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Conversion of substituted 5-aryloxypyrazole-carbaldehydes into reduced 3,4′-bipyrazoles: synthesis and characterization, and the structures of four precursors and two products, and their supramolecular assembly in zero, one and two dimensions

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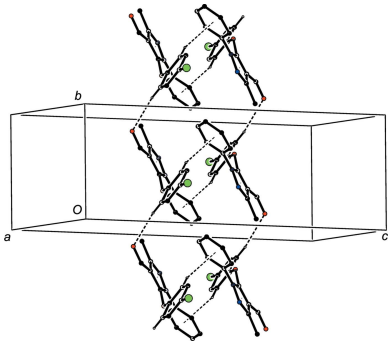
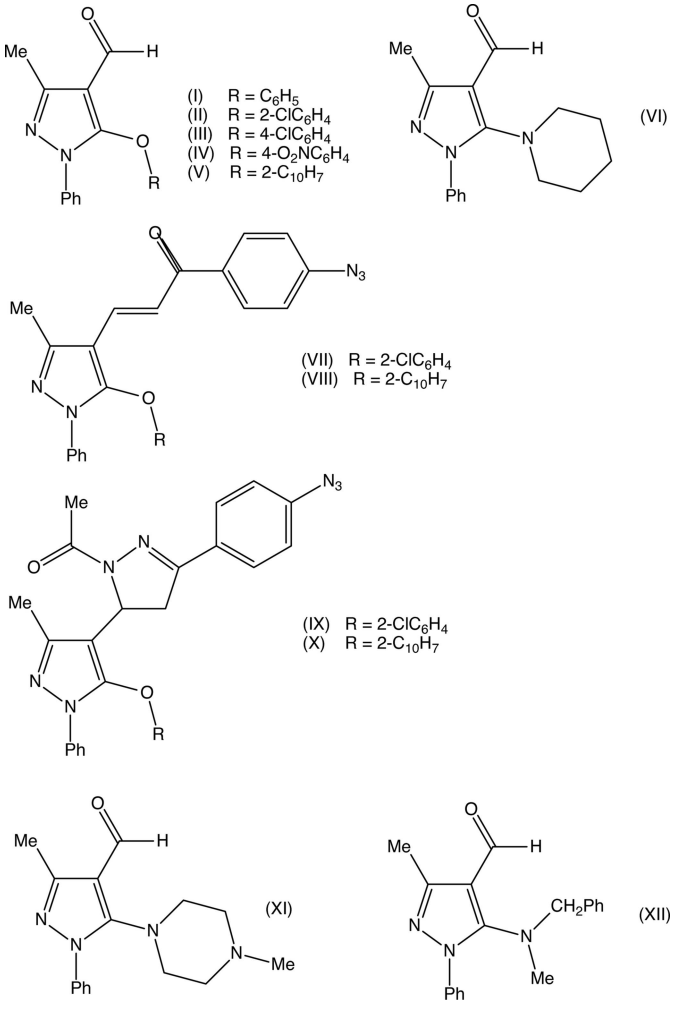
The reaction of 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde with phenols under basic conditions yields the corresponding 5-aryloxy derivatives; the subsequent reaction of these carbaldehydes with substituted acetophenones yields the corresponding chalcones, which in turn undergo cyclocondensation reactions with hydrazine in the presence of acetic acid to form *N*-acetylated reduced bipyrazoles. Structures are reported for three 5-aryloxycarbaldehydes and the 5-piperidino analogue, and for two reduced bipyrazole products. 5-(2-Chlorophenoxy)-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde, $C_{17}H_{13}ClN_2O_2$, (II), which crystallizes with $Z' = 2$ in the space group $P\overline{1}$, exhibits orientational disorder of the carbaldehyde group in each of the two independent molecules. Each of 3-methyl-5-(4-nitrophenoxy)-1-phenyl-1*H*-pyrazole-4-carbaldehyde, $C_{17}H_{13}N_3O_4$, (IV), 3-methyl-5-(naphthalen-2-yloxy)-1-phenyl-1*H*-pyrazole-4-carbaldehyde, $C_{21}H_{16}N_2O_2$, (V), and 3-methyl-1-phenyl-5-(piperidin-1-yl)-1*H*-pyrazole-4-carbaldehyde, $C_{16}H_{19}N_3O$, (VI), (3*RS*)-2-acetyl-5-(4-azidophenyl)-5′-(2-chlorophenoxy)-3′-methyl-1′-phenyl-3,4-dihydro-1′*H*,2*H*-[3,4′-bipyrazole] $C_{27}H_{22}ClN_7O_2$, (IX) and (3*RS*)-2-acetyl-5-(4-azidophenyl)-3′-methyl-5′-(naphthalen-2-yloxy)-1′-phenyl-3,4-dihydro-1′*H*,2*H*-[3,4′-bipyrazole] $C_{31}H_{25}N_7O_2$, (X), has $Z' = 1$, and each is fully ordered. The new compounds have all been fully characterized by analysis, namely IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. In each of (II), (V) and (IX), the molecules are linked into ribbons, generated respectively by combinations of C—H···N, C—H···π and C—Cl···π interactions in (II), C—H···O and C—H···π hydrogen bonds in (V), and C—H···N and C—H···O hydrogen bonds in (IX). The molecules of compounds (IV) and (IX) are both linked into sheets, by multiple C—H···O and C—H···π hydrogen bonds in (IV), and by two C—H···π hydrogen bonds in (IX). A single C—H···N hydrogen bond links the molecules of (X) into centrosymmetric dimers. Comparisons are made with the structures of some related compounds.



1. Introduction

Pyrazole derivatives exhibit a wide variety of biological activity, including antibacterial and antifungal activity (Satheesha Rai *et al.*, 2008; Isloor *et al.*, 2009; Vijesh *et al.*, 2013) and analgesic and anti-inflammatory activity (Girisha *et al.*, 2010; Isloor *et al.*, 2010; Vijesh *et al.*, 2013). In addition, the *N*-phenylpyrazole fragment is present in a number of drugs (Kramer, 2015; Alam *et al.*, 2016). As part of our programme

on the synthesis and structural characterization of pyrazole derivatives with potential biological activity, we report here the synthesis and structures of several 5-substituted 1-phenylpyrazole-4-carbaldehydes which have been used as precursors for the synthesis of reduced 3,4′-bipyrazoles, approached *via* the intermediate chalcones. Thus, we report the synthesis of the precursors (II), (IV), (V) and (VI), the chalcone intermediates (VII) and (VIII), and the bipyrazole products (IX) and (X), together with the structures of compounds (II), (IV)–(VI), (IX) and (X) (Scheme 1 and Figs. 1–6), which we compare with the recently reported structures of the related precursors (I) (Shahani *et al.*, 2011), (III) (Vinutha *et al.*, 2014; Glidewell *et al.*, 2019), (XI) (Sunitha *et al.*, 2016) and (XII) (Cuartas, *et al.*, 2017), and with those of a related intermediate



Scheme 1

chalcone and two reduced bipyridyl products (Cuartas *et al.*, 2017). The compounds were prepared by nucleophilic substitution of 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde with an amine or a phenol under basic conditions to yield the precursor carbaldehydes (I)–(VI); reaction of such a precursor with an acetyl compound produces chalcone intermediates (VII) and (VIII), cyclocondensation of which with hydrazine produces the reduced bipyrazole products (IX) and (X) (Scheme 1).

2. Experimental

2.1. Synthesis and crystallization

For the synthesis of the aryloxy derivatives (II), (IV) and (V), a mixture of 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (1.0 g, 4.5 mmol), the appropriate phenol (6.8 mmol) and solid potassium hydroxide (0.38 g, 6.8 mmol) in dimethyl sulfoxide (10 ml) was heated at 333 K for 6 h. The mixtures were then cooled to ambient temperature and poured onto crushed ice, after which the resulting solids were collected by filtration, washed with water and dried in air. Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation, at ambient temperature and in the presence of air, of solutions in ethanol. Compound (II): yield 79%, m.p. 364–366 K. Compound (IV): yield 68%, m.p. 378–379 K. Compound (V): yield 80%, m.p. 408–410 K.

For the synthesis of compound (VI), potassium carbonate (0.94 g, 6.8 mmol) was added to a well-stirred solution of piperidine (0.58 g, 6.8 mmol) in ethanol (25 ml) and stirring was continued for 30 min at ambient temperature. To this suspension, 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (1.0 g, 4.5 mmol) was added and the mixture was heated under reflux for 2 h. The mixture was cooled to ambient temperature and the excess solvent was removed under reduced pressure. The resulting solid was washed with cold water and recrystallized from ethanol to give crystals suitable for single-crystal X-ray diffraction (yield 68%, m.p. 385–387 K).

For the synthesis of the bipyrazoles (IX) and (X), the appropriate precursor [(II) for (IX) or (V) for (X)] (6.2 mmol) was added to a well-stirred solution of 4-azidoacetophenone (1.0 g, 6.2 mmol) and potassium hydroxide (0.34 g, 6.2 mmol) in ethanol (20 ml), and stirring was continued at ambient temperature for 30 min. The resulting solids were collected by filtration, washed with cold water and recrystallized from ethanol–dimethylformamide (3:1 *v*/*v*) to give the intermediates 1-(4-azidophenyl)-3-[5-(2-chlorophenoxy)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl]prop-2-en-1-one, (VII), and 1-(4-azidophenyl)-3-[5-(naphthalen-2-yloxy)-3-methyl-1-phenyl-1*H*-pyrazol-4-yl]prop-2-en-1-one, (VIII), respectively. Despite repeated attempts using a wide variety of solvents, we have been unable to grow crystals of compounds (VII) and (VIII) suitable for single-crystal X-ray diffraction. Compound (VII): yield 77%, m.p. 435–438 K. Compound (VIII): yield 74%, m.p. 489–490 K.

A mixture containing one of these chalcones (10 mmol) and hydrazine hydrate (15 mmol) in acetic acid (15 ml) was stirred overnight at 353 K, poured onto crushed ice (50 g) and allowed to warm to ambient temperature. The resulting solids were collected by filtration, dried in air and crystallized from ethanol–dimethylformamide (3:1 *v*/*v*) to give the products (IX) and (X); crystals suitable for single-crystal X-ray diffraction were selected directly from the prepared samples. Compound (IX): yield 72%, m.p. 412–414 K. Compound (X): yield, 68%, m.p. 452–453 K.

Full characterization data (analysis, IR, ^{1}H and ^{13}C NMR and mass spectrometry) are provided in the supporting information for compounds (II) and (IV)–(X).

Table 1
Experimental details.

Experiments were carried out at 296 K with Mo $K\alpha$ radiation using a Bruker APEXII CCD diffractometer. Absorption was corrected for by multi-scan methods (*SADABS*; Bruker, 2015). H-atom parameters were constrained.

