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5-Chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde: sheets built from C—H···O and C—H···π(arene) hydrogen bonds

Jorge Trilleras,[a] Jairo Quiroga,[a] Justo Cobo,[b] John N. Low[c] and Christopher Glidewell[d]*

[a]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [d]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.033
wR factor = 0.085
Data-to-parameter ratio = 16.7

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

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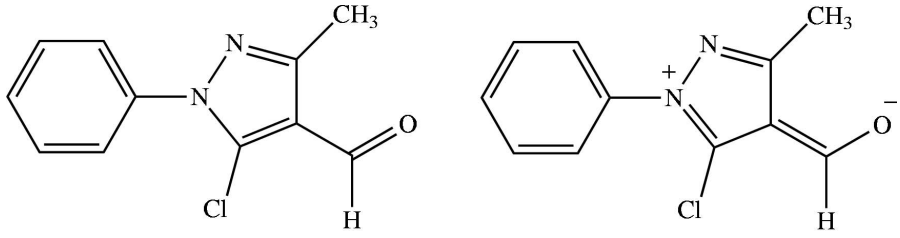
Molecules of the title compound, $C_{11}H_9ClN_2O$, are linked into sheets by a combination of one C—H···O hydrogen bond and one C—H···π(arene) hydrogen bond.

Comment

The title compound, (I), was prepared under Vilsmeyer conditions in which chlorination of C5 occurs in addition to the expected formylation, giving a versatile intermediate for the synthesis of fused pyrazolo heterocycles *via* cyclo-condensation reactions (Paul *et al.*, 2001).



(I) (I*a*)

The aldehydic fragment is almost coplanar with the adjacent pyrazole ring, but the two ring planes are inclined at 71.3 (2)° (Table 1). Within the pyrazolecarbaldehyde portion of the molecule, the bonds N1—C5 and C4—C41 are both short for their types (Allen *et al.*, 1987), while bonds C4—C5 and C41—O4 are both long for their types, suggesting some contribution to the overall molecular–electronic structure from the charge-separated form (I*a*) (see scheme).

The molecules of (I) are linked into sheets by a combination of one C—H···O hydrogen bond and one C—H···π(arene) hydrogen bond (Table 2); each of these hydrogen bonds

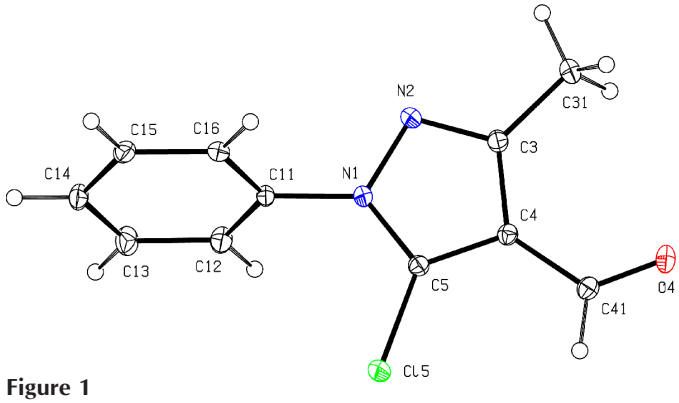


Figure 1
The molecule of compound (I), showing the atom-labelling scheme. For the sake of clarity, only one set of methyl H atoms is shown; displacement ellipsoids are drawn at the 30% probability level.

