

5-Chloro-3-methyl-4-[3-(4-nitrophenyl)-4,5-dihydro-1H-pyrazol-5-yl]-1-phenyl-1H-pyrazole: a chain of fused hydrogen-bonded rings

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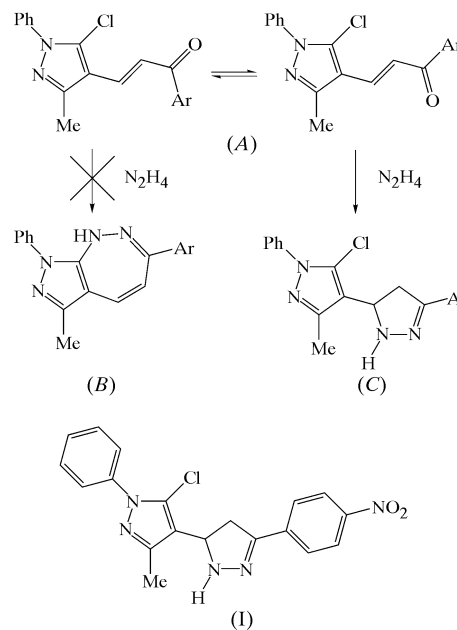
In the title compound, C₁₉H₁₆ClN₅O₂, the molecules are linked into chains of edge-fused rings by a combination of two independent C—H···O hydrogen bonds, augmented by a centrosymmetric π – π stacking interaction.

Comment

With the aim of preparing new classes of fused pyrazole systems such as pyrazolo[3,4-c][1,2]diazepines, we have investigated the reactions of hydrazine with chalcones, (A) (see scheme), such as (*E*)-3-(5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-(4-nitrophenyl)-2-propen-1-one, but instead of the expected condensation at the carbonyl group followed by nucleophilic displacement of the Cl to yield the pyrazolodiazepine, (B), we have observed a different cyclocondensation involving only the α,β -unsaturated component, yielding the unfused pyrazole, (C). We report here the structure of an example of type (C), *viz.* the title compound, (I).

The molecule of (I) contains two linked heterocyclic rings, namely a pyrazole ring (N11/N12/C13–C15), with chloro, methyl and phenyl substituents, and a dihydropyrazole ring (N21/N22/C23–C25), with a 4-nitrophenyl substituent (Fig. 1). The N11–N12 bond is shorter than the N21–N22 bond, while the N12–C13 bond is longer than the N22–C23 bond (Table 1), consistent with a degree of cyclic aromatic delocalization in the pyrazole ring. The dihydropyrazole ring adopts a non-planar conformation, with a modest fold across the vector N21···C24, with a total puckering amplitude (Cremer & Pople, 1975) of 0.263 Å. The ring-puckering parameter φ_2

for the atom sequence N21–N22–C23–C24–C25 is 327.0 (4)°, compared with a value of (36*n*)° for an idealized envelope conformation. While the 4-nitrophenyl ring and the mean plane of the dihydropyrazole ring are almost coplanar, with a dihedral between these planes of only 7.5 (2)°, the corresponding dihedral angle between the pyrazole ring and the unsubstituted phenyl ring is 68.3 (2)°. The dihedral angle between the mean planes of the heterocyclic rings is 74.5 (2)°.



The molecules of (I) are linked by two independent C—H···O hydrogen bonds (Table 2). Atom C25 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor to atom O232 in the molecule at (1 – *x*, 1 – *y*, 1 – *z*), so generating a centrosymmetric $R_2^2(20)$ (Bernstein *et al.*, 1995) ring centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). This dimeric motif is reinforced by an aromatic π – π stacking interaction. The nitrated phenyl rings in the molecules at (*x*, *y*, *z*) and (1 – *x*, 1 – *y*, 1 – *z*) are strictly parallel, with an interplanar spacing of 3.421 (2) Å. The corresponding ring-centroid separation is 3.678 (2) Å, with a nearly ideal ring offset of 1.351 (2) Å.

In addition, in a rather weak hydrogen bond, atom C126 in the molecule at (*x*, *y*, *z*) acts as donor to atom N12 in the molecule at (1 + *x*, *y*, *z*), so generating by translation a C(5)

