

(E)-1-[(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methylidene]-2-phenylhydrazine: sheets built from π -stacked hydrogen-bonded chains

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The reaction between 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde and phenylhydrazine proceeds *via* condensation to provide the title compound, C₁₇H₁₅ClN₄, (I), rather than *via* the alternative routes of simple nucleophilic substitution or cyclocondensation. With the exception of the phenyl group bonded directly to the pyrazole ring, the non-H atoms of (I) are nearly coplanar, with an r.m.s. deviation of 0.058 Å. The molecules are linked into *C*(7) chains by a single N—H···N hydrogen bond, and the chains are linked by π – π stacking interactions to form sheets.

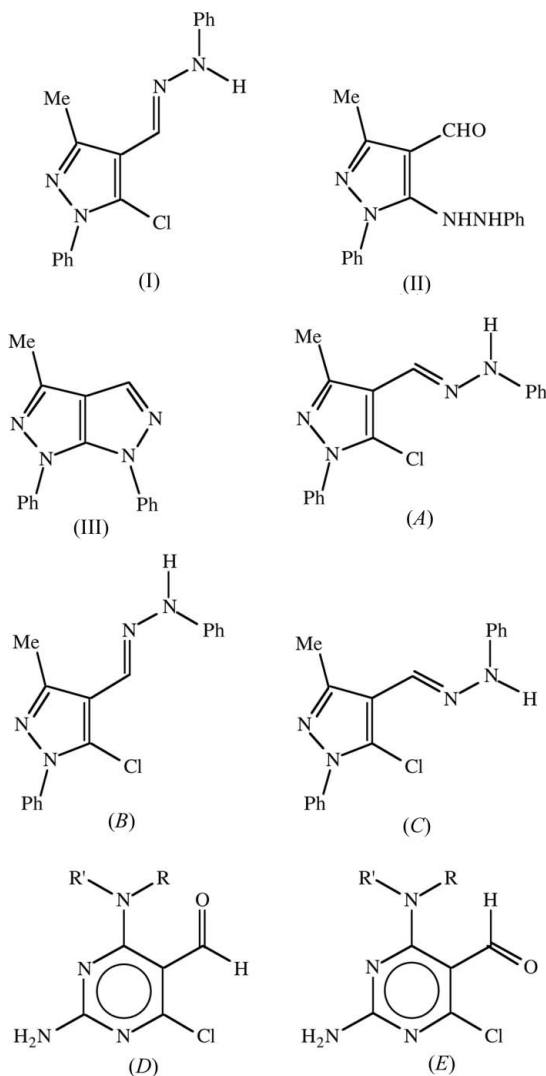
Keywords: crystal structure; π -stacked hydrogen-bonded chains; condensation reaction; phenylhydrazine derivative.

1. Introduction

Pyrazole rings are present in numerous natural products, as well as in synthetic pharmacophores with biological activity, and the structural diversity and biological importance of pyrazole derivatives have made them attractive targets for synthesis. Substituted 4-formylpyrazoles can be used as precursors in the synthesis of fused pyrazole systems, and it has been reported that nucleophilic displacement of chloro substituents by nucleophiles based on heteroatoms such as N, O or S can lead either to simple substitution or to intramolecular cyclization (Kaushik *et al.*, 2010; Maluleka & Mphahlele, 2013).

We report here the structure of (E)-1-[(5-chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methylidene]-2-phenylhydrazine, (I) (Fig. 1), which was prepared by the reaction between 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde and phenylhydrazine, where the reaction turns out to involve straightforward condensation to form compound (I), rather than

nucleophilic substitution to form a hydrazinopyrazole, (II) (see Scheme). No evidence was found for a cyclocondensation reaction, involving both condensation and substitution, which would lead to the formation of a pyrazolo[3,4-*b*]pyrazole derivative, (III) (see Scheme). This observation is consistent with our previous observation (Díaz *et al.*, 2010) of condensation rather than substitution in the reaction between 6-chloro-4-(4-chlorophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbaldehyde and benzene-1,2-diamine, whereas reactions between amines and chloropyrimidine-carbaldehydes reliably lead to substitution rather than condensation (Cobo *et al.*, 2008; Trilleras *et al.*, 2009).



