19) | C13—C14—C15—C16 | 0.2 (4) |
| C1—C2—C3—N1 | 0.2 (3) | C14—C15—C16—C17 | 1.2 (4) |
| C1—C2—C3—C4 | -179.6 (3) | C15—C16—C17—C12 | -1.3 (3) |
| C1—C2—C5—N3 | 172.0 (2) | | |

Fig. 1