	(II)	(IV)	(V)
Crystal data			
Chemical formula	$C_{17}H_{13}ClN_2O_2$	$C_{17}H_{13}N_3O_4$	$C_{21}H_{16}N_2O_2$
M_r	312.74	323.30	328.36
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a, b, c (Å)	10.3034 (4), 11.4856 (4), 14.4725 (5)	14.1163 (9), 11.7268 (7), 9.3982 (5)	7.7302 (6), 17.2550 (16), 13.1989 (11)
α, β, γ (°)	81.013 (2), 69.861 (2), 69.990 (2)	90, 94.259 (3), 90	90, 106.079 (2), 90
V (Å^3)	1509.47 (10)	1551.47 (16)	1691.7 (2)
Z	4	4	4
μ (mm^{-1})	0.26	0.10	0.08
Crystal size (mm)	0.19 × 0.16 × 0.13	0.20 × 0.15 × 0.15	0.20 × 0.16 × 0.14
Data collection			
T_{min}, T_{max}	0.902, 0.967	0.945, 0.985	0.954, 0.988
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35720, 6296, 4051	28186, 3956, 2361	34394, 4311, 2711
R_{int}	0.042	0.037	0.049
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.629	0.672	0.672
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.112, 1.03	0.043, 0.121, 1.01	0.047, 0.130, 1.03
No. of reflections	6296	3956	4311
No. of parameters	425	219	227
No. of restraints	2	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.26	0.19, −0.15	0.17, −0.25

	(VI)	(IX)	(X)
Crystal data			
Chemical formula	$C_{16}H_{19}N_3O$	$C_{27}H_{22}ClN_7O_2$	$C_{31}H_{25}N_7O_2$
M_r	269.34	511.97	527.58
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
a, b, c (Å)	8.9432 (7), 16.0546 (14), 10.1155 (8)	10.8804 (4), 11.3363 (4), 11.5737 (4)	10.4911 (11), 11.2048 (12), 13.5943 (17)
α, β, γ (°)	90, 97.777 (2), 90	97.294 (2), 90.050 (2), 117.840 (2)	105.323 (3), 93.505 (3), 117.460 (3)
V (Å^3)	1439.0 (2)	1249.15 (8)	1335.9 (3)
Z	4	2	2
μ (mm^{-1})	0.08	0.19	0.09
Crystal size (mm)	0.20 × 0.15 × 0.10	0.19 × 0.17 × 0.14	0.15 × 0.13 × 0.12
Data collection			
T_{min}, T_{max}	0.950, 0.992	0.930, 0.973	0.926, 0.990
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27358, 3000, 1869	31603, 5197, 3299	16901, 5470, 2883
R_{int}	0.047	0.044	0.038
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.629	0.629	0.629
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.141, 1.05	0.045, 0.126, 1.01	0.055, 0.178, 1.01
No. of reflections	3000	5197	5470
No. of parameters	183	336	363
No. of restraints	0	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.18	0.26, −0.26	0.25, −0.25

Computer programs: *APEX2* (Bruker, 2015), *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *PLATON* (Spek, 2009).

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 they were then treated as riding atoms in geometrically idealized positions, with C—H = 0.93 (aromatic and formyl), 0.96 (CH_3), 0.97 (CH_2) or 0.98 Å (aliphatic), and with U_{iso}(H) = kU_{eq}(C), where k = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms. Small numbers of low-angle reflections which had been attenuated by the beam stop [reflection 100 in each of (IV) and (IX), 010 in (II), 001 in (X) and 011 in (V)] were omitted from the final refinements. It was apparent from an early stage that in each of the two independent molecules of compound (II) the formyl group was disordered over two sets of atomic sites having unequal occupancies. For the minor-disorder component of each molecule, the bonded distances and the 1,3 nonbonded distances were restrained to be the same as the corresponding distances in the major form, subject

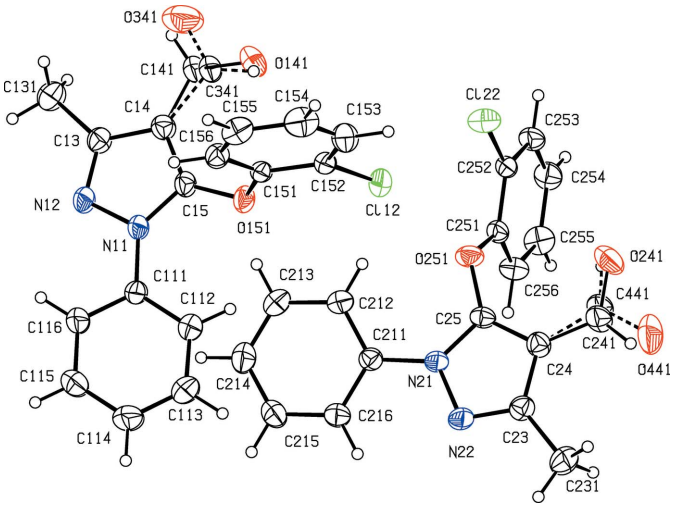


Figure 1
The structures of the two independent molecules in compound (II), showing the atom-labelling scheme and the disorder of the carbaldehyde groups. The major disorder components are drawn using full lines and the minor components are drawn using broken lines. Displacement ellipsoids are drawn at the 30% probability level.

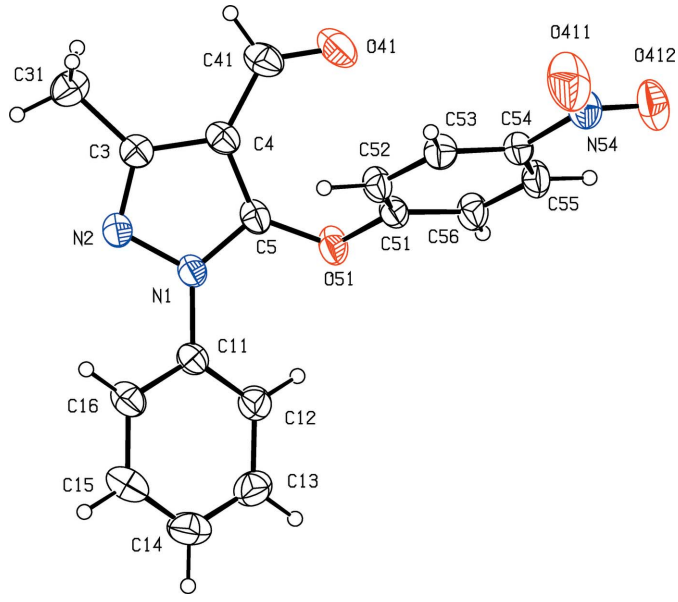


Figure 2
The molecular structure of compound (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

to s.u. values of 0.01 and 0.02 Å, respectively. In addition, the anisotropic displacement parameters for corresponding pairs of partial-occupancy formyl C-atom sites (C141/C341 and C241/C441) were constrained to be the same; subject to these conditions, the occupancies of the two sets of atomic sites refined to 0.682 (6) and 0.318 (6) in molecule 1, and to 0.536 (5) and 0.464 (5) in molecule 2.

3. Results and discussion

Compound (II) crystallizes with $Z' = 2$ in the space group $P\overline{1}$, but a search for possible additional symmetry revealed none; all of the other compounds discussed here crystallize with $Z' = 1$. In addition, both molecules in compound (II) exhibit orientation disorder of the carbaldehyde units, where the two disorder components are related by a rotation of *ca* 180° about the exocyclic C—C bonds (Fig. 1); in the crystal selected for data collection, the occupancies of the disorder components are 0.682 (6) and 0.318 (6) in the type 1 molecule containing atom N11, and 0.536 (5) and 0.464 (5) in the type 2 molecule containing atom N21. By contrast, the molecules in all of the other compounds considered here are fully ordered.

None of the compounds exhibits any internal symmetry, so that all of them are conformationally chiral, but the space groups (Table 1) confirm that all have crystallized as racemic mixtures. The reference molecules were selected such that all have the same sign for the torsion angle N*x*2—N*x*1—C*x*11—C*x*12, where *x* is 1 or 2 for compound (II), and nul otherwise. In addition, compounds (IX) and (X) both contain a stereogenic centre at atom C43 (Figs. 5 and 6), and in the selected reference molecules, this atom has the *S* configuration. In each of the products (IX) and (X), the reduced pyrazole ring is very slightly puckered out of planarity, with ring-puckering amplitudes (Cremer & Pople, 1975) of 0.120 (3) Å in (IX) and 0.094 (3) Å in (X), with ring conformations intermediate between the envelope and half-chair forms.

The two independent molecules of compound (II) are involved in entirely different types of hydrogen bonding (Table 2). Inversion-related pairs of type 1 molecules are linked by a pair of C—H···N hydrogen bonds to form a cyclic centrosymmetric dimer characterized by an $R_2^2(14)$ (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995) motif and centred at $(\frac{1}{2}, 0, 1)$. The type 2 molecules form a second type of centrosymmetric dimer containing inversion-related C—H···π(arene) hydrogen bonds and centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. These two hydrogen-bonded dimers are linked by a C—Cl···π(pyr-

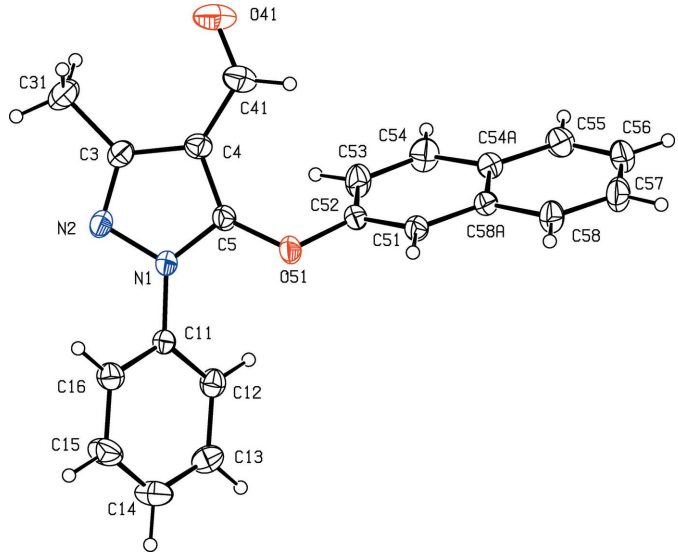


Figure 3
The molecular structure of compound (V), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

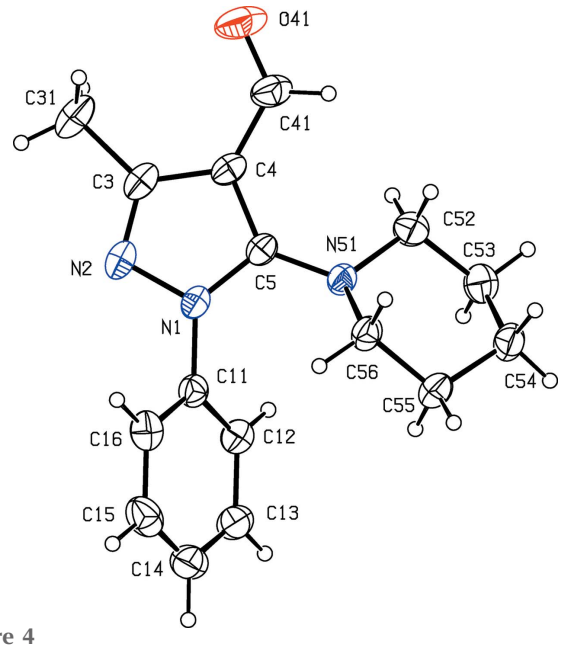


Figure 4
The molecular structure of compound (VI), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 2
Hydrogen-bond parameters (Å, °).