2. Experimental

2.1. Synthesis and crystallization

A catalytic quantity of acetic acid was added to a solution of 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (221 mg, 1 mmol) and phenylhydrazine (108 mg, 1 mmol) in ethanol (5 ml), and this mixture was then heated under reflux for 2 h. The solution was allowed to cool to ambient temperature and the resulting solid product, (I), was collected by

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₁₇ H ₁₅ ClN ₄
<i>M_r</i>	310.78
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.773 (2), 9.9525 (18), 13.760 (3)
β (°)	114.519 (10)
<i>V</i> (Å ³)	1466.9 (5)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.26
Crystal size (mm)	0.36 × 0.33 × 0.21
Data collection	
Diffractometer	Bruker–Nonius KappaCCD diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)
<i>T_{min}</i> , <i>T_{max}</i>	0.901, 0.946
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	23842, 3355, 2305
<i>R_{int}</i>	0.087
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.053, 0.139, 1.04
No. of reflections	3355
No. of parameters	200
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.36, -0.49

Computer programs: *COLLECT* (Hooft, 1998), *DIRAX/LSQ* (Duisenberg *et al.*, 2000), *EVALCCD* (Duisenberg *et al.*, 2003), *SIR2004* (Burla *et al.*, 2005), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

filtration and washed with cold hexane (yield 63%, m.p. 452–455 K). MS (70 eV), *m/z*: 310 (*M*⁺), 275, 193, 132, 91, 77, 69, 51, 41. Yellow crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in the presence of air, of a solution in dimethylformamide–ethanol (3:7 *v/v*).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps and then treated as riding atoms. H atoms bonded to C atoms were permitted to ride in geometrically idealized positions, with C–H = 0.95 (aromatic and alkenic) or 0.98 Å (methyl) and $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for the methyl group, which was permitted to rotate but not to tilt, and 1.2 for the phenyl and alkenic groups. The H atom bonded to atom N42 was similarly permitted to ride, with an N–H distance of 0.88 Å and $U_{iso}(H) = 1.2U_{eq}(N)$.

3. Results and discussion

Within the pyrazole ring of compound (I), the N2–C3 and N1–C5 bond lengths differ by less than 0.04 Å (Table 2), despite the fact that these two bonds are formally double and single bonds, respectively; both these bonds are very significantly longer than the isolated N41=C41 double bond. Similarly, the C3–C4 and C4–C5 distances differ by less than 0.06 Å, although these two bonds are formally single and double bonds, respectively. These observations point to the

Table 2
Selected geometric parameters (Å, °).

N1–N2	1.373 (3)	C4–C5	1.379 (3)
N2–C3	1.328 (3)	C5–N1	1.363 (3)
C3–C4	1.424 (3)	C41–N41	1.289 (3)
N2–N1–C11–C12	–131.2 (2)	C41–N41–N42–C421	–176.2 (2)
C5–C4–C41–N41	176.9 (2)	N41–N42–C421–C422	–10.3 (3)
C4–C41–N41–N42	–175.5 (2)		

development of a significant degree of aromatic delocalization within the pyrazole ring.

Apart from the pendent phenyl ring (atoms C11–C16), the non-H atoms in the molecule of (I) do not deviate markedly from coplanarity; the maximum deviation from the mean plane of these atoms is exhibited by atom N42, whose deviation is 0.127 (2) Å, and the r.m.s. deviation is 0.058 Å. In addition, the dihedral angle between the planes of the pyrazole and terminal phenyl ring (atoms C421–C426) is only 1.9 (2)°, whereas that between the pyrazole and C11–C16 phenyl rings is 48.5 (2)°. The coplanarity, apart from the C11–C16 phenyl ring, is most plausibly associated with the π – π stacking interactions between inversion-related pairs of molecules, as discussed below, while the twist of the C11–C16 ring out of the plane of the rest of the molecule may be influenced by the contact between atoms C151 and H12, where the observed nonbonded distance in (I) of 2.94 Å is almost identical to the sum of the van der Waals radii (2.95 Å; Bondi, 1964; Rowland & Taylor, 1996). The molecules of (I) thus exhibit no internal symmetry, and hence they are conformationally chiral; however, the centrosymmetric space group confirms that equal numbers of the two conformational enantiomers are present in the crystal.

