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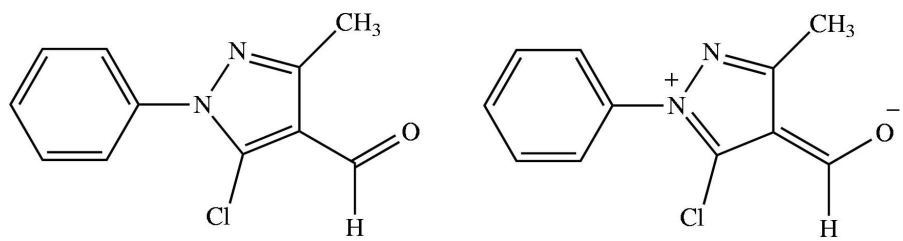
Molecules of the title compound, $C_{11}H_9ClN_2O$, are linked into sheets by a combination of one C—H···O hydrogen bond and one C—H···π(arene) hydrogen bond.

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

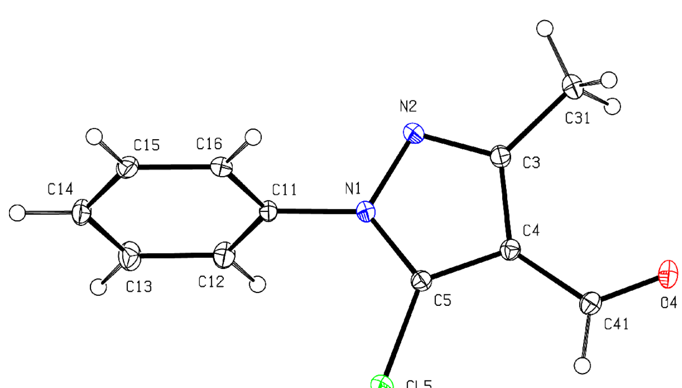


Figure 1
The molecule of compound (I), showing the atom-labelling scheme. For the sake of clarity, only one set of methyl H atoms is shown; displacement ellipsoids are drawn at the 30% probability level.

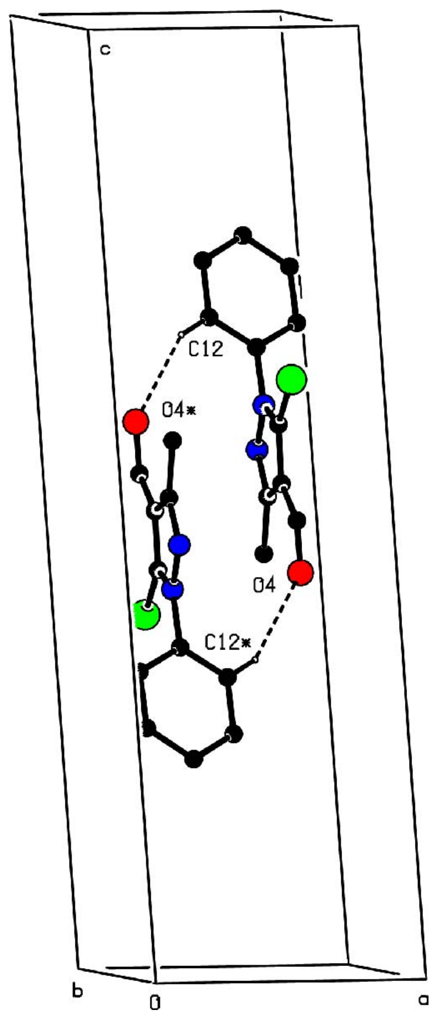


Figure 2
Part of the crystal structure of compound (I), showing the formation of an $R_2^2(16)$ ring centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). For the sake of clarity, H atoms not involved in this motif have been omitted. Atoms marked with an asterisk (*) are at the symmetry position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