*Cg*1 represents the centroid of the C211–C216 ring, *Cg*2 the centroid of the C11–C16 ring and *Cg*3 the centroid of the N1/N2/C3–C5 ring.

Compound	D—H···A	D—H	H···A	D···A	D—H···A
(II)	C156—H156···N12^{i}	0.93	2.59	3.433 (3)	152
	C255—H255···*Cg*1^{ii}	0.93	2.80	3.635 (3)	140
(III)	C52—H52···O41^{iii}	0.93	2.59	3.509 (3)	171
	C56—H56···*Cg*2^{ii}	0.93	2.64	3.483 (3)	152
(IV)	C14—H14···O412^{iv}	0.93	2.57	3.330 (3)	139
	C52—H52···O41^{v}	0.93	2.53	3.456 (2)	174
	C55—H55···O411^{vi}	0.93	2.50	3.259 (3)	139
	C53—H53···*Cg*2^{vii}	0.93	2.84	3.564 (2)	135
(V)	C51—H51···O41^{viii}	0.93	2.50	3.386 (2)	160
	C12—H12···*Cg*3^{ii}	0.93	2.96	3.4804 (17)	117
	C53—H53···*Cg*2^{ii}	0.93	2.78	3.6477 (19)	155
(VI)	C15—H15···*Cg*3^{ix}	0.93	2.97	3.848 (3)	159
	C52—H52*A*···*Cg*2^{x}	0.97	2.96	3.761 (3)	140
(IX)	C14—H14···N451^{xi}	0.93	2.58	3.378 (5)	144
	C55—H55···O421^{xii}	0.93	2.59	3.228 (4)	126
(X)	C44—H44*A*···N2^{ii}	0.97	2.60	3.397 (4)	139

Symmetry codes: (i) $-x+1, y, -z+2$; (ii) $-x+1, -y+1, -z+1$; (iii) $x, y-1, z$; (iv) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (v) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (vi) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (vii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (viii) $x+1, y, z$; (ix) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (x) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (xi) $-x+1, -y+1, -z$; (xii) $-x+2, -y+2, -z+1$.

(pyrazole) interaction, where the Cl···centroid distance of 3.4275 (11) Å is somewhat shorter than the typical value of 3.6 Å (Imai *et al.*, 2008) found for C—Cl···π(arene) interactions. Propagation of these interactions by inversion and translation then generates a complex chain of rings running parallel to the [01$\bar{1}$] direction (Fig. 7).

The supramolecular assembly in compound (IV) takes the form of a complex sheet built from three independent C—H···O hydrogen bonds, together with a C—H···π(arene) hydrogen bond (Table 2), but the analysis of the assembly can be simplified by the identification of simple substructures (Ferguson *et al.*, 1998*a*,*b*; Gregson *et al.*, 2000). The hydrogen bond having atom C14 as the donor links molecules related by the 2_1 screw axis along ($\frac{1}{2}, y, \frac{1}{4}$) to form a *C*(14) chain running parallel to the [010] direction, and that having atom C55 as the donor links molecules related by the 2_1 screw axis along ($\frac{1}{2}, y, \frac{3}{4}$) into a *C*(5) chain, also running parallel to [010]. In combination, these two motifs give rise to a sheet of $R_4^4(34)$ rings lying parallel to (100) and spanning the entire domain $0 < x < 1$ (Fig. 8). A second sheet of this type, related to the first by inversion also spans the domain $0 < x < 1$, so that these two sheets are interwoven. The two sheets are linked into a bilayer structure by a chain-of-rings motif built from C—H···O and C—H···π(arene) hydrogen bonds and running parallel to the [001] direction (Fig. 9); however, there are no direction-specific interactions between adjacent bilayers, so that the supramolecular assembly is strictly two-dimensional.

The molecules of compound (V) are linked into a ribbon in the form of a chain of rings by a combination of C—H···O and

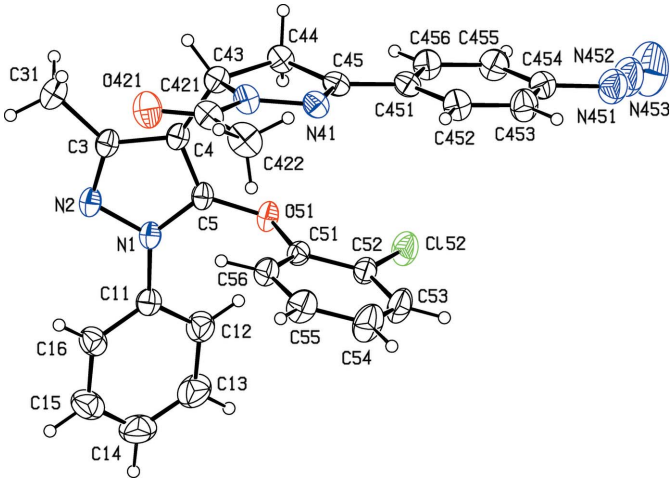


Figure 5
The molecular structure of compound (IX), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

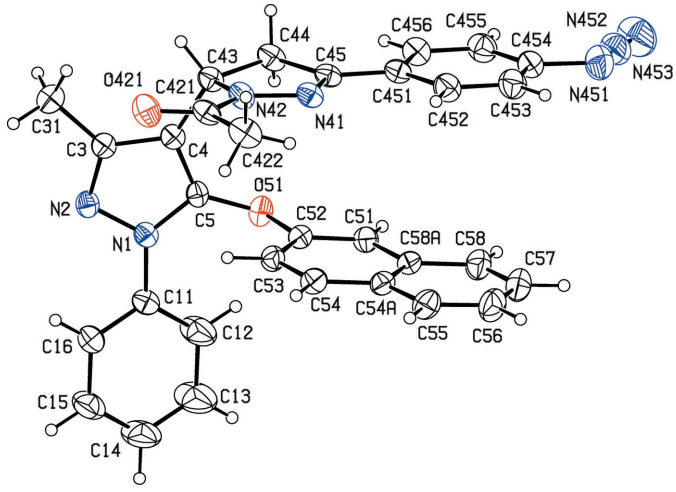


Figure 6
The molecular structure of compound (X), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

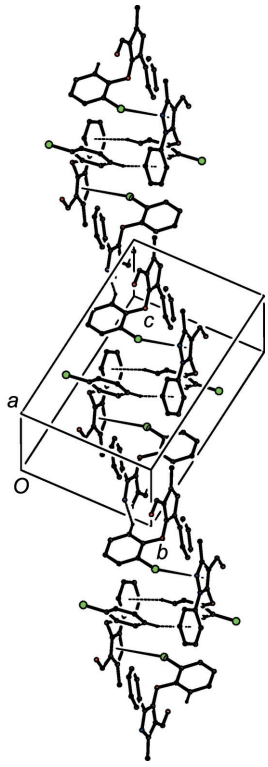


Figure 7
Part of the crystal structure of compound (II), showing the formation of a chain running parallel to the [01$\bar{1}$] direction and built from C—H···N and C—H···π(arene) hydrogen bonds and C—Cl···π(pyrazole) interactions. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

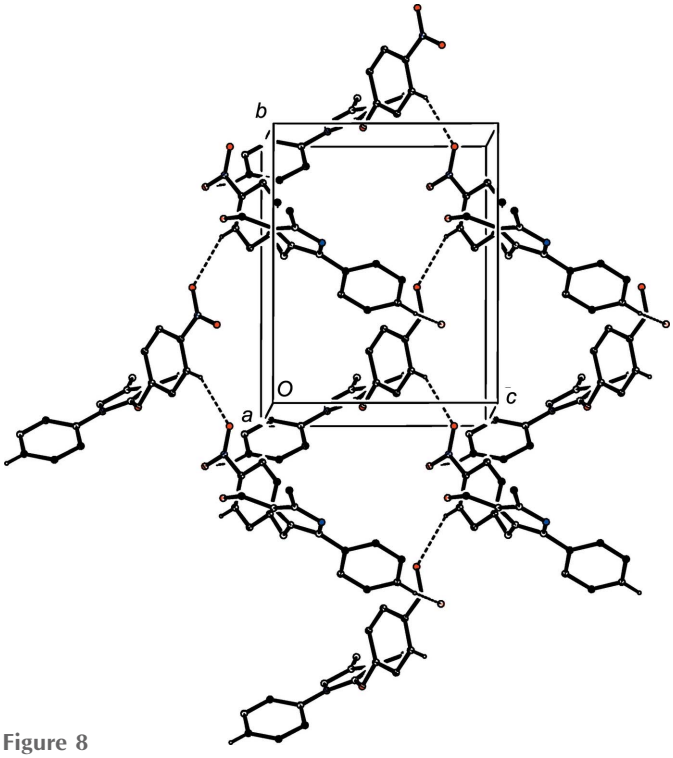


Figure 8
Part of the crystal structure of compound (IV), showing the formation of a sheet lying parallel to (100) and built from C—H···O hydrogen bonds. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

C—H···π(arene) hydrogen bonds (Table 2). Molecules related by translation are linked into $C(8)$ chains by the C—H···O hydrogen bonds, and inversion-related pairs of such chains are linked by the C—H···π(arene) hydrogen bond to form a chain of rings running parallel to the [100] direction (Fig. 10).

Two C—H···π hydrogen bonds, one having the pyrazole ring as the acceptor and the other having the *N*-phenyl ring as the acceptor, link the molecules of compound (VI) into sheets whose formation is readily analysed in terms of two one-dimensional (1D) substructures. Molecules related by the *n*-glide plane at $y = \frac{3}{4}$ are linked by the C—H···π(pyrazole) hydrogen bond to form a chain running parallel to the [101] direction, and molecules related by the 2_1 screw axis along $(\frac{1}{4}, y, \frac{3}{4})$ are linked by the C—H···π(arene) hydrogen bond to form a second chain, this time running parallel to the [010] direction. The combination of chains along [010] and [101] generates a sheet lying parallel to (10$\bar{1}$) (Fig. 11).

