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Low-temperature crystal structure of 4-chloro-1*H*-pyrazole

Kelly Rue and Raphael G. Raptis*

Department of Chemistry and Biochemistry, 11200 SW 8th Street, Miami, FL 33199, USA. *Correspondence e-mail: rraptis@fiu.edu

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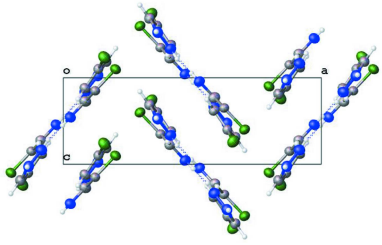
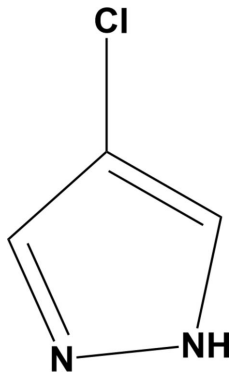
The structure of 4-chloro-1*H*-pyrazole, $C_3H_3ClN_2$, at 170 K has orthorhombic (*Pnma*) symmetry and is isostructural to its bromo analogue. Data were collected at low temperature since 4-chloro-1*H*-pyrazole sublimes when subjected to the localized heat produced by X-rays. The structure displays intermolecular N—H···N hydrogen bonding and the packing features a trimeric molecular assembly bisected by a mirror plane (*m* normal to *b*) running through one chlorine atom, one carbon atom and one N—N bond. The asymmetric unit therefore consists of one and one-half 4-chloro-1*H*-pyrazole molecules. Thus, the N—H proton is crystallographically disordered over two positions of 50% occupancy each.

1. Chemical context

Pyrazoles are a family of five-membered, π-excess aromatic heterocycles with adjacent nitrogen atoms (Krishnakumar *et al.*, 2011; Karrouchi *et al.*, 2018). They serve as scaffolds for numerous pharmaceutically active compounds and agrochemicals as they are stable and amenable to substitution (Naim *et al.*, 2016). They readily coordinate to metals, forming a large group of complexes where typically pyrazoles are monodentate or bridging bidentate pyrazolido ligands (Pettinari *et al.*, 2010; Viciano-Chumillas *et al.*, 2010). In the solid state, pyrazoles form hydrogen-bonded aggregates whose topology depends on the steric bulk of peripheral substituents and the acidity of the N1—H proton and basicity of the N2 atom. For example, 4-bromo-pyrazole and 3-methyl-pyrazole form approximately planar triangular assemblies (Foces-Foces *et al.*, 1999; Goddard *et al.*, 1999), 3,5-diphenyl-pyrazole and 3,5-bis(trifluoromethyl)pyrazole form tetranuclear assemblies (Raptis *et al.*, 1993; Alkorta *et al.*, 1999), while pyrazole forms a one-dimensional polymeric chain (Krebs Larsen *et al.*, 1970).





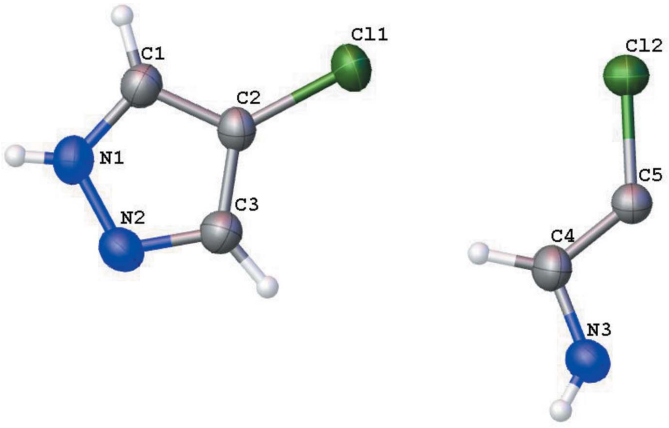


Figure 1
Perspective view of the asymmetric unit of 4-chloro-1*H*-pyrazole. Displacement ellipsoids are shown at 50% probability and half the disordered protons are removed for clarity.

2. Structural commentary

4-Chloro-1*H*-pyrazole crystallizes with one and one-half molecules in the asymmetric unit (Z' = 1.5) as shown in Fig. 1. The second molecule is bisected by a mirror plane normal to *b* (x, 3/4, z), which runs through C5, Cl2, and the N3—N3^{i} bond [symmetry code: (i) $x, \frac{1}{2} - y, z$]. As a result of this mirror plane, the NH protons are crystallographically disordered over two positions. As with the bromo analogue (Foces-Foces *et al.*, 1999), 4-chloro-1*H*-pyrazole crystallizes in the *Pnma* space group and forms trimeric units (Fig. 2).