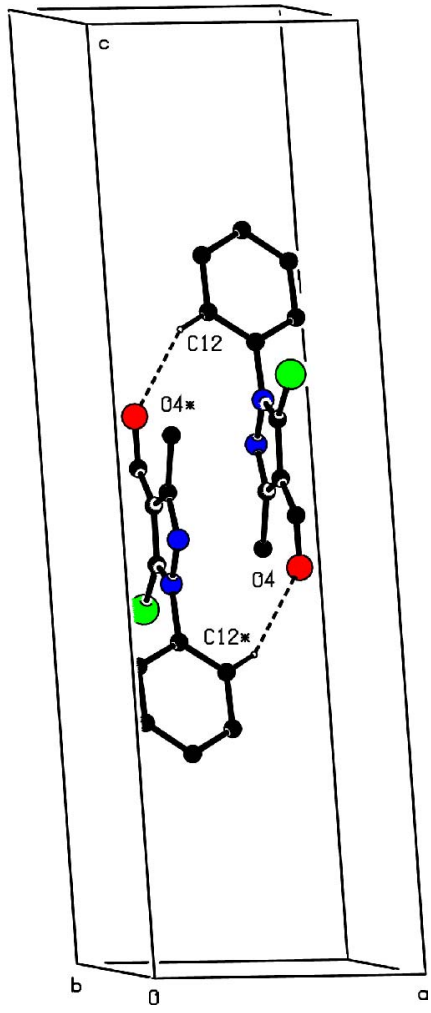


Figure 2
Part of the crystal structure of compound (I), showing the formation of an $R_2^2(16)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. For the sake of clarity, H atoms not involved in this motif have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

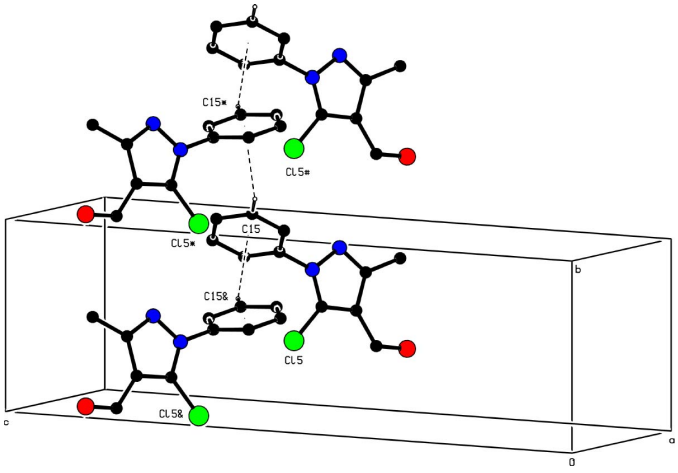


Figure 3
Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain along [010]. For the sake of clarity, H atoms not involved in this motif have been omitted. Atoms marked with an asterisk (*), a hash (#) or an ampersand (&) are at the symmetry positions $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $(x, 1 + y, z)$ and $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

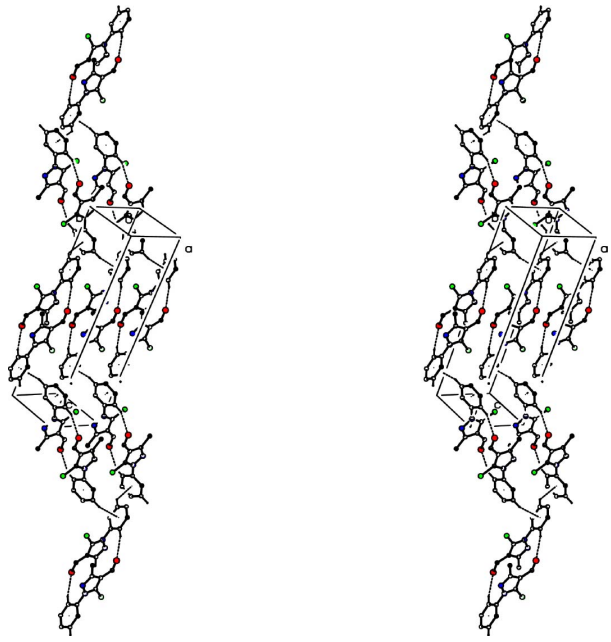


Figure 4
Stereoview of part of the crystal structure of compound (I), showing the formation of a $(10\bar{2})$ sheet. For the sake of clarity, H atoms not involved in these motifs have been omitted.