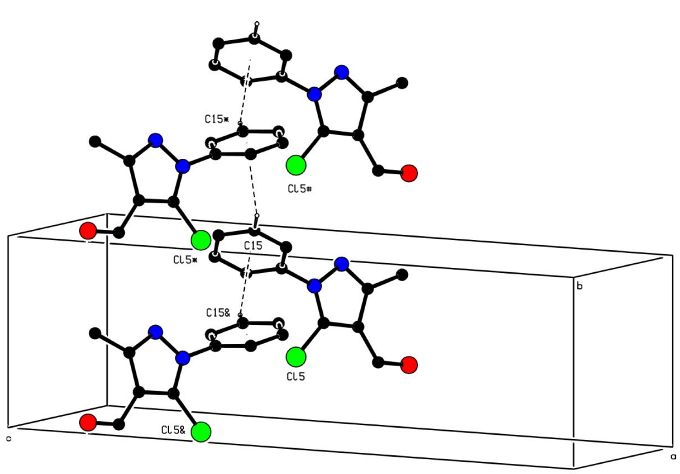


Figure 3
Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain along [010]. For the sake of clarity, H atoms not involved in this motif have been omitted. Atoms marked with an asterisk (*), a hash (#) or an ampersand (&) are at the symmetry positions $(1 - x,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

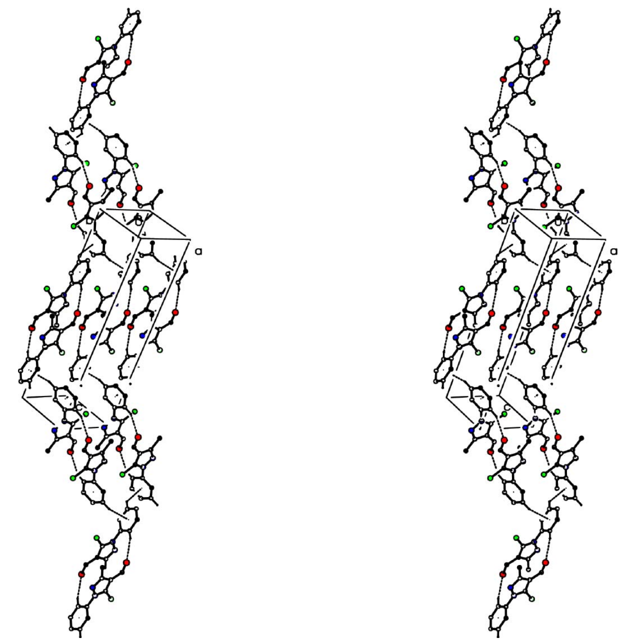


Figure 4
Stereoview of part of the crystal structure of compound (I), showing the formation of a $(10\bar{2})$ sheet. For the sake of clarity, H atoms not involved in these motifs have been omitted.

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

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

Data collection

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

Refinement

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

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).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England. JC thanks the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. JQ and HS thank COLCIENCIAS and UNIVALLE (Universidad del Valle, Colombia) for financial support.

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supporting information

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$V = 998.49$ (5) Å^3
$Z = 4$
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Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2291 reflections
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$T = 120$ K
Lath, colourless
0.42 × 0.24 × 0.10 mm

Data collection

Bruker–Nonius 95mm CCD camera on κ goniostat diffractometer
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Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
$T_{min} = 0.866$, $T_{max} = 0.966$
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2291 independent reflections
1995 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -28 \rightarrow 29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.085$
$S = 1.02$
2289 reflections
137 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.5856P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.011 (2)