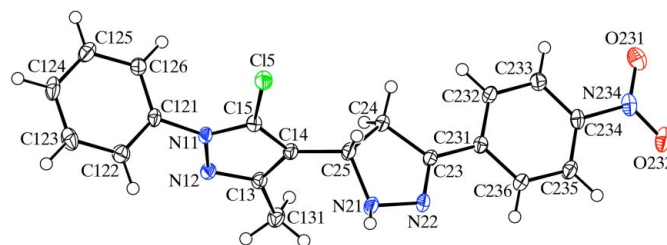
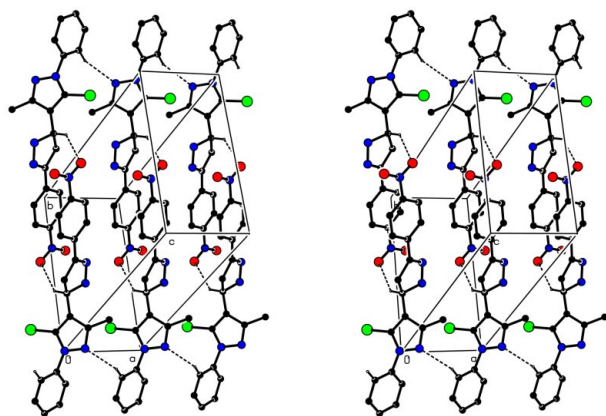


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.


Figure 2

A stereoview of part of the crystal structure of (I), showing the formation of a [100] chain of alternating $R_2^2(20)$ and $R_4^4(40)$ rings. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

chain running parallel to the [100] direction. The combination of the $R_2^2(20)$ and $C(5)$ motifs then generates a chain of edge-fused centrosymmetric rings running parallel to the [100] direction, with $R_2^2(20)$ rings centred at $(n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) and $R_4^4(40)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 2).

There are no direction-specific interactions between adjacent chains. It is noteworthy that the N—H bond plays no role in the intermolecular aggregation. The potential hydrogen-bond acceptors closest to atom N21 in the molecule at (x, y, z) are the O atoms in the molecule at $(1 - x, 1 - y, 1 - z)$, i.e. the other component of the $R_2^2(20)$ dimer, where the two relevant N...O distances are 3.477 (2) and 3.539 (2) Å, associated with H...O distances of 3.29 and 3.02 Å, respectively. Moreover, N—H... π (arene) hydrogen bonds are absent from the crystal structure of (I).

Experimental

Hydrazine hydrate (0.10 g of a 55% aqueous solution, 1.72 mmol) was added dropwise to a solution of (*E*)-3-(5-chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-1-(4-nitrophenyl)-2-propen-1-one (0.150 g, 0.428 mmol) in methanol (30 ml) and the mixture was stirred at room temperature for 15 min. The solid product was collected by filtration, washed with cold methanol and then recrystallized from methanol, giving crystals of (I) suitable for single-crystal X-ray diffraction (yield 84%; m.p. 455–456 K). MS (EI 30 eV), m/z (%): 383/381 (35/100, M^+), 346 (87, $M \pm \text{Cl}$), 330 (20), 77 (51).

Crystal data

$\text{C}_{19}\text{H}_{16}\text{ClN}_5\text{O}_2$
 $M_r = 381.82$
 Triclinic, $P\bar{1}$
 $a = 5.5055$ (2) Å
 $b = 11.8317$ (3) Å
 $c = 13.5668$ (4) Å
 $\alpha = 83.3210$ (17)°
 $\beta = 78.9560$ (17)°
 $\gamma = 86.3960$ (18)°
 $V = 860.73$ (5) Å³

$Z = 2$
 $D_x = 1.473$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3876 reflections
 $\theta = 3.1\text{--}27.5^\circ$
 $\mu = 0.25$ mm⁻¹
 $T = 120$ (2) K
 Block, yellow
 0.42 × 0.34 × 0.16 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\text{min}} = 0.928$, $T_{\text{max}} = 0.961$
 19351 measured reflections
 3950 independent reflections

3076 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 27.6^\circ$
 $h = -7 \rightarrow 7$
 $k = -15 \rightarrow 15$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.102$
 $S = 1.06$
 3950 reflections
 245 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.3277P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.34$ e Å⁻³

Table 1

Selected bond lengths (Å).

N11—N12	1.3681 (18)	N21—N22	1.3924 (19)
N12—C13	1.331 (2)	N22—C23	1.290 (2)
C13—C14	1.418 (2)	C23—C24	1.509 (2)
C14—C15	1.378 (2)	C24—C25	1.539 (2)
C15—N11	1.354 (2)	C25—N21	1.495 (2)

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C25—H25...O232 ⁱ	1.00	2.49	3.278 (2)	136
C126—H126...N12 ⁱⁱ	0.95	2.60	3.463 (2)	151

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

Crystals of compound (I) are triclinic. The space group $P\bar{1}$ was selected and confirmed by the successful structure analysis. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (aliphatic CH), and an N—H distance of 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$, or $1.5U_{\text{eq}}(\text{C})$ for the methyl group.

Data collection: COLLECT (Nonius, 1998); 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 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1888). Services for accessing these data are described at the back of the journal.

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