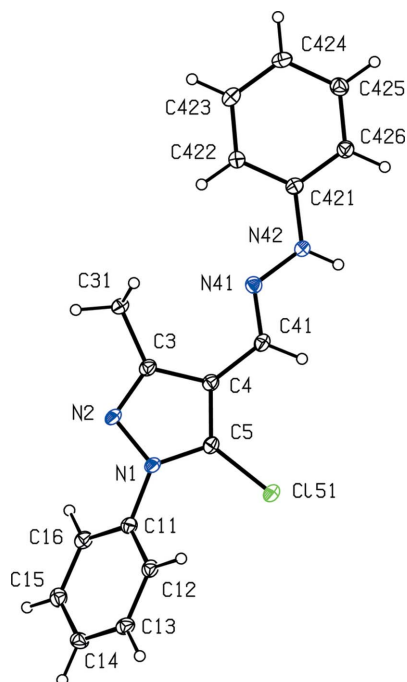


Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 3

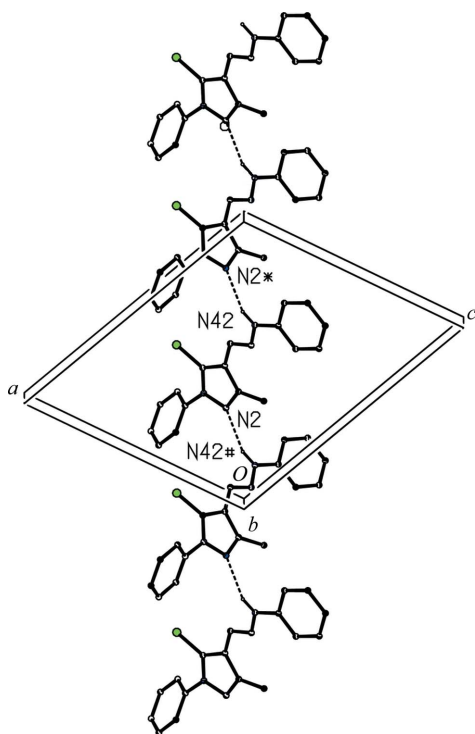
Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 represent the centroids of the C421–C426 and C11–C16 rings, respectively.

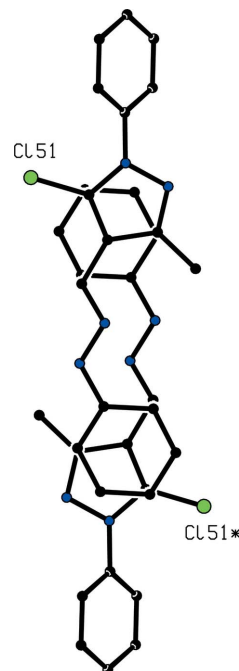
<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N42–H42···N2 ⁱ	0.88	2.26	3.100 (3)	159
C13–H13···Cg1 ⁱⁱ	0.95	2.73	3.392 (2)	127
C31–H31A···Cg2 ⁱⁱⁱ	0.98	2.92	3.373 (2)	109

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

It is of interest to consider what factors might be responsible for the adoption of the observed conformation for (I), as opposed to the other possible conformations, *viz.* (A)–(C) (see Scheme), which all have nearly planar skeletons, apart from the C11–C16 phenyl ring. The alternative orientation of the C=N unit relative to the C–Cl bond in forms (I) and (A) is reminiscent of the two alternative orientations (D) and (E) of the formyl group observed in an extended series of chloropyrimidine carbaldehydes (Cobo *et al.*, 2008). A number of factors were considered (Cobo *et al.*, 2008) as plausible contributors to the observation of these alternative conformations, and two of these factors, namely electrostatics and intermolecular hydrogen-bond formation, are relevant to the present example. It may be assumed that the C5–Cl51 bond is polarized, with the Cl atom carrying a partial negative charge; since in the imino unit atom N41 also carries a partial negative charge, the mutual repulsion of these charges favours forms (I)


Figure 2

Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded *C*(7) chain along [101]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$ and $(x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2})$, respectively.