Also disordered in this structure are the C and N atoms. Without disorder, pyrazoles have one 'pyrrole-like' side and one 'pyridine-like' side, as was discussed in the neutron diffraction study of 1*H*-pyrazole (Krebs Larsen *et al.*, 1970). The C—N, C—C, and C—H bonds on either side of the molecule are crystallographically distinct and resemble either pyrrole or pyridine. However, due to the disorder of the N—H protons in the current structure, only average positions of the C and N atoms have been obtained. Therefore, the C—N, C—C, and C—H bonds on either side of the molecule are indistinguishable. This is most apparent in the C—N bonds. In the current structure, the C—N bonds are 1.335 (2), 1.334 (2), and 1.334 (2) Å for C1—N1, C3—N2, and C4 —N3, respectively. In the 1*H*-pyrazole structure, the C—N bond lengths are 1.356 and 1.350 Å for the 'pyrrole-like' side and the 'pyridine-like' side, respectively. The C—N bond lengths of the current structure are in agreement with those previously reported in the 4-bromo analogue with C—N bond lengths of 1.343 (10), 1.331 (10), and 1.327 (10) Å (Foces-Foces *et al.*, 1999). Furthermore, these bond lengths are also in agreement with the 4-chloro-1*H*-pyrazol-2-ium chloride salt, which exhibits C—N bond lengths of 1.334 (2) and 1.331 (2) Å (Farmiloe *et al.*, 2019). The N—N bonds of the present molecule are 1.346 (2) and 1.345 (3) Å, for N1—N2 and N3—N3^{i}, respectively, and are similar to those of 4-methyl-1*H*-pyrazole (which is refined without proton disorder in $Pca2_1$) with N—N bond lengths of 1.343 (2), 1.344 (2), and 1.349 (2) Å (Goddard *et al.*, 1999). However, the N—N bonds of the 4-bromo analogue are slightly shorter at 1.335 (9) Å each (Foces-Foces *et al.*, 1999).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N1^{i}	0.88	2.03	2.885 (3)	165
N2—H2···N3^{ii}	0.88	1.99	2.8582 (19)	169
N3—H3A···N2^{ii}	0.88	1.99	2.8582 (19)	169

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

3. Supramolecular features

Pyrazoles are known to crystallize in a variety of hydrogen-bonded motifs – dimers, trimers, tetramers, and catemers (Infantes & Motherwell, 2004; Pérez & Riera, 2009). The current structure of 4-chloro-1*H*-pyrazole crystallizes in trimeric units, as do the 4-bromo and 4-methyl analogues. The intermolecular N1···N1^{i}, N2···N3^{ii}, and N3···N2^{ii} [symmetry codes: (i) $x, -y + \frac{3}{2}, z$; (ii) $-x + 1, -y + 1, -z$] are 2.885 (3), 2.858 (2), and 2.858 (2), respectively, as shown in Table 1.

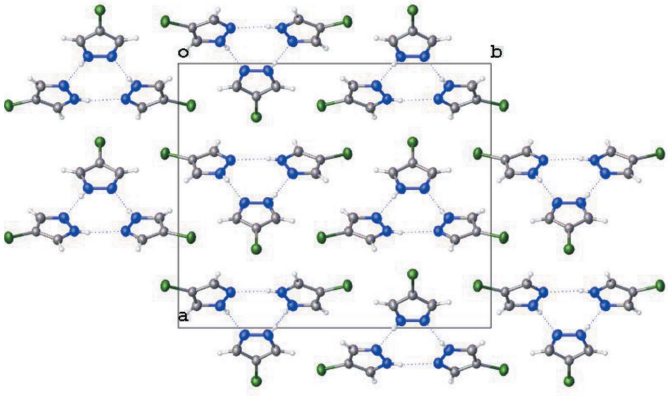


Figure 2
Packing of 4-chloro-1*H*-pyrazole, viewed parallel to the *c* axis, showing the formation of trimeric units. Half the disordered protons have been removed for clarity.