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cl5	0.76255 (6)	0.36211 (5)	0.624349 (15)	0.02455 (13)	
O4	0.74674 (16)	0.36571 (16)	0.42194 (4)	0.0228 (2)	
N1	0.76095 (17)	0.73981 (17)	0.59171 (5)	0.0162 (3)	
N2	0.75951 (18)	0.86419 (18)	0.54330 (5)	0.0187 (3)	
C3	0.7526 (2)	0.7469 (2)	0.49587 (6)	0.0174 (3)	
C4	0.7505 (2)	0.5448 (2)	0.51250 (6)	0.0154 (3)	
C5	0.7562 (2)	0.5510 (2)	0.57448 (6)	0.0157 (3)	
C11	0.7702 (2)	0.8177 (2)	0.65140 (6)	0.0165 (3)	
C12	0.5997 (2)	0.8051 (2)	0.68381 (6)	0.0221 (3)	
C13	0.6118 (2)	0.8772 (2)	0.74201 (7)	0.0258 (3)	
C14	0.7905 (2)	0.9625 (2)	0.76634 (6)	0.0228 (3)	
C15	0.9595 (2)	0.9760 (2)	0.73277 (6)	0.0207 (3)	
C16	0.9504 (2)	0.9021 (2)	0.67492 (6)	0.0179 (3)	
C31	0.7486 (3)	0.8339 (2)	0.43451 (6)	0.0253 (3)	
C41	0.7478 (2)	0.3679 (2)	0.47649 (6)	0.0180 (3)	
H12	0.4767	0.7485	0.6667	0.026*	
H13	0.4968	0.8678	0.7652	0.031*	
H14	0.7976	1.0119	0.8060	0.027*	
H15	1.0815	1.0359	0.7494	0.025*	
H16	1.0659	0.9094	0.6519	0.022*	
H31A	0.7515	0.9778	0.4374	0.038*	0.50
H31B	0.6237	0.7925	0.4113	0.038*	0.50
H31C	0.8679	0.7882	0.4146	0.038*	0.50
H31D	0.7439	0.7279	0.4048	0.038*	0.50
H31E	0.8717	0.9132	0.4309	0.038*	0.50
H31F	0.6275	0.9174	0.4276	0.038*	0.50
H41	0.7467	0.2449	0.4966	0.022*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl5	0.0400 (2)	0.0170 (2)	0.01678 (19)	0.00039 (15)	0.00269 (14)	0.00238 (13)
O4	0.0258 (5)	0.0266 (6)	0.0159 (5)	−0.0007 (4)	0.0003 (4)	−0.0060 (4)
N1	0.0203 (6)	0.0159 (6)	0.0124 (5)	−0.0006 (5)	0.0009 (4)	0.0001 (4)
N2	0.0256 (6)	0.0164 (6)	0.0144 (5)	−0.0007 (5)	0.0022 (4)	0.0018 (4)
C3	0.0183 (7)	0.0189 (7)	0.0150 (6)	−0.0007 (6)	0.0018 (5)	−0.0009 (5)
C4	0.0140 (6)	0.0166 (7)	0.0156 (6)	−0.0009 (5)	0.0006 (5)	−0.0010 (5)
C5	0.0157 (6)	0.0158 (7)	0.0156 (6)	−0.0010 (5)	0.0008 (5)	0.0003 (5)
C11	0.0236 (7)	0.0138 (7)	0.0122 (6)	0.0010 (5)	0.0005 (5)	−0.0007 (5)
C12	0.0214 (7)	0.0251 (8)	0.0197 (7)	−0.0021 (6)	0.0020 (5)	−0.0049 (6)
C13	0.0263 (8)	0.0305 (9)	0.0216 (7)	0.0002 (7)	0.0081 (6)	−0.0053 (6)
C14	0.0324 (8)	0.0206 (8)	0.0153 (6)	0.0025 (6)	0.0013 (6)	−0.0048 (6)
C15	0.0262 (7)	0.0165 (7)	0.0185 (7)	−0.0022 (6)	−0.0040 (5)	−0.0002 (5)
C16	0.0221 (7)	0.0153 (7)	0.0165 (6)	−0.0008 (6)	0.0018 (5)	0.0022 (5)
C31	0.0374 (9)	0.0237 (8)	0.0149 (7)	−0.0008 (7)	0.0023 (6)	0.0009 (6)

C41	0.0166 (7)	0.0182 (7)	0.0192 (7)	−0.0006 (6)	0.0006 (5)	−0.0018 (5)

Geometric parameters (Å, º)