Figure 3

Part of the crystal structure of compound (I), showing the π – π stacking interactions between a pair of inversion-related molecules. For the sake of clarity, the unit-cell outline and all H atoms have been omitted. The atom marked with an asterisk (*) is at the symmetry position $(-x + 1, -y + 1, -z + 1)$.

and (B) over forms (A) and (C). So far as hydrogen bonding is concerned, the formation of an intermolecular N–H···N hydrogen bond, as discussed below, is most likely to be the principal factor favouring the observed conformation (Fig. 1) over the alternative conformation, *i.e.* (B).

The supramolecular assembly of (I) is determined by a combination of an N–H···N hydrogen bond (Table 3) and a π – π stacking interaction. The N–H···N hydrogen bond links molecules related by the *n*-glide plane at $y = 0.25$ into a *C*(7) (Bernstein *et al.*, 1995) chain running parallel to the [101] direction, in which the two conformational enantiomorphs alternate (Fig. 2). Chains of this type are linked by π – π stacking interactions. In the pair of inversion-related molecules at (x, y, z) and $(-x + 1, -y + 1, -z + 1)$, the pyrazole ring of one molecule and the C421–C426 phenyl ring of the other are nearly parallel, with a dihedral angle between their planes of $1.9(2)^\circ$. The distance between the centroids of these two rings is $3.470(2)$ Å and the shortest perpendicular distance from the centroid of one ring to the plane of the other is $3.385(2)$ Å, giving a ring-centroid offset of *ca.* 1.13 Å. Hence, the molecules in each such pair are linked by two π – π stacking interactions (Fig. 3). The two molecules in the reference π -stacked pair at (x, y, z) and $(-x + 1, -y + 1, -z + 1)$ form parts, respectively, of the hydrogen-bonded chains across the *n*-glide planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. Similarly, the molecule at $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$, which lies in the chain across the *n*-glide plane at $y = \frac{1}{4}$, forms π – π stacking interactions with the molecule at $(-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2})$, which itself forms part of the hydrogen-bonded chain across the *n*-glide plane at $y = -\frac{1}{4}$. In

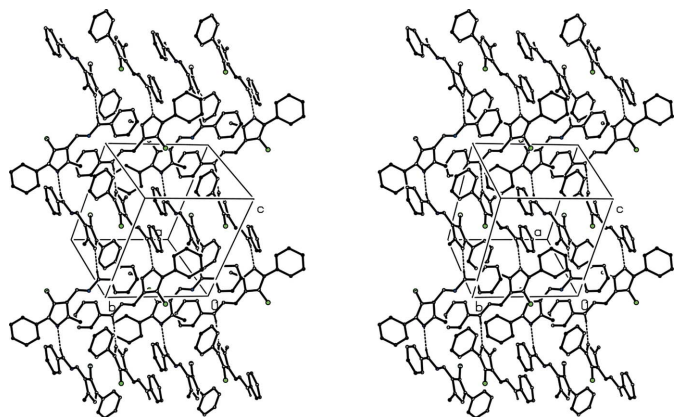


Figure 4

A stereoview of part of the crystal structure of compound (I), showing the formation of a π -stacked sheet of hydrogen-bonded chains. For the sake of clarity, H atoms bonded to C atoms have been omitted.

this way, the hydrogen-bonded chains parallel to [101] are linked into a π -stacked sheet lying parallel to (10 $\bar{1}$) (Fig. 4).