The structures of the reduced bipyrazoles (IX) and (X) contain no C—H···π hydrogen bonds. In compound (IX), a combination of C—H···N and C—H···O hydrogen bonds (Table 2) links the molecules into a chain of rings running parallel to [111] in which $R_2^2(22)$ rings containing C—H···O hydrogen bonds and centred at $(n, n, n - \frac{1}{2})$ alternate with $R_2^2(32)$ rings containing C—H···N hydrogen bonds and centred at $(n + \frac{1}{2}, n + \frac{1}{2}, n)$, where *n* represents an integer in each case (Fig. 12). By contrast, the very simple supra-

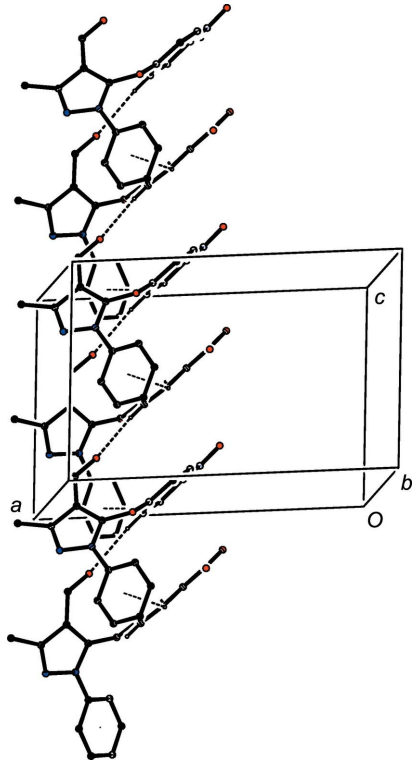


Figure 9
Part of the crystal structure of compound (IV), showing the formation of a chain of rings running parallel to [001] and built from C—H···O and C—H···π(arene) hydrogen bonds. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

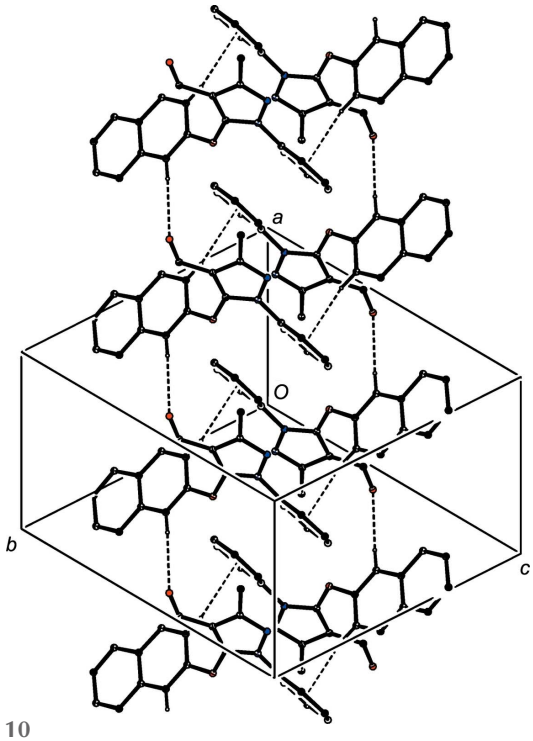


Figure 10
Part of the crystal structure of compound (V), showing the formation of a chain of rings running parallel to the [100] direction and built from C—H···O and C—H···π(arene) hydrogen bonds. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

molecular assembly in compound (X) is based on a single hydrogen bond of C—H···N type which links inversion-related pairs of molecules into centrosymmetric $R_2^2(12)$ dimers (Fig. 13).

Overall, therefore, the supramolecular assembly is finite, or zero-dimensional (0D), in compound (X), 1D in each of compounds (II), (V) and (IX), and two-dimensional (2D) in compounds (IV) and (VI).

It is worthwhile briefly comparing the supramolecular assembly in the compounds reported here with that in the structures of some related compounds. In the starting material 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde, inversion-related pairs of molecules are linked by paired C—H···O hydrogen bonds to form $R_2^2(16)$ dimers, which are linked into sheets by a C—H···π(arene) hydrogen bond (Trilleras *et al.*, 2005). 3-Methyl-5-phenoxy-1-phenyl-1*H*-pyrazole-4-carbaldehyde, (I) (see Scheme 1), can be regarded as the unsubstituted parent compound for the substituted compounds (II)–(V). Both C—H···N and C—H···O hydrogen bonds are absent from the structure, but inversion-related pairs of molecules are linked into centrosymmetric dimers by C—H···π(arene) hydrogen bonds (Shahani *et al.*, 2011).

The structure of 5-(4-chlorophenoxy)-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde, (III), has been reported recently (Vinutha *et al.*, 2014), but the structure description given was both sparse and incomplete. We have now taken the opportunity to redetermine this structure, using a rather larger data

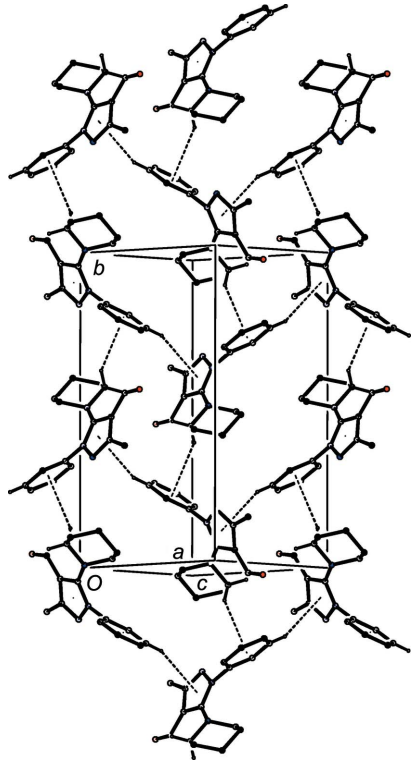


Figure 11
Part of the crystal structure of compound (VI), showing the formation of a sheet lying parallel to (10$\bar{1}$) and built from C—H···π(pyrazole) and C—H···π(arene) hydrogen bonds. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

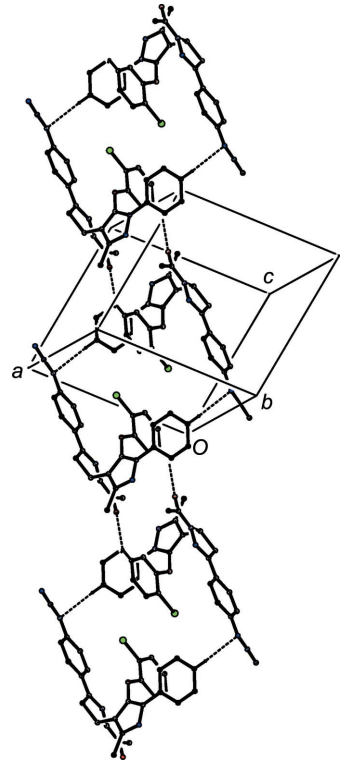


Figure 12
Part of the crystal structure of compound (IX), showing the formation of a chain of rings running parallel to the [111] direction and built from C—H···O and C—H···N hydrogen bonds. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

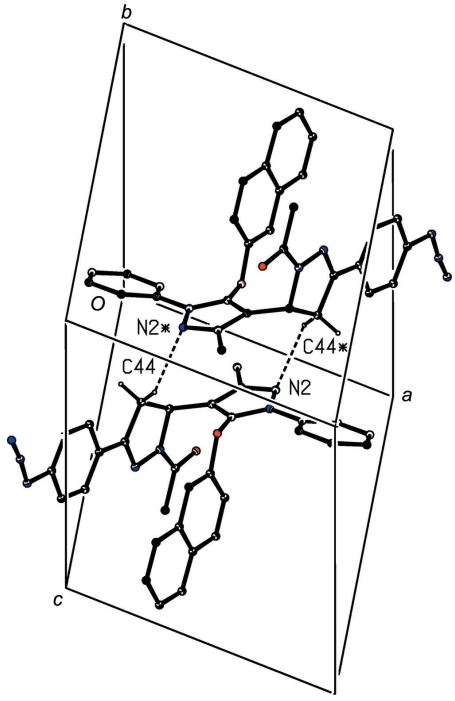


Figure 13
Part of the crystal structure of compound (X), showing the formation of a cyclic dimer. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($-x+1$, $-y+1$, $-z+1$).

set and it is this determination to which we now refer (Glidewell *et al.*, 2019). A combination of C—H···O and C—H···π(arene) hydrogen bonds links the molecules of (III) into a chain of rings running parallel to the [010] direction, in which centrosymmetric dimers built from C—H···π(arene) hydrogen bonds and centred at ($\frac{1}{2}$, $n+\frac{1}{2}$, $\frac{1}{2}$) alternate with centrosymmetric rings containing four hydrogen bonds, two each of

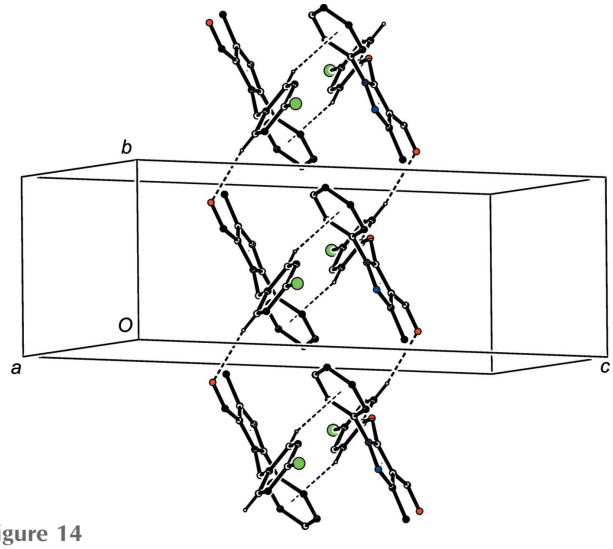


Figure 14
Part of the crystal structure of compound (III), showing the formation of a chain of rings running parallel to the [010] direction and built from C—H···O and C—H···π(arene) hydrogen bonds. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

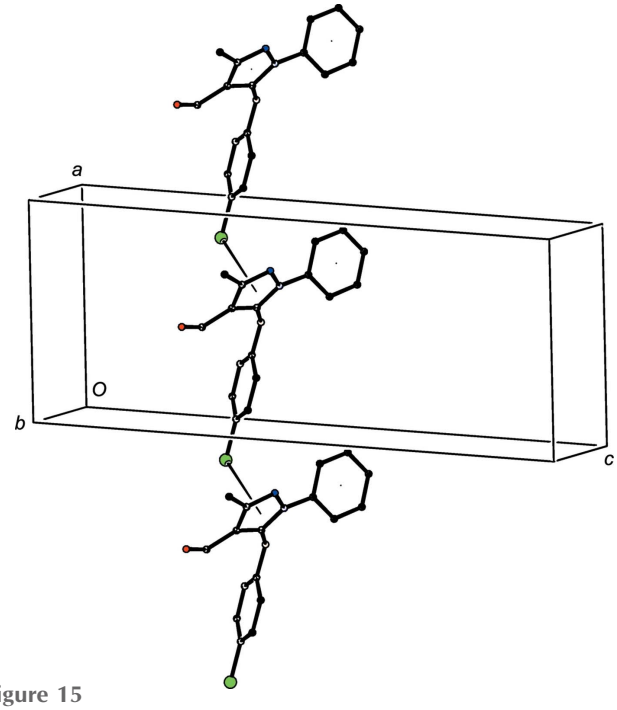


Figure 15
Part of the crystal structure of compound (III), showing the formation of a chain parallel to the [100] direction and built from C—Cl···π(pyrazole) interactions. The Cl···(ring centroid) contacts are drawn as tapered lines and, for the sake of clarity, H atoms have all been omitted.