generates a characteristic simple substructure and the sheet formation is most readily analysed in terms of these two substructures. In the first substructure, aryl atom C12 in the molecule at (x, y, z) acts as hydrogen-bond donor to aldehydic atom O4 in the molecule at $(1 - x, 1 - y, 1 - z)$, so generating a centrosymmetric $R_2^2(16)$ ring (Bernstein *et al.*, 1995) centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). In the second substructure, aryl atom C15 in the molecule at (x, y, z) acts as hydrogen-bond donor to the ring C11–C16 in the molecule at $(2 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, so forming a chain running parallel to the [010] direction and generated by the 2_1 screw axis along $(1, y, \frac{3}{4})$ (Fig. 3). Each $R_2^2(16)$ dimer thus acts as a double donor and a double acceptor of C—H$\cdots\pi$(arene) hydrogen bonds, such that the dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ acts as donor to the dimers centred at $(\frac{3}{2}, 1, 1)$ and $(-\frac{1}{2}, 0, 0)$ and as acceptor from the dimers centred at $(\frac{3}{2}, 0, 1)$ and $(-\frac{1}{2}, 1, 0)$. In this manner, a sheet parallel to $(10\bar{2})$ is formed (Fig. 4); taking the $R_2^2(16)$ dimers as the nodes of the resulting net, this is then of (6,3)-type. However, there are no direction-specific interactions between adjacent sheets.

Experimental

For the preparation of (I), phosphoryl chloride (0.35 mol, 32 ml) was added dropwise to ice-cold dimethylformamide (0.16 mol, 12 ml). To this mixture was added 3-methyl-1-phenyl-5-pyrazolone (0.05 mol) and the reaction mixture was then heated under reflux for 1 h. After cooling, the reaction mixture was poured into ice-cold water (300 ml). The solid which precipitated was collected by filtration, washed with water, dried and recrystallized from ethanol to give pale-yellow crystals (m.p. 417 K) suitable for single-crystal X-ray diffraction (yield 90%). MS (70 eV) *m/z* (%): 221 (38), 222/220 (31/94, M^+), 77 (100), 51 (98).

Crystal data

$C_{11}H_9ClN_2O$	D_x = 1.468 Mg m^{-3}
M_r = 220.65	Mo Kα radiation
Monoclinic, $P2_1/c$	Cell parameters from 2291 reflections
a = 6.5683 (2) Å	θ = 3.1–27.5°
b = 6.7921 (2) Å	μ = 0.35 mm^{-1}
c = 22.4418 (6) Å	T = 120 (2) K
β = 94.206 (2)°	Lath, colourless
V = 998.49 (5) Å^3	0.42 × 0.24 × 0.10 mm
Z = 4	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	2291 independent reflections
φ and ω scans	1995 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	R_{int} = 0.031
T_{min} = 0.866, T_{max} = 0.966	θ_{max} = 27.5°
10 853 measured reflections	$h = -8 \rightarrow 8$
	$k = -8 \rightarrow 8$
	$l = -28 \rightarrow 29$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.5856P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.033	$(\Delta/\sigma)_{max}$ = 0.002
$wR(F^2)$ = 0.085	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
S = 1.02	$\Delta\rho_{min}$ = −0.25 e Å^{-3}
2289 reflections	Extinction correction: *SHELXL97*
137 parameters	Extinction coefficient: 0.011 (2)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.3759 (16)	N1—C11	1.4372 (17)
N2—C3	1.3276 (18)	C4—C41	1.4471 (19)
C3—C4	1.423 (2)	C41—O4	1.2239 (17)
C4—C5	1.3892 (18)	C5—Cl5	1.7009 (14)
C5—N1	1.3394 (18)		
N2—N1—C11—C12	109.18 (15)	C3—C4—C41—O4	0.0 (2)

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

Cg is the centroid of ring C11–C16.

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···O4^{i}	0.95	2.51	3.371 (2)	151
C15—H15···Cg^{ii}	0.95	2.72	3.498 (2)	140

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Two very low angle reflections ($\bar{2}02$) and (01) were omitted from the final refinement because of partial attenuation and/or extinction.All H atoms were located in difference maps and then treated as riding atoms, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic and aldehyde H atoms or C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. The methyl group was modelled using six H-atom sites, all with occupancy 0.5.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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