There are two further direction-specific intermolecular contacts, both of the C—H $\cdots\pi$ (arene) type (Table 3), which require comment. Both of these contacts have C—H \cdots (ring-centroid) angles which are less than 130° and, on this basis, neither is likely to be structurally significant (Wood *et al.*, 2009). In addition, the contact having the smaller D—H \cdots A angles also has a rather long H \cdots A distance and it involves one of the C—H bonds of the methyl group. When a methyl group, having local C_3 symmetry, is bonded to a planar ring, having approximate local C_2 symmetry, the resulting sixfold rotational barrier is extremely low, *i.e.* of the order of only a few $J\ mol^{-1}$ (Tannenbaum *et al.*, 1956; Naylor & Wilson, 1957), so that such a methyl group is likely to be undergoing very rapid rotation about the bond connecting the two entities in question, here the C3—C31 bond, even in the solid state at low temperatures (Riddell & Rogerson, 1996, 1997). Hence, we conclude that neither of the C—H $\cdots\pi$ (arene) contacts is structurally significant. Thus, although the C11—C16 phenyl rings lie at the ends of the π -stacked dimers (Fig. 3), they play no structural role, other than defining a lower bound for the axial approach of such dimers to one another (*cf.* Fig. 4). Perhaps surprisingly, imine-type atom N41 plays no role in the hydrogen-bonded assembly; the shortest intermolecular contacts involving this atom are to atom H12 at ($-x + 1, -y, -z + 1$), with an H \cdots N distance of 2.83 Å, well outside the

sum of the van der Waals radii, and to the associated atom C12 at ($-x + 1, -y, z + 1$), with a C \cdots N distance of 3.419 (3) Å, corresponding to a C—H \cdots N angle of only 121°. The long H \cdots N distance and the very small C—H \cdots N angle mean that this contact is not structurally significant (Wood *et al.*, 2009). There are no short intermolecular contacts involving the Cl atom.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3218). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2014). **C70**, 216-219 [doi:10.1107/S2053229614000680]

(*E*)-1-[(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methylidene]-2-phenylhydrazine: sheets built from π -stacked hydrogen-bonded chains

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Computing details

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

(*E*)-1-[(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methylidene]-2-phenylhydrazine

Crystal data

$C_{17}H_{15}ClN_4$	$F(000) = 648$
$M_r = 310.78$	$D_x = 1.407 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2yn	Cell parameters from 3355 reflections
$a = 11.773 (2) \text{ \AA}$	$\theta = 2.6\text{--}27.5^\circ$
$b = 9.9525 (18) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$c = 13.760 (3) \text{ \AA}$	$T = 120 \text{ K}$
$\beta = 114.519 (10)^\circ$	Block, yellow
$V = 1466.9 (5) \text{ \AA}^3$	$0.36 \times 0.33 \times 0.21 \text{ mm}$
$Z = 4$	

Data collection

Bruker–Nonius KappaCCD diffractometer	$T_{\min} = 0.901$, $T_{\max} = 0.946$
Radiation source: Bruker–Nonius FR591 rotating anode	23842 measured reflections
Graphite monochromator	3355 independent reflections
Detector resolution: $9.091 \text{ pixels mm}^{-1}$	2305 reflections with $I > 2\sigma(I)$
φ & ω scans	$R_{\text{int}} = 0.087$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.6^\circ$
	$h = -15 \rightarrow 15$
	$k = -12 \rightarrow 12$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.053$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.139$	H-atom parameters constrained
$S = 1.04$	
3355 reflections	
200 parameters	
0 restraints	