C—H···π(arene) and C—H···O types and centred at ($\frac{1}{2}$, n, $\frac{1}{2}$), where n represents an integer in each case (Fig. 14). In addition, molecules related by translation along [100] are linked into chains (Fig. 15) by a C—Cl···π(pyrazole) interaction, with geometric parameters Cl···Cg^{i} = 3.5143 (11) Å and C—Cl···Cg^{i} = 112.54 (8)° [Cg represents the centroid of the pyrazole ring; symmetry code: (i) $x-1$, y, z]. The combination of the chains along [100] and [010] generates a sheet lying parallel to (001).

The molecules of compound (XI) are linked by a single C—H···O hydrogen bond to form chains (Sunitha *et al.*, 2016), and those of compound (XII) are linked into a chain of rings by a combination of C—H···N and C—H···π(arene) hydrogen bonds (Cuartas *et al.*, 2017). Two reduced 3,4′-bipyrazoles derived from compound (XII) are linked, respectively, into a chain of rings and a sheet (Cuartas *et al.*, 2017).

In summary, C—H···N hydrogen bonds are present in the structures of compounds (I), (II), (IX), (X) and (XII), C—H···O hydrogen bonds are present in (III) (V), (IX) and (XI), C—H···π hydrogen bonds are present in (I)–(VI) and (XII), but C—Cl···π interactions are present only in (II). Thus, quite modest changes in molecular constitution can give rise to significant changes in the spectrum of direction-specific intermolecular interactions and hence in the patterns of supramolecular assembly.

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supporting information

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Conversion of substituted 5-aryloxypyrazolecarbaldehydes into reduced 3,4′-bipyrazoles: synthesis and characterization, and the structures of four precursors and two products, and their supramolecular assembly in zero, one and two dimensions

Haruvegowda Kiran Kumar, Hemmige S. Yathirajan, Nagaraj Manju, Balakrishna Kalluraya, Ravindranath S. Rathore and Christopher Glidewell

Computing details

For all structures, data collection: *APEX2* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b) and *PLATON* (Spek, 2009).

5-(2-Chlorophenoxy)-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (II)

Crystal data

$C_{17}H_{13}ClN_2O_2$
M_r = 312.74
Triclinic, $P\overline{1}$
a = 10.3034 (4) Å
b = 11.4856 (4) Å
c = 14.4725 (5) Å
α = 81.013 (2)°
β = 69.861 (2)°
γ = 69.990 (2)°
V = 1509.47 (10) Å^3
Z = 4
$F(000)$ = 648
D_x = 1.376 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7620 reflections
θ = 1.5–28.5°
μ = 0.26 mm^{-1}
T = 296 K
Block, colourless
0.19 × 0.16 × 0.13 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
Detector resolution: 0.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.902, T_{max} = 0.967
35720 measured reflections
6296 independent reflections
4051 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 26.6°, θ_{min} = 1.5°
h = −12→12
k = −14→14
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.112$
$S = 1.03$
6296 reflections
425 parameters
2 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 0.7109P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Experimental. Characterisation data for compounds (II) and (IV) - (X).

Compound (II). . IR (KBr, cm^{-1}) 1717 (C=O), 1566 (C=N). NMR ($CDCl_3$) δ(^{1}H) 2.56 (s, 3H, CH_3), 6.92 (dd, 1H, J=0.80 Hz, J= 6.44 Hz, H2 of 2-chlorophenyl), 7.09 (m, 1H, 2-chlorophenyl), 7.17 (m, 1H, 2-chlorophenyl), 7.34 (t, 1H, 2-chlorophenyl), 7.43 (t, 3H, H3,H4,H5 of N-phenyl), 7.69 (d, 2H, J=6.40 Hz, H2, H6 of N-phenyl), 9.54 (s, 1H, aldehyde); δ(^{13}C) 14.60 (CH_3), 108.77, 117.17, 122.87, 122.87, 123.58, 125.79, 128.12, 128.27, 129.28, 131.25, 136.80, 150.86, 151.88, 152.21, 182.73 (aldehyde). MS (m/z) 313/315 (M^+ + 1). Analysis: found C 65.3, H 4.3, N 8.9%; $C_{17}H_{13}ClN_2O_2$ requires C 65.3, H 4.2, N 9.0%.

Compound (IV). IR (KBr, cm^{-1}) 1667 (C=O), 1610 (C=N), 1545 (NO_2), 1340 (NO_2). NMR ($CDCl_3$) δ(^{1}H) 2.61 (s, 3H, CH_3), 7.12 (d, 2H, J= 4.44 Hz, H2,H6 of N-phenyl), 7.43-7.46 (m, 3H, H3,H4,H5 of N-phenyl), 7.59 (d, 2H, J=7.42 Hz) and 8.23 (d, 2H, J= 7.42 Hz) (AB, 4-nitrophenyl), 9.78 (s, 1H, aldehyde); δ(^{13}C) 13.96 (CH_3), 109.36, 116.17, 122.85, 126.25, 128.62, 129.50, 136.34, 144.16, 149.16, 151.30, 160.70, 182.43 (aldehyde). MS (m/z) 324 (M^+ + 1). Analysis: found C 63.3, H 4.0, N 12.7%; $C_{17}H_{13}N_3O_4$ requires C 63.2, H 4.1, N 13.0%.

Compound (V). IR (KBr, cm^{-1}) 1719 (C=O), 1555 (C=N). NMR ($CDCl_3$) δ(^{1}H) 2.31 (s, 3H, CH_3), 7.28 (m, 3H, Ar-H), 7.40 (m, 4H, Ar-H), 7.68 (d, 2H, J=6.80 Hz, Ar-H), 7.71 (d, 1H, J=6.40 Hz, Ar-H), 7.83 (d, 1H, J=6.40 Hz, Ar-H), 7.85 (d, 1H, J=7.20 Hz, Ar-H), 9.65 (s, 1H, aldehyde); δ(^{13}C) 14.62 (CH_3), 109.09, 111.60, 116.87, 122.77, 125.57, 127.25, 127.32, 127.86, 128.07, 129.29, 130.61, 130.77, 133.90, 136.92, 150.93, 152.39, 154.88, 183.09 (aldehyde). MS (m/z) 329 (M^+ + 1). Analysis: found C 76.8, H 5.0, N 8.6%; $C_{21}H_{16}N_2O_2$ requires C 76.8, H 4.9, N 8.5%.

Compound (VI). IR (KBr, cm^{-1}) 1722 (C=O), 1534 (C=N). NMR ($CDCl_3$) δ(^{1}H) 2.32 (s, 3H, CH_3), 2.98-3.67 (m, 10H, piperidine), 6.97 (d, 2H, J= 7.87 Hz, H2,H6 of N-phenyl), 7.24 (m, 3H, H3,H4,H5 of N-phenyl), 9.70 (s, 1H, aldehyde); δ(^{13}C) 12.97 (CH_3), 45.65 (CH_2), 57.51(CH_2), 125.76, 126.8,127.43, 128.69, 129.86, 136.43, 145.39, 148.21, 151.27, 183.43 (aldehyde). MS (m/z) 270 (M^+ + 1). Analysis: found C 71.4, H 7.0, N 15.5%; $C_{16}H_{19}N_3O$ requires C 71.3, H 7.1, N 15.6%.

Compound (VII). IR (KBr, cm^{-1}) 2359 (azide), 1650 (C=O), 1592 (C=N). NMR ($CDCl_3$) δ(^{1}H) 2.52 (s, 3H, CH_3), 6.62 (d, 1H, Ar-H), 6.90 (d, 1H, J= 15.80 Hz, oalkenic H), 6.98 (d, 2H, J=8.64 Hz, H2, H6 of azidophenyl), 7.03 (m, 2H, Ar-H), 7.28 (d, 2H, J= 8.64 Hz, H3,H5 of azidophenyl), 7.36 (m, 2H, Ar-H), 7.55 (d, 1H, J=15.80 Hz, alkenic H), 7.60 (m, 4H, Ar-H). MS (m/z) 456 (M^+ + 1) for $C_{25}H_{18}{}^{35}ClN_5O_2$. Analysis: found C 66.0, H 4.0, N 15.5%; $C_{25}H_{18}ClN_5O_2$ requires C 65.9, H 4.0, N 15.4%.

Compound (VIII). IR (KBr, cm^{-1}) 2354 (azide), 1676 (C=O), 1565 (C=N). NMR ($CDCl_3$) δ(^{1}H) : 2.56 (s, 3H, CH_3), 6.67 (m, 2H, Ar-H), 6.96 (d, 1H, J= 15.80 Hz, alkenic H), 7.06 (d, 2H, J=8.58 Hz, H2,H6 of azidophenyl), 7.10 (m, 3H, Ar-H), 7.26 (d, 2H, J= 8.64 Hz, H3,H5 of azidophenyl), 7.43 (m, 2H, Ar-H), 7.58 (d, 1H, J=15.80 Hz, alkenic H), 7.60 (m, 5H, Ar-H). MS (m/z) 472 (M^+ + 1). Analysis: found C 74.0, H 4.4, N 14.7%; $C_{29}H_{21}N_5O_2$ requires C 73.9, H 6.5, N 14.9%.

Compound (IX). IR (KBr, cm^{-1}) 2359 (azide), 1650 (C=O), 1592 (C=N). NMR ($CDCl_3$) δ(^{1}H) 2.02 (s, 3H, acyl CH_3), 2.42 (s,3H, CH_3), 3.26 (dd, J=5.1 Hz & 17.4 Hz, 1H, -CH_2), 3.57 (dd, J=12.3 Hz and 17.4 Hz, 1H, -CH_2), 5.37 (dd, J=5.1

Hz and 12.3 Hz, 1H, -CH), 6.62 (d, J=8.1 Hz, 1H, Ar-H), 7.18 (d, J= 7.8 Hz, 2H, H2 and H6 of azidophenyl), 7.32 (m, 4H, Ar-H), 7.38 (m, 4H, Ar-H), 7.44(d, J= 7.8 Hz, 2H, H3 and H5 of azidophenyl); δ(^{13}C) 12.93 (CH_3, acetyl), 22.46 (CH_3, pyrazole), 52.18 (CH_2, pyrazoline), 54.91 (-CH, pyrazoline), 109.09, 111.60, 116.87, 122.77, 125.57, 127.25, 127.32, 127.86, 128.07, 129.29, 130.61, 130.77, 131.28 133.90, 136.92, 138.54, 150.93, 152.39, 155.87, 158.92, 171.24 (C=O). MS (m/z) 512/514 (M^+ + 1). Analysis: found C 63.4, H 4.3, N 19.2%; $C_{27}H_{22}ClN_7O_2$ requires C 63.3, H 4.4, N 19.2%.