N1—N2	1.3759 (16)	C13—H13	0.95
N2—C3	1.3276 (18)	C14—C15	1.389 (2)
C3—C4	1.423 (2)	C14—H14	0.95
C4—C5	1.3892 (18)	C15—C16	1.3889 (19)
C5—N1	1.3394 (18)	C15—H15	0.95
N1—C11	1.4372 (17)	C16—H16	0.95
C4—C41	1.4471 (19)	C3—C31	1.4969 (19)
C41—O4	1.2239 (17)	C31—H31A	0.98
C5—Cl5	1.7009 (14)	C31—H31B	0.98
C11—C12	1.382 (2)	C31—H31C	0.98
C11—C16	1.385 (2)	C31—H31D	0.98
C12—C13	1.392 (2)	C31—H31E	0.98
C12—H12	0.95	C31—H31F	0.98
C13—C14	1.385 (2)	C41—H41	0.95
C5—N1—N2	111.17 (11)	C3—C31—H31C	109.5
C5—N1—C11	128.32 (11)	H31A—C31—H31C	109.5
N2—N1—C11	120.50 (11)	H31B—C31—H31C	109.5
C12—C11—C16	121.87 (13)	C3—C31—H31D	109.5
C12—C11—N1	119.16 (12)	H31A—C31—H31D	141.1
C16—C11—N1	118.97 (12)	H31B—C31—H31D	56.3
C11—C12—C13	118.65 (14)	H31C—C31—H31D	56.3
C11—C12—H12	120.7	C3—C31—H31E	109.5
C13—C12—H12	120.7	H31A—C31—H31E	56.3
C14—C13—C12	120.37 (14)	H31B—C31—H31E	141.1
C14—C13—H13	119.8	H31C—C31—H31E	56.3
C12—C13—H13	119.8	H31D—C31—H31E	109.5
C13—C14—C15	120.11 (13)	C3—C31—H31F	109.5
C13—C14—H14	119.9	H31A—C31—H31F	56.3
C15—C14—H14	119.9	H31B—C31—H31F	56.3
C16—C15—C14	120.11 (13)	H31C—C31—H31F	141.1
C16—C15—H15	119.9	H31D—C31—H31F	109.5
C14—C15—H15	119.9	H31E—C31—H31F	109.5
C11—C16—C15	118.88 (13)	C5—C4—C3	103.49 (12)
C11—C16—H16	120.6	C5—C4—C41	125.64 (13)
C15—C16—H16	120.6	C3—C4—C41	130.86 (12)
C3—N2—N1	105.22 (11)	O4—C41—C4	124.60 (13)
N2—C3—C4	111.66 (12)	O4—C41—H41	117.7
N2—C3—C31	119.86 (13)	C4—C41—H41	117.7
C4—C3—C31	128.48 (12)	N1—C5—C4	108.45 (12)
C3—C31—H31A	109.5	N1—C5—Cl5	122.23 (10)
C3—C31—H31B	109.5	C4—C5—Cl5	129.31 (11)
H31A—C31—H31B	109.5		

C5—N1—C11—C12	−72.01 (19)	N1—N2—C3—C31	179.84 (12)
N2—N1—C11—C12	109.18 (15)	N2—C3—C4—C5	0.17 (16)
C5—N1—C11—C16	107.61 (17)	C31—C3—C4—C5	180.00 (14)
N2—N1—C11—C16	−71.21 (17)	N2—C3—C4—C41	−178.57 (13)
C16—C11—C12—C13	−1.0 (2)	C31—C3—C4—C41	1.3 (2)
N1—C11—C12—C13	178.63 (13)	C5—C4—C41—O4	−178.50 (13)
C11—C12—C13—C14	1.1 (2)	C3—C4—C41—O4	0.0 (2)
C12—C13—C14—C15	−0.3 (2)	N2—N1—C5—C4	−0.25 (15)
C13—C14—C15—C16	−0.7 (2)	C11—N1—C5—C4	−179.15 (13)
C12—C11—C16—C15	0.1 (2)	N2—N1—C5—Cl5	178.44 (9)
N1—C11—C16—C15	−179.54 (12)	C11—N1—C5—Cl5	−0.5 (2)
C14—C15—C16—C11	0.8 (2)	C3—C4—C5—N1	0.05 (15)
C5—N1—N2—C3	0.35 (15)	C41—C4—C5—N1	178.88 (12)
C11—N1—N2—C3	179.35 (12)	C3—C4—C5—Cl5	−178.52 (11)
N1—N2—C3—C4	−0.31 (15)	C41—C4—C5—Cl5	0.3 (2)

Hydrogen-bond geometry (Å, º)

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) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+2, *y*+1/2, −*z*+3/2.