$$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 1.0139P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.48333 (18)	0.02131 (19)	0.30004 (15)	0.0219 (4)
N2	0.36968 (18)	0.0719 (2)	0.28775 (16)	0.0240 (5)
C3	0.3935 (2)	0.1558 (2)	0.36891 (19)	0.0235 (5)
C4	0.5236 (2)	0.1625 (2)	0.43589 (18)	0.0220 (5)
C5	0.5762 (2)	0.0749 (2)	0.38850 (18)	0.0225 (5)
C11	0.4900 (2)	-0.0694 (2)	0.22207 (18)	0.0226 (5)
C12	0.5563 (2)	-0.1895 (2)	0.25351 (19)	0.0241 (5)
H12	0.5999	-0.2106	0.3272	0.029*
C13	0.5580 (2)	-0.2777 (2)	0.1764 (2)	0.0265 (5)
H13	0.6041	-0.3590	0.1972	0.032*
C14	0.4930 (2)	-0.2481 (2)	0.06943 (19)	0.0266 (6)
H14	0.4937	-0.3097	0.0169	0.032*
C15	0.4265 (2)	-0.1286 (3)	0.03817 (19)	0.0269 (6)
H15	0.3820	-0.1083	-0.0355	0.032*
C16	0.4255 (2)	-0.0393 (2)	0.11489 (19)	0.0253 (5)
H16	0.3804	0.0426	0.0939	0.030*
C31	0.2907 (2)	0.2303 (3)	0.3812 (2)	0.0276 (6)
H31A	0.2107	0.2050	0.3234	0.041*
H31B	0.3039	0.3271	0.3781	0.041*
H31C	0.2897	0.2078	0.4502	0.041*
C41	0.5880 (2)	0.2501 (2)	0.52585 (18)	0.0235 (5)
H41	0.6765	0.2484	0.5613	0.028*
N41	0.52473 (19)	0.33070 (19)	0.55775 (15)	0.0231 (5)
N42	0.58770 (19)	0.4184 (2)	0.63754 (15)	0.0247 (5)
H42	0.6696	0.4234	0.6639	0.030*
C421	0.5209 (2)	0.5003 (2)	0.67712 (18)	0.0226 (5)
C422	0.3908 (2)	0.5105 (2)	0.62639 (18)	0.0243 (5)
H422	0.3456	0.4617	0.5626	0.029*
C423	0.3279 (2)	0.5922 (3)	0.6696 (2)	0.0281 (6)
H423	0.2395	0.5983	0.6351	0.034*
C424	0.3921 (2)	0.6649 (2)	0.7624 (2)	0.0282 (6)
H424	0.3485	0.7203	0.7917	0.034*
C425	0.5219 (2)	0.6551 (2)	0.8117 (2)	0.0278 (6)
H425	0.5671	0.7049	0.8750	0.033*
C426	0.5857 (2)	0.5736 (2)	0.76949 (19)	0.0248 (5)
H426	0.6741	0.5679	0.8040	0.030*
Cl51	0.73009 (5)	0.04036 (6)	0.42363 (5)	0.02856 (19)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0167 (10)	0.0229 (11)	0.0274 (10)	0.0005 (8)	0.0105 (8)	-0.0022 (8)
N2	0.0159 (10)	0.0279 (11)	0.0300 (11)	0.0021 (8)	0.0111 (9)	-0.0013 (9)