Compound (X). IR (KBr, cm^{-1}) 2365 (azide), 1698 (C=O),1587 (C=N). NMR ($CDCl_3$) δ(^{1}H) 2.12 (s, 3H, acyl CH_3), 2.42 (s, 3H, CH_3), 3.27 (dd, J=5.2 Hz and 17.1 Hz, 1H, -CH_2), 3.53 (dd, J=12.4 Hz and 17.1 Hz, 1H, -CH_2), 5.33 (dd, J=5.0 Hz and 12.4 Hz, 1H, -CH), 6.62 (m, 3H, Ar-H), 7.13 (d, J=7.7 Hz, 2H, H2,H6 of azidophenyl), 7.28 (m, 4H, Ar-H), 7.39 (m, 5H, Ar-H), 7.40 (d, J=7.6 Hz, 2H, H3,H5 of azidophenyl); δ(^{13}C) 12.28 (CH_3 acetyl), 22.40 (CH_3, pyrazole), 51.12 (CH_2, pyrazoline), 53.78 (-CH, pyrazoline), 108.13, 111.60, 117.85, 121.77, 127.56, 127.88, 128.42, 128.68, 128.97, 129.39, 130.68, 131.54, 132.23, 132.69, 133.77, 134.28 135.87, 136.72, 137.54, 149.93, 152.22, 155.86, 157.92, 172.30 (C=O). MS (m/z) 528 (M^+ + 1). Analysis: found C 70.4, H 4.6, N 18.8%; $C_{31}H_{25}N_7O_2$ requires C 70.6, H 4.8, N 18.6%.

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N11	0.46537 (19)	0.20203 (16)	0.97485 (11)	0.0428 (4)	
N12	0.4865 (2)	0.14789 (18)	1.06314 (12)	0.0481 (5)	
C13	0.6283 (3)	0.1122 (2)	1.04671 (15)	0.0471 (5)	
C14	0.7027 (2)	0.1431 (2)	0.94887 (15)	0.0478 (5)	
C15	0.5939 (2)	0.1991 (2)	0.90689 (14)	0.0436 (5)	
C111	0.3208 (2)	0.2481 (2)	0.96916 (14)	0.0427 (5)	
C112	0.2864 (3)	0.3315 (3)	0.8960 (2)	0.0814 (9)	
H112	0.3575	0.3598	0.8483	0.098*	
C113	0.1451 (3)	0.3729 (4)	0.8937 (2)	0.1052 (13)	
H113	0.1222	0.4283	0.8432	0.126*	
C114	0.0389 (3)	0.3349 (3)	0.9633 (2)	0.0826 (9)	
H114	−0.0562	0.3641	0.9612	0.099*	
C115	0.0738 (3)	0.2535 (3)	1.0363 (2)	0.0741 (8)	
H115	0.0016	0.2271	1.0847	0.089*	
C116	0.2138 (3)	0.2094 (2)	1.03989 (17)	0.0596 (7)	
H116	0.2360	0.1534	1.0903	0.072*	
C131	0.6907 (3)	0.0485 (3)	1.12701 (17)	0.0652 (7)	
H13A	0.6134	0.0426	1.1862	0.098*	
H13B	0.7447	0.0952	1.1386	0.098*	
H13C	0.7541	−0.0332	1.1079	0.098*	
O151	0.60317 (16)	0.24826 (13)	0.81410 (10)	0.0502 (4)	
C151	0.6655 (2)	0.1640 (2)	0.73937 (14)	0.0392 (5)	
C152	0.7316 (2)	0.2059 (2)	0.64638 (15)	0.0437 (5)	
Cl12	0.74176 (7)	0.35534 (6)	0.62745 (5)	0.0646 (2)	

C153	0.7915 (3)	0.1277 (3)	0.56909 (17)	0.0627 (7)	
H153	0.8371	0.1554	0.5063	0.075*	
C154	0.7838 (3)	0.0093 (3)	0.5845 (2)	0.0704 (8)	
H154	0.8236	−0.0431	0.5322	0.085*	
C155	0.7176 (3)	−0.0324 (2)	0.6772 (2)	0.0604 (7)	
H155	0.7133	−0.1132	0.6875	0.072*	
C156	0.6578 (2)	0.0449 (2)	0.75491 (17)	0.0486 (5)	
H156	0.6123	0.0169	0.8176	0.058*	
C141	0.8530 (8)	0.1221 (15)	0.9098 (7)	0.056 (2)	0.682 (6)
H141	0.9112	0.0811	0.9492	0.067*	0.682 (6)
O141	0.9129 (3)	0.1571 (3)	0.8223 (2)	0.0759 (12)	0.682 (6)
C341	0.865 (2)	0.133 (4)	0.886 (2)	0.056 (2)	0.318 (6)
H341	0.8920	0.1666	0.8217	0.067*	0.318 (6)
O341	0.9538 (8)	0.0736 (8)	0.9322 (6)	0.108 (3)	0.318 (6)
N21	0.35991 (17)	0.30621 (16)	0.36519 (12)	0.0399 (4)	
N22	0.25244 (19)	0.36825 (17)	0.32225 (13)	0.0464 (4)	
C23	0.3205 (2)	0.4062 (2)	0.23383 (16)	0.0466 (5)	
C24	0.4720 (2)	0.3700 (2)	0.21647 (16)	0.0470 (5)	
C25	0.4906 (2)	0.30728 (19)	0.30224 (16)	0.0412 (5)	
C211	0.3173 (2)	0.25752 (19)	0.46428 (15)	0.0414 (5)	
C212	0.4180 (3)	0.1774 (2)	0.50657 (19)	0.0653 (7)	
H212	0.5163	0.1524	0.4705	0.078*	
C213	0.3710 (3)	0.1348 (3)	0.6031 (2)	0.0796 (9)	
H213	0.4389	0.0821	0.6320	0.096*	
C214	0.2275 (3)	0.1683 (3)	0.65666 (19)	0.0686 (7)	
H214	0.1974	0.1383	0.7214	0.082*	
C215	0.1287 (3)	0.2464 (3)	0.61408 (18)	0.0627 (7)	
H215	0.0303	0.2693	0.6502	0.075*	
C216	0.1720 (2)	0.2920 (2)	0.51849 (17)	0.0525 (6)	
H216	0.1034	0.3459	0.4906	0.063*	
C231	0.2365 (3)	0.4796 (3)	0.16684 (19)	0.0674 (7)	
H23A	0.2393	0.5633	0.1593	0.101*	
H23B	0.1374	0.4795	0.1944	0.101*	
H23C	0.2787	0.4432	0.1037	0.101*	
O251	0.61405 (15)	0.24538 (14)	0.32537 (12)	0.0525 (4)	
C251	0.6978 (2)	0.3141 (2)	0.33282 (15)	0.0417 (5)	
C252	0.8440 (2)	0.2532 (2)	0.31538 (14)	0.0414 (5)	
Cl22	0.91523 (7)	0.10054 (6)	0.28375 (5)	0.06481 (19)	
C253	0.9323 (2)	0.3149 (2)	0.32515 (16)	0.0532 (6)	
H253	1.0313	0.2744	0.3131	0.064*	
C254	0.8744 (3)	0.4354 (2)	0.35251 (18)	0.0579 (6)	
H254	0.9342	0.4764	0.3593	0.070*	
C255	0.7287 (3)	0.4961 (2)	0.36995 (19)	0.0615 (7)	
H255	0.6899	0.5782	0.3882	0.074*	
C256	0.6397 (3)	0.4354 (2)	0.36030 (18)	0.0551 (6)	
H256	0.5408	0.4762	0.3723	0.066*	
C241	0.5717 (19)	0.386 (3)	0.1239 (9)	0.056 (2)	0.536 (5)
H241	0.5400	0.4223	0.0703	0.067*	0.536 (5)

O241	0.7078 (4)	0.3480 (4)	0.1156 (3)	0.0786 (15)	0.536 (5)
C441	0.599 (2)	0.392 (3)	0.1335 (10)	0.056 (2)	0.464 (5)
H441	0.6916	0.3673	0.1403	0.067*	0.464 (5)
O441	0.5767 (6)	0.4465 (6)	0.0535 (4)	0.113 (2)	0.464 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N11	0.0443 (10)	0.0524 (11)	0.0300 (9)	−0.0158 (9)	−0.0112 (8)	0.0035 (8)
N12	0.0519 (12)	0.0614 (12)	0.0318 (9)	−0.0195 (10)	−0.0155 (8)	0.0057 (8)
C13	0.0515 (14)	0.0541 (14)	0.0388 (12)	−0.0170 (11)	−0.0174 (10)	−0.0015 (10)
C14	0.0457 (13)	0.0535 (14)	0.0423 (12)	−0.0145 (11)	−0.0118 (10)	−0.0034 (10)
C15	0.0487 (13)	0.0452 (13)	0.0325 (11)	−0.0145 (10)	−0.0077 (10)	−0.0011 (9)
C111	0.0422 (12)	0.0479 (13)	0.0356 (11)	−0.0110 (10)	−0.0129 (9)	−0.0005 (9)
C112	0.0538 (16)	0.103 (2)	0.0669 (18)	−0.0174 (16)	−0.0176 (14)	0.0357 (16)
C113	0.064 (2)	0.143 (3)	0.078 (2)	−0.012 (2)	−0.0293 (17)	0.050 (2)
C114	0.0500 (16)	0.113 (3)	0.0722 (19)	−0.0116 (16)	−0.0251 (15)	0.0127 (18)
C115	0.0460 (15)	0.102 (2)	0.0664 (17)	−0.0250 (15)	−0.0129 (13)	0.0129 (16)
C116	0.0484 (14)	0.0775 (18)	0.0460 (13)	−0.0194 (13)	−0.0133 (11)	0.0129 (12)
C131	0.0687 (17)	0.0828 (19)	0.0498 (14)	−0.0209 (15)	−0.0307 (13)	0.0031 (13)
O151	0.0590 (10)	0.0459 (9)	0.0311 (7)	−0.0088 (7)	−0.0052 (7)	0.0018 (6)
C151	0.0341 (11)	0.0475 (13)	0.0320 (10)	−0.0079 (9)	−0.0111 (9)	0.0005 (9)
C152	0.0381 (12)	0.0499 (13)	0.0367 (11)	−0.0085 (10)	−0.0112 (9)	0.0032 (9)
Cl12	0.0620 (4)	0.0567 (4)	0.0602 (4)	−0.0174 (3)	−0.0106 (3)	0.0168 (3)
C153	0.0635 (16)	0.080 (2)	0.0361 (13)	−0.0148 (14)	−0.0116 (11)	−0.0040 (12)
C154	0.0738 (19)	0.077 (2)	0.0599 (17)	−0.0080 (15)	−0.0254 (14)	−0.0264 (15)
C155	0.0668 (17)	0.0510 (15)	0.0746 (18)	−0.0167 (13)	−0.0360 (14)	−0.0057 (13)
C156	0.0488 (13)	0.0539 (14)	0.0459 (12)	−0.0179 (11)	−0.0192 (11)	0.0044 (11)
C141	0.048 (2)	0.072 (4)	0.042 (6)	−0.021 (2)	−0.009 (3)	0.008 (4)
O141	0.0554 (18)	0.098 (2)	0.059 (2)	−0.0294 (16)	0.0018 (14)	0.0044 (16)
C341	0.048 (2)	0.072 (4)	0.042 (6)	−0.021 (2)	−0.009 (3)	0.008 (4)
O341	0.059 (5)	0.133 (7)	0.128 (7)	−0.015 (4)	−0.039 (4)	−0.006 (5)
N21	0.0334 (9)	0.0457 (10)	0.0446 (10)	−0.0131 (8)	−0.0175 (8)	0.0005 (8)
N22	0.0387 (10)	0.0550 (12)	0.0527 (11)	−0.0157 (9)	−0.0249 (9)	0.0045 (9)
C23	0.0479 (13)	0.0491 (13)	0.0492 (13)	−0.0172 (11)	−0.0216 (11)	0.0000 (10)
C24	0.0467 (13)	0.0522 (14)	0.0446 (12)	−0.0192 (11)	−0.0142 (10)	−0.0010 (10)
C25	0.0333 (11)	0.0424 (12)	0.0511 (12)	−0.0118 (9)	−0.0153 (10)	−0.0062 (10)
C211	0.0394 (12)	0.0421 (12)	0.0467 (12)	−0.0150 (10)	−0.0168 (10)	−0.0004 (9)
C212	0.0447 (14)	0.0747 (18)	0.0599 (15)	−0.0051 (13)	−0.0168 (12)	0.0132 (13)
C213	0.0627 (18)	0.089 (2)	0.0703 (18)	−0.0095 (16)	−0.0279 (15)	0.0285 (16)
C214	0.0727 (19)	0.0770 (19)	0.0540 (15)	−0.0289 (15)	−0.0204 (14)	0.0171 (13)
C215	0.0492 (15)	0.0786 (19)	0.0573 (15)	−0.0269 (14)	−0.0099 (12)	0.0060 (13)
C216	0.0411 (13)	0.0624 (15)	0.0563 (14)	−0.0176 (11)	−0.0192 (11)	0.0036 (11)
C231	0.0672 (17)	0.0818 (19)	0.0606 (16)	−0.0228 (15)	−0.0361 (14)	0.0128 (14)
O251	0.0354 (8)	0.0493 (9)	0.0780 (11)	−0.0147 (7)	−0.0248 (8)	0.0028 (8)
C251	0.0347 (11)	0.0538 (14)	0.0396 (11)	−0.0187 (10)	−0.0134 (9)	0.0049 (10)
C252	0.0334 (11)	0.0525 (13)	0.0358 (11)	−0.0128 (10)	−0.0105 (9)	0.0031 (9)
Cl22	0.0488 (4)	0.0603 (4)	0.0825 (5)	−0.0051 (3)	−0.0261 (3)	−0.0094 (3)