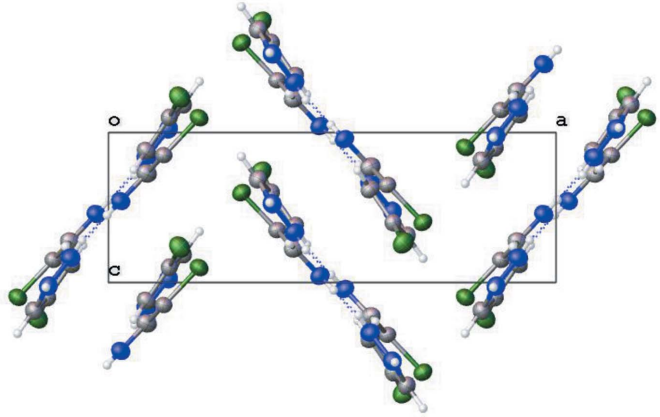


Figure 3
Packing of 4-chloro-1*H*-pyrazole, viewed parallel to the *b* axis, showing the formation of a herringbone motif.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_3H_3ClN_2$
M_r	102.52
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	170
a, *b*, *c* (Å)	14.9122 (10), 17.6410 (9), 4.9878 (3)
V (Å^3)	1312.13 (14)
Z	12
Radiation type	Mo *Kα*
μ (mm^{-1})	0.69
Crystal size (mm)	0.29 × 0.14 × 0.08
Data collection	
Diffractometer	Bruker D8 CMOS
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2019)
T_{min}, T_{max}	0.760, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25891, 1798, 1481
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.682
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.092, 1.06
No. of reflections	1798
No. of parameters	97
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.26

Computer programs: *APEX3* (Brker, 2020), *CrysAlis PRO* (Rigaku OD, 2019), *SHELXS* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), and *OLEX2* (Dolomanov *et al.*, 2009).

These values are in agreement with other intermolecular hydrogen-bond interactions of pyrazoles. Just as with the 4-bromo derivative, 4-chloro-1*H*-pyrazole packs in a herringbone arrangement when viewed down the *b* axis (Fig. 3). The current structure exhibits no π-stacking interactions.

4. Synthesis and crystallization

4-Chloro-1*H*-pyrazole was purchased commercially and crystals were grown from the slow evaporation of a methylene chloride solution.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The data were collected at 170 K on a Bruker D8 CMOS diffractometer equipped with a Photon II detector. *CrysAlis PRO* was used for scaling and absorption correction. All C—H protons were refined freely while the N—H protons were fixed using an AFIX command and constrained to half occupancy due to the proton disorder.

To remove the proton disorder, an attempt was made to refine the molecule in the non-centrosymmetric $Pn2_1a$ space group, which is also consistent with the systematic absences. In $Pn2_1a$, hydrogen atoms were refined in both possible positions – on the odd-labeled N atoms or on the even-labeled N atoms. However, as Foces-Foces *et al.* (1999) found with the 4-bromo-analogue, refinement in the lower symmetry space group did not improve the refinement. For the trial $Pn2_1a$ structure with protons on the even-labeled N atoms, the R_1 and wR_2 values slightly increased to 3.67% and 9.67%, respectively, and the shifting of the carbon atoms could not be consolidated. For the trial $Pn2_1a$ structure with protons on the odd-labeled N atoms, the R_1 and wR_2 values increased even more to 3.71% and 9.69%, respectively, and the coordinates of the non-protonated N atoms could not converge. Therefore, the best refined model was chosen to be in the centrosymmetric *Pnma* space group with NH protons disordered over two positions.

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Kelly Rue and Raphael G. Raptis

Computing details

Data collection: *APEX3* (Bruker, 2020); cell refinement: *CrysAlis PRO* (Rigaku OD, 2019); data reduction: *CrysAlis PRO* (Rigaku OD, 2019); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018*/3 (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

4-Chloro-1*H*-pyrazole

Crystal data

$C_3H_3ClN_2$
M_r = 102.52
Orthorhombic, *Pnma*
a = 14.9122 (10) Å
b = 17.6410 (9) Å
c = 4.9878 (3) Å
V = 1312.13 (14) Å^3
Z = 12
F(000) = 624
D_x = 1.557 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6701 reflections
θ = 2.3–30.2°
μ = 0.69 mm^{-1}
T = 170 K
Rect. Prism, clear colourless
0.28 × 0.14 × 0.08 mm

Data collection

Bruker D8 CMOS diffractometer
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2019)
T_{min} = 0.760, T_{max} = 1.000
25891 measured reflections
1798 independent reflections
1481 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 29.0°, θ_{min} = 2.3°
h = −20→20
k = −23→23
l = −6→6