C3	0.0202 (12)	0.0233 (13)	0.0289 (13)	-0.0008 (10)	0.0122 (10)	0.0001 (10)
C4	0.0205 (12)	0.0223 (12)	0.0243 (12)	-0.0010 (10)	0.0105 (10)	0.0006 (9)
C5	0.0184 (12)	0.0240 (12)	0.0255 (12)	-0.0011 (10)	0.0093 (10)	0.0009 (10)
C11	0.0191 (12)	0.0234 (12)	0.0287 (13)	-0.0050 (10)	0.0133 (10)	-0.0040 (10)
C12	0.0199 (12)	0.0271 (13)	0.0260 (13)	-0.0017 (10)	0.0104 (10)	0.0001 (10)
C13	0.0237 (13)	0.0245 (13)	0.0359 (14)	-0.0017 (10)	0.0168 (11)	-0.0018 (11)
C14	0.0272 (14)	0.0294 (14)	0.0280 (13)	-0.0046 (11)	0.0161 (11)	-0.0062 (10)
C15	0.0236 (13)	0.0334 (14)	0.0248 (12)	-0.0043 (11)	0.0111 (11)	-0.0002 (10)
C16	0.0227 (12)	0.0241 (13)	0.0307 (13)	0.0004 (10)	0.0127 (11)	0.0017 (10)
C31	0.0204 (13)	0.0312 (14)	0.0324 (13)	0.0014 (11)	0.0122 (11)	-0.0062 (11)
C41	0.0180 (12)	0.0277 (13)	0.0247 (12)	0.0005 (10)	0.0089 (10)	0.0019 (10)
N41	0.0230 (11)	0.0244 (11)	0.0218 (10)	-0.0007 (9)	0.0092 (9)	-0.0003 (8)
N42	0.0184 (10)	0.0301 (11)	0.0253 (10)	0.0004 (9)	0.0089 (9)	-0.0054 (8)
C421	0.0231 (12)	0.0226 (12)	0.0239 (12)	0.0007 (10)	0.0116 (10)	0.0021 (9)
C422	0.0226 (12)	0.0255 (12)	0.0233 (12)	0.0006 (10)	0.0082 (10)	-0.0017 (10)
C423	0.0223 (13)	0.0295 (14)	0.0328 (14)	0.0042 (11)	0.0118 (11)	0.0040 (11)
C424	0.0280 (14)	0.0267 (13)	0.0349 (14)	0.0041 (11)	0.0182 (12)	-0.0013 (11)
C425	0.0290 (14)	0.0272 (13)	0.0288 (13)	-0.0035 (11)	0.0136 (11)	-0.0031 (10)
C426	0.0228 (13)	0.0270 (13)	0.0249 (12)	-0.0003 (10)	0.0101 (10)	-0.0002 (10)
CI51	0.0179 (3)	0.0327 (4)	0.0342 (3)	0.0014 (3)	0.0099 (3)	-0.0041 (3)

Geometric parameters (Å, °)

N1—N2	1.373 (3)	C31—H31A	0.9800
N1—C11	1.429 (3)	C31—H31B	0.9800
N2—C3	1.328 (3)	C31—H31C	0.9800
C3—C4	1.424 (3)	C41—N41	1.289 (3)
C3—C31	1.488 (3)	C41—H41	0.9500
C4—C5	1.379 (3)	N41—N42	1.357 (3)
C5—N1	1.363 (3)	N42—C421	1.391 (3)
C4—C41	1.445 (3)	N42—H42	0.8800
C5—CI51	1.705 (2)	C421—C426	1.387 (3)
C11—C16	1.383 (3)	C421—C422	1.399 (3)
C11—C12	1.395 (3)	C422—C423	1.388 (3)
C12—C13	1.384 (3)	C422—H422	0.9500
C12—H12	0.9500	C423—C424	1.387 (4)
C13—C14	1.379 (4)	C423—H423	0.9500
C13—H13	0.9500	C424—C425	1.394 (4)
C14—C15	1.391 (4)	C424—H424	0.9500
C14—H14	0.9500	C425—C426	1.386 (3)
C15—C16	1.384 (3)	C425—H425	0.9500
C15—H15	0.9500	C426—H426	0.9500
C16—H16	0.9500		
C5—N1—N2	110.27 (18)	C3—C31—H31A	109.5
C5—N1—C11	130.1 (2)	C3—C31—H31B	109.5
N2—N1—C11	119.58 (18)	H31A—C31—H31B	109.5
C3—N2—N1	105.78 (18)	C3—C31—H31C	109.5
N2—C3—C4	111.6 (2)	H31A—C31—H31C	109.5
N2—C3—C31	120.7 (2)	H31B—C31—H31C	109.5