C253	0.0371 (12)	0.0729 (18)	0.0538 (14)	−0.0200 (12)	−0.0199 (11)	0.0049 (12)
C254	0.0547 (15)	0.0691 (18)	0.0645 (16)	−0.0314 (14)	−0.0263 (13)	0.0019 (13)
C255	0.0649 (17)	0.0568 (16)	0.0699 (17)	−0.0198 (13)	−0.0263 (13)	−0.0094 (13)
C256	0.0394 (13)	0.0600 (16)	0.0645 (15)	−0.0101 (11)	−0.0181 (11)	−0.0068 (12)
C241	0.045 (6)	0.081 (3)	0.053 (3)	−0.031 (5)	−0.022 (3)	0.004 (3)
O241	0.045 (2)	0.109 (3)	0.073 (2)	−0.032 (2)	−0.0038 (18)	0.003 (2)
C441	0.045 (6)	0.081 (3)	0.053 (3)	−0.031 (5)	−0.022 (3)	0.004 (3)
O441	0.110 (4)	0.153 (5)	0.066 (3)	−0.057 (4)	−0.020 (3)	0.044 (3)

Geometric parameters (Å, º)

N11—C15	1.344 (3)	N21—C25	1.344 (3)
N11—N12	1.385 (2)	N21—N22	1.384 (2)
N11—C111	1.428 (3)	N21—C211	1.430 (3)
N12—C13	1.319 (3)	N22—C23	1.318 (3)
C13—C14	1.414 (3)	C23—C24	1.411 (3)
C13—C131	1.492 (3)	C23—C231	1.491 (3)
C14—C15	1.375 (3)	C24—C25	1.374 (3)
C14—C141	1.400 (8)	C24—C241	1.410 (11)
C14—C341	1.58 (2)	C24—C441	1.508 (13)
C15—O151	1.357 (2)	C25—O251	1.354 (2)
C111—C112	1.368 (3)	C211—C216	1.377 (3)
C111—C116	1.370 (3)	C211—C212	1.380 (3)
C112—C113	1.378 (4)	C212—C213	1.381 (3)
C112—H112	0.9300	C212—H212	0.9300
C113—C114	1.354 (4)	C213—C214	1.360 (4)
C113—H113	0.9300	C213—H213	0.9300
C114—C115	1.357 (4)	C214—C215	1.363 (3)
C114—H114	0.9300	C214—H214	0.9300
C115—C116	1.372 (3)	C215—C216	1.377 (3)
C115—H115	0.9300	C215—H215	0.9300
C116—H116	0.9300	C216—H216	0.9300
C131—H13A	0.9600	C231—H23A	0.9600
C131—H13B	0.9600	C231—H23B	0.9600
C131—H13C	0.9600	C231—H23C	0.9600
O151—C151	1.394 (2)	O251—C251	1.392 (2)
C151—C156	1.376 (3)	C251—C252	1.376 (3)
C151—C152	1.378 (3)	C251—C256	1.376 (3)
C152—C153	1.378 (3)	C252—C253	1.383 (3)
C152—Cl12	1.728 (2)	C252—Cl22	1.721 (2)
C153—C154	1.369 (4)	C253—C254	1.368 (3)
C153—H153	0.9300	C253—H253	0.9300
C154—C155	1.374 (4)	C254—C255	1.372 (3)
C154—H154	0.9300	C254—H254	0.9300
C155—C156	1.376 (3)	C255—C256	1.379 (3)
C155—H155	0.9300	C255—H255	0.9300
C156—H156	0.9300	C256—H256	0.9300
C141—O141	1.272 (10)	C241—O241	1.286 (17)

C141—H141	0.9300	C241—H241	0.9300
C341—O341	1.271 (13)	C441—O441	1.283 (17)
C341—H341	0.9300	C441—H441	0.9300
C15—N11—N12	109.92 (17)	C25—N21—N22	109.99 (16)
C15—N11—C111	131.34 (17)	C25—N21—C211	131.70 (17)
N12—N11—C111	118.73 (16)	N22—N21—C211	118.27 (16)
C13—N12—N11	105.69 (16)	C23—N22—N21	105.52 (17)
N12—C13—C14	111.49 (19)	N22—C23—C24	111.66 (18)
N12—C13—C131	120.3 (2)	N22—C23—C231	120.1 (2)
C14—C13—C131	128.3 (2)	C24—C23—C231	128.2 (2)
C15—C14—C141	130.6 (4)	C25—C24—C241	132.2 (9)
C15—C14—C13	104.06 (19)	C25—C24—C23	104.14 (18)
C141—C14—C13	125.3 (4)	C241—C24—C23	123.1 (8)
C15—C14—C341	119.0 (8)	C25—C24—C441	120.9 (9)
C13—C14—C341	136.8 (8)	C23—C24—C441	134.9 (9)
N11—C15—O151	121.68 (19)	N21—C25—O251	120.89 (18)
N11—C15—C14	108.84 (18)	N21—C25—C24	108.69 (18)
O151—C15—C14	129.5 (2)	O251—C25—C24	130.25 (19)
C112—C111—C116	119.5 (2)	C216—C211—C212	119.5 (2)
C112—C111—N11	121.6 (2)	C216—C211—N21	118.85 (18)
C116—C111—N11	118.93 (18)	C212—C211—N21	121.68 (19)
C111—C112—C113	119.3 (3)	C211—C212—C213	119.2 (2)
C111—C112—H112	120.4	C211—C212—H212	120.4
C113—C112—H112	120.4	C213—C212—H212	120.4
C114—C113—C112	121.5 (3)	C214—C213—C212	121.4 (2)
C114—C113—H113	119.2	C214—C213—H213	119.3
C112—C113—H113	119.2	C212—C213—H213	119.3
C113—C114—C115	118.7 (3)	C213—C214—C215	119.0 (2)
C113—C114—H114	120.7	C213—C214—H214	120.5
C115—C114—H114	120.7	C215—C214—H214	120.5
C114—C115—C116	121.1 (3)	C214—C215—C216	121.1 (2)
C114—C115—H115	119.4	C214—C215—H215	119.5
C116—C115—H115	119.4	C216—C215—H215	119.5
C111—C116—C115	119.9 (2)	C215—C216—C211	119.8 (2)
C111—C116—H116	120.1	C215—C216—H216	120.1
C115—C116—H116	120.1	C211—C216—H216	120.1
C13—C131—H13A	109.5	C23—C231—H23A	109.5
C13—C131—H13B	109.5	C23—C231—H23B	109.5
H13A—C131—H13B	109.5	H23A—C231—H23B	109.5
C13—C131—H13C	109.5	C23—C231—H23C	109.5
H13A—C131—H13C	109.5	H23A—C231—H23C	109.5
H13B—C131—H13C	109.5	H23B—C231—H23C	109.5
C15—O151—C151	116.19 (16)	C25—O251—C251	117.88 (16)
C156—C151—C152	120.2 (2)	C252—C251—C256	120.3 (2)
C156—C151—O151	122.55 (18)	C252—C251—O251	116.61 (19)
C152—C151—O151	117.18 (19)	C256—C251—O251	123.02 (19)
C151—C152—C153	119.7 (2)	C251—C252—C253	119.5 (2)

C151—C152—Cl12	119.99 (17)	C251—C252—Cl22	120.09 (17)
C153—C152—Cl12	120.30 (18)	C253—C252—Cl22	120.40 (17)
C154—C153—C152	120.1 (2)	C254—C253—C252	120.1 (2)
C154—C153—H153	120.0	C254—C253—H253	119.9
C152—C153—H153	120.0	C252—C253—H253	119.9
C153—C154—C155	120.2 (2)	C253—C254—C255	120.3 (2)
C153—C154—H154	119.9	C253—C254—H254	119.8
C155—C154—H154	119.9	C255—C254—H254	119.8
C154—C155—C156	120.2 (2)	C254—C255—C256	119.9 (2)
C154—C155—H155	119.9	C254—C255—H255	120.0
C156—C155—H155	119.9	C256—C255—H255	120.0
C151—C156—C155	119.6 (2)	C251—C256—C255	119.8 (2)
C151—C156—H156	120.2	C251—C256—H256	120.1
C155—C156—H156	120.2	C255—C256—H256	120.1
O141—C141—C14	122.4 (5)	O241—C241—C24	118.2 (12)
O141—C141—H141	118.8	O241—C241—H241	120.9
C14—C141—H141	118.8	C24—C241—H241	120.9
O341—C341—C14	112.0 (19)	O441—C441—C24	118.2 (15)
O341—C341—H341	124.0	O441—C441—H441	120.9
C14—C341—H341	124.0	C24—C441—H441	120.9