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.092
S = 1.06
1798 reflections
97 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.5547P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.65912 (3)	0.45830 (2)	0.73672 (9)	0.04510 (15)	
C1	0.66638 (11)	0.61504 (9)	0.6893 (4)	0.0375 (3)	
C2	0.63595 (10)	0.54554 (8)	0.6008 (3)	0.0330 (3)	
N1	0.63427 (9)	0.66822 (7)	0.5248 (3)	0.0390 (3)	
H1A	0.644141	0.717242	0.538844	0.047*	0.5
C3	0.58468 (11)	0.56001 (10)	0.3776 (3)	0.0389 (4)	
N2	0.58435 (9)	0.63462 (8)	0.3340 (3)	0.0405 (3)	
H2	0.556236	0.657939	0.202649	0.049*	0.5
Cl2	0.70256 (4)	0.250000	0.59928 (11)	0.03892 (16)	
C5	0.62343 (15)	0.250000	0.3495 (4)	0.0326 (4)	
N3	0.52730 (9)	0.28813 (7)	0.0432 (3)	0.0395 (3)	
H3A	0.494432	0.317237	−0.061095	0.047*	0.5
C4	0.58543 (12)	0.31226 (10)	0.2276 (3)	0.0396 (4)	
H3	0.5571 (14)	0.5266 (11)	0.253 (4)	0.043 (5)*	
H1	0.7031 (12)	0.6279 (11)	0.839 (4)	0.040 (5)*	
H4	0.5962 (12)	0.3661 (12)	0.261 (4)	0.051 (6)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0525 (3)	0.0303 (2)	0.0525 (3)	0.00392 (16)	−0.00952 (19)	0.00342 (16)
C1	0.0379 (8)	0.0335 (8)	0.0412 (8)	−0.0017 (6)	−0.0027 (7)	−0.0020 (7)
C2	0.0340 (7)	0.0281 (7)	0.0371 (8)	0.0020 (6)	0.0008 (6)	−0.0006 (6)
N1	0.0408 (7)	0.0330 (6)	0.0431 (7)	−0.0007 (6)	0.0017 (6)	−0.0012 (6)
C3	0.0429 (9)	0.0345 (8)	0.0391 (8)	0.0028 (6)	−0.0053 (7)	−0.0032 (7)
N2	0.0450 (8)	0.0383 (7)	0.0384 (7)	0.0053 (6)	−0.0022 (6)	0.0028 (6)
Cl2	0.0416 (3)	0.0395 (3)	0.0356 (3)	0.000	−0.0053 (2)	0.000
C5	0.0359 (11)	0.0311 (10)	0.0309 (10)	0.000	−0.0011 (9)	0.000
N3	0.0432 (7)	0.0370 (7)	0.0384 (7)	0.0068 (6)	−0.0036 (6)	−0.0001 (6)
C4	0.0483 (10)	0.0306 (8)	0.0401 (8)	0.0052 (7)	−0.0035 (7)	−0.0040 (7)

Geometric parameters (Å, º)

Cl1—C2	1.7169 (15)	N2—H2	0.8800
C1—C2	1.380 (2)	Cl2—C5	1.716 (2)
C1—N1	1.335 (2)	C5—C4	1.377 (2)
C1—H1	0.952 (19)	C5—C4^{i}	1.377 (2)
C2—C3	1.374 (2)	N3—N3^{i}	1.345 (3)
N1—H1A	0.8800	N3—H3A	0.8800

N1—N2	1.3457 (19)	N3—C4	1.334 (2)
C3—N2	1.334 (2)	C4—H4	0.98 (2)
C3—H3	0.951 (19)		
C2—C1—H1	130.6 (11)	N1—N2—H2	125.7
N1—C1—C2	108.04 (14)	C3—N2—N1	108.50 (14)
N1—C1—H1	121.4 (11)	C3—N2—H2	125.7
C1—C2—Cl1	127.15 (13)	C4^{i}—C5—Cl2	127.11 (10)
C3—C2—Cl1	126.74 (12)	C4—C5—Cl2	127.11 (10)
C3—C2—C1	106.09 (14)	C4—C5—C4^{i}	105.8 (2)
C1—N1—H1A	125.6	N3^{i}—N3—H3A	125.7
C1—N1—N2	108.87 (13)	C4—N3—N3^{i}	108.61 (9)
N2—N1—H1A	125.6	C4—N3—H3A	125.7
C2—C3—H3	131.0 (12)	C5—C4—H4	129.2 (11)
N2—C3—C2	108.49 (15)	N3—C4—C5	108.50 (15)
N2—C3—H3	120.2 (12)	N3—C4—H4	122.3 (11)
Cl1—C2—C3—N2	−178.73 (13)	N1—C1—C2—Cl1	178.76 (12)
C1—C2—C3—N2	0.03 (19)	N1—C1—C2—C3	0.01 (18)
C1—N1—N2—C3	0.07 (18)	Cl2—C5—C4—N3	179.74 (15)
C2—C1—N1—N2	−0.05 (18)	N3^{i}—N3—C4—C5	−0.20 (16)
C2—C3—N2—N1	−0.06 (19)	C4^{i}—C5—C4—N3	0.3 (3)

Symmetry code: (i) *x*, −*y*+1/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N1^{ii}	0.88	2.03	2.885 (3)	165
N2—H2···N3^{iii}	0.88	1.99	2.8582 (19)	169
N3—H3*A*···N2^{iii}	0.88	1.99	2.8582 (19)	169

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