C4—C3—C31	127.6 (2)	N41—C41—C4	119.7 (2)
C5—C4—C3	103.8 (2)	N41—C41—H41	120.1
C5—C4—C41	127.4 (2)	C4—C41—H41	120.1
C3—C4—C41	128.5 (2)	C41—N41—N42	118.5 (2)
N1—C5—C4	108.6 (2)	N41—N42—C421	119.1 (2)
N1—C5—C151	122.60 (18)	N41—N42—H42	120.5
C4—C5—C151	128.74 (19)	C421—N42—H42	120.5
C16—C11—C12	120.3 (2)	C426—C421—N42	118.8 (2)
C16—C11—N1	119.2 (2)	C426—C421—C422	119.4 (2)
C12—C11—N1	120.4 (2)	N42—C421—C422	121.8 (2)
C13—C12—C11	119.3 (2)	C423—C422—C421	119.8 (2)
C13—C12—H12	120.3	C423—C422—H422	120.1
C11—C12—H12	120.3	C421—C422—H422	120.1
C14—C13—C12	120.3 (2)	C424—C423—C422	121.1 (2)
C14—C13—H13	119.8	C424—C423—H423	119.5
C12—C13—H13	119.8	C422—C423—H423	119.5
C13—C14—C15	120.3 (2)	C423—C424—C425	118.7 (2)
C13—C14—H14	119.9	C423—C424—H424	120.6
C15—C14—H14	119.9	C425—C424—H424	120.6
C16—C15—C14	119.7 (2)	C426—C425—C424	120.8 (2)
C16—C15—H15	120.2	C426—C425—H425	119.6
C14—C15—H15	120.2	C424—C425—H425	119.6
C11—C16—C15	120.0 (2)	C425—C426—C421	120.3 (2)
C11—C16—H16	120.0	C425—C426—H426	119.9
C15—C16—H16	120.0	C421—C426—H426	119.9
C5—N1—N2—C3	-0.2 (3)	N1—C11—C12—C13	177.9 (2)
C11—N1—N2—C3	-177.6 (2)	C11—C12—C13—C14	-1.1 (4)
N1—N2—C3—C4	0.3 (3)	C12—C13—C14—C15	0.8 (4)
N1—N2—C3—C31	179.8 (2)	C13—C14—C15—C16	-0.2 (4)
N2—C3—C4—C5	-0.3 (3)	C12—C11—C16—C15	0.0 (4)
C31—C3—C4—C5	-179.8 (2)	N1—C11—C16—C15	-177.3 (2)
N2—C3—C4—C41	173.9 (2)	C14—C15—C16—C11	-0.2 (4)
C31—C3—C4—C41	-5.6 (4)	C5—C4—C41—N41	176.9 (2)
N2—N1—C5—C4	0.0 (3)	C3—C4—C41—N41	4.1 (4)
C11—N1—C5—C4	177.1 (2)	C4—C41—N41—N42	-175.5 (2)
N2—N1—C5—C151	-176.57 (16)	C41—N41—N42—C421	-176.2 (2)
C11—N1—C5—C151	0.5 (4)	N41—N42—C421—C426	169.6 (2)
C3—C4—C5—N1	0.1 (3)	N41—N42—C421—C422	-10.3 (3)
C41—C4—C5—N1	-174.1 (2)	C426—C421—C422—C423	-0.8 (4)
C3—C4—C5—C151	176.48 (19)	N42—C421—C422—C423	179.1 (2)
C41—C4—C5—C151	2.2 (4)	C421—C422—C423—C424	0.4 (4)
C5—N1—C11—C16	-130.8 (3)	C422—C423—C424—C425	0.3 (4)
N2—N1—C11—C16	46.0 (3)	C423—C424—C425—C426	-0.5 (4)
C5—N1—C11—C12	52.0 (3)	C424—C425—C426—C421	0.0 (4)
N2—N1—C11—C12	-131.2 (2)	N42—C421—C426—C425	-179.3 (2)
C16—C11—C12—C13	0.7 (4)	C422—C421—C426—C425	0.7 (4)

Hydrogen-bond geometry (Å, °)

*Cg*1 and *Cg*2 represent the centroids of the C421–C426 and C11–C16 rings, respectively.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N42—H42···N2 ⁱ	0.88	2.26	3.100 (3)	159
C13—H13··· <i>Cg</i> 1 ⁱⁱ	0.95	2.73	3.392 (2)	127
C31—H31 <i>A</i> ··· <i>Cg</i> 2 ⁱⁱⁱ	0.98	2.92	3.373 (2)	109

Symmetry codes: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $-x+1, -y, -z+1$; (iii) $-x+1/2, y+1/2, -z+1/2$.