C15—N11—N12—C13	−0.5 (2)	C25—N21—N22—C23	−0.2 (2)
C111—N11—N12—C13	178.80 (18)	C211—N21—N22—C23	177.93 (18)
N11—N12—C13—C14	0.8 (3)	N21—N22—C23—C24	0.3 (2)
N11—N12—C13—C131	−179.6 (2)	N21—N22—C23—C231	−178.8 (2)
N12—C13—C14—C15	−0.8 (3)	N22—C23—C24—C25	−0.4 (3)
C131—C13—C14—C15	179.6 (2)	C231—C23—C24—C25	178.7 (2)
N12—C13—C14—C141	177.3 (9)	N22—C23—C24—C241	172.2 (13)
C131—C13—C14—C141	−2.3 (10)	C231—C23—C24—C241	−8.8 (14)
N12—C13—C14—C341	176 (2)	N22—C23—C24—C441	−176.2 (17)
C131—C13—C14—C341	−3 (2)	C231—C23—C24—C441	2.9 (17)
N12—N11—C15—O151	−178.96 (18)	N22—N21—C25—O251	−175.75 (17)
C111—N11—C15—O151	1.9 (3)	C211—N21—C25—O251	6.5 (3)
N12—N11—C15—C14	0.0 (2)	N22—N21—C25—C24	0.0 (2)
C111—N11—C15—C14	−179.2 (2)	C211—N21—C25—C24	−177.8 (2)
C141—C14—C15—N11	−177.5 (10)	C241—C24—C25—N21	−171.4 (14)
C13—C14—C15—N11	0.5 (2)	C23—C24—C25—N21	0.2 (2)
C341—C14—C15—N11	−177.4 (18)	C441—C24—C25—N21	176.8 (15)
C141—C14—C15—O151	1.3 (11)	C241—C24—C25—O251	3.8 (14)
C13—C14—C15—O151	179.3 (2)	C23—C24—C25—O251	175.4 (2)
C341—C14—C15—O151	1.4 (19)	C441—C24—C25—O251	−8.0 (15)
C15—N11—C111—C112	−19.3 (4)	C25—N21—C211—C216	166.6 (2)
N12—N11—C111—C112	161.6 (2)	N22—N21—C211—C216	−11.1 (3)
C15—N11—C111—C116	161.9 (2)	C25—N21—C211—C212	−13.3 (3)
N12—N11—C111—C116	−17.2 (3)	N22—N21—C211—C212	169.0 (2)
C116—C111—C112—C113	−1.4 (5)	C216—C211—C212—C213	−0.9 (4)
N11—C111—C112—C113	179.9 (3)	N21—C211—C212—C213	178.9 (2)
C111—C112—C113—C114	1.3 (6)	C211—C212—C213—C214	1.3 (5)

C112—C113—C114—C115	−0.4 (6)	C212—C213—C214—C215	−0.6 (5)
C113—C114—C115—C116	−0.3 (5)	C213—C214—C215—C216	−0.4 (4)
C112—C111—C116—C115	0.6 (4)	C214—C215—C216—C211	0.6 (4)
N11—C111—C116—C115	179.4 (2)	C212—C211—C216—C215	0.0 (4)
C114—C115—C116—C111	0.2 (5)	N21—C211—C216—C215	−179.9 (2)
N11—C15—O151—C151	−110.9 (2)	N21—C25—O251—C251	−117.7 (2)
C14—C15—O151—C151	70.4 (3)	C24—C25—O251—C251	67.6 (3)
C15—O151—C151—C156	29.1 (3)	C25—O251—C251—C252	−153.77 (19)
C15—O151—C151—C152	−153.42 (19)	C25—O251—C251—C256	29.0 (3)
C156—C151—C152—C153	−0.7 (3)	C256—C251—C252—C253	−0.3 (3)
O151—C151—C152—C153	−178.17 (19)	O251—C251—C252—C253	−177.63 (18)
C156—C151—C152—Cl12	−179.69 (16)	C256—C251—C252—Cl22	178.53 (17)
O151—C151—C152—Cl12	2.8 (3)	O251—C251—C252—Cl22	1.3 (2)
C151—C152—C153—C154	0.6 (4)	C251—C252—C253—C254	0.4 (3)
Cl12—C152—C153—C154	179.7 (2)	Cl22—C252—C253—C254	−178.51 (17)
C152—C153—C154—C155	−0.5 (4)	C252—C253—C254—C255	−0.3 (4)
C153—C154—C155—C156	0.4 (4)	C253—C254—C255—C256	0.3 (4)
C152—C151—C156—C155	0.6 (3)	C252—C251—C256—C255	0.3 (3)
O151—C151—C156—C155	177.94 (19)	O251—C251—C256—C255	177.4 (2)
C154—C155—C156—C151	−0.5 (4)	C254—C255—C256—C251	−0.3 (4)
C15—C14—C141—O141	1 (2)	C25—C24—C241—O241	−9 (3)
C13—C14—C141—O141	−176.7 (9)	C23—C24—C241—O241	−179.1 (12)
C341—C14—C141—O141	0 (10)	C441—C24—C241—O241	35 (8)
C15—C14—C341—O341	−176.6 (18)	C25—C24—C441—O441	177.0 (16)
C141—C14—C341—O341	3 (9)	C241—C24—C441—O441	34 (8)
C13—C14—C341—O341	6 (4)	C23—C24—C441—O441	−8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C156—H156···N12^{i}	0.93	2.59	3.433 (3)	152
C255—H255···*Cg*3^{ii}	0.93	2.80	3.635 (3)	140

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

3-Methyl-5-(4-nitrophenoxy)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (IV)

Crystal data

$C_{17}H_{13}N_3O_4$
M_r = 323.30
Monoclinic, $P2_1/c$
a = 14.1163 (9) Å
b = 11.7268 (7) Å
c = 9.3982 (5) Å
β = 94.259 (3)°
V = 1551.47 (16) Å^3
Z = 4
$F(000)$ = 672
D_x = 1.384 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4821 reflections
θ = 1.4–30.8°
μ = 0.10 mm^{-1}
T = 296 K
Block, colourless
0.20 × 0.15 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
Detector resolution: 0.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.945, T_{max} = 0.985
28186 measured reflections
3956 independent reflections
2361 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 28.6°, θ_{min} = 2.3°
h = −18→18
k = −15→15
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.121
S = 1.01
3956 reflections
219 parameters
0 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.5804P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0064 (11)

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}
N1	0.86994 (10)	0.04307 (11)	0.28782 (14)	0.0439 (3)
N2	0.96335 (10)	0.07594 (12)	0.28157 (15)	0.0467 (4)
C3	0.98509 (13)	0.12942 (14)	0.40292 (19)	0.0463 (4)
C4	0.90857 (13)	0.13138 (14)	0.49144 (18)	0.0471 (4)
C5	0.83639 (13)	0.07652 (14)	0.41151 (18)	0.0457 (4)
C11	0.82349 (12)	−0.01374 (14)	0.16813 (18)	0.0442 (4)
C12	0.75167 (13)	−0.09122 (16)	0.1842 (2)	0.0552 (5)
H12	0.7326	−0.1081	0.2745	0.066*
C13	0.70832 (15)	−0.14363 (18)	0.0648 (2)	0.0674 (6)
H13	0.6590	−0.1950	0.0747	0.081*
C14	0.73745 (17)	−0.1204 (2)	−0.0681 (2)	0.0711 (6)
H14	0.7083	−0.1564	−0.1479	0.085*
C15	0.80937 (17)	−0.04447 (18)	−0.0831 (2)	0.0680 (6)
H15	0.8290	−0.0291	−0.1735	0.082*
C16	0.85318 (15)	0.00968 (16)	0.03427 (19)	0.0561 (5)
H16	0.9021	0.0614	0.0235	0.067*
C31	1.08136 (14)	0.18030 (18)	0.4311 (2)	0.0648 (5)
H31A	1.1212	0.1570	0.3580	0.097*

H31B	1.1086	0.1548	0.5223	0.097*
H31C	1.0763	0.2619	0.4314	0.097*
C41	0.91097 (17)	0.17425 (17)	0.6348 (2)	0.0625 (5)
H41	0.9677	0.2070	0.6710	0.075*
O41	0.84724 (12)	0.17227 (14)	0.71320 (15)	0.0781 (5)
O51	0.74717 (9)	0.04733 (10)	0.43900 (14)	0.0592 (4)
C51	0.68931 (12)	0.12862 (15)	0.49678 (18)	0.0463 (4)
C52	0.69553 (13)	0.24277 (15)	0.46518 (18)	0.0496 (4)
H52	0.7389	0.2687	0.4028	0.060*
C53	0.63630 (13)	0.31763 (15)	0.52768 (19)	0.0512 (4)
H53	0.6394	0.3954	0.5091	0.061*
C54	0.57244 (12)	0.27586 (16)	0.61811 (18)	0.0484 (4)
C55	0.56359 (13)	0.16141 (17)	0.6451 (2)	0.0544 (5)
H55	0.5183	0.1352	0.7042	0.065*
C56	0.62287 (13)	0.08639 (16)	0.5831 (2)	0.0536 (5)
H56	0.6182	0.0084	0.5991	0.064*
N54	0.51327 (12)	0.35609 (18)	0.69134 (19)	0.0662 (5)
O411	0.52206 (15)	0.45668 (17)	0.6681 (2)	0.1137 (7)
O412	0.45836 (11)	0.31846 (16)	0.77356 (18)	0.0883 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0479 (8)	0.0408 (7)	0.0444 (8)	−0.0016 (6)	0.0128 (6)	−0.0032 (6)
N2	0.0457 (8)	0.0458 (8)	0.0497 (8)	0.0006 (6)	0.0112 (7)	0.0000 (7)
C3	0.0540 (10)	0.0347 (8)	0.0504 (10)	0.0017 (7)	0.0051 (8)	0.0018 (8)
C4	0.0629 (11)	0.0341 (8)	0.0452 (9)	−0.0001 (8)	0.0097 (8)	−0.0014 (7)
C5	0.0568 (11)	0.0336 (8)	0.0488 (10)	−0.0012 (7)	0.0182 (8)	−0.0013 (7)
C11	0.0487 (10)	0.0370 (9)	0.0474 (9)	0.0063 (7)	0.0067 (8)	−0.0055 (7)
C12	0.0553 (11)	0.0525 (11)	0.0588 (11)	−0.0019 (9)	0.0108 (9)	−0.0076 (9)
C13	0.0568 (12)	0.0620 (13)	0.0828 (16)	−0.0055 (10)	0.0017 (11)	−0.0178 (11)
C14	0.0757 (15)	0.0687 (14)	0.0666 (14)	0.0113 (12)	−0.0108 (11)	−0.0214 (11)
C15	0.0945 (17)	0.0621 (13)	0.0476 (11)	0.0078 (12)	0.0066 (11)	−0.0088 (10)
C16	0.0712 (13)	0.0485 (10)	0.0500 (11)	−0.0004 (9)	0.0147 (9)	−0.0047 (9)
C31	0.0585 (12)	0.0596 (12)	0.0754 (14)	−0.0064 (10)	−0.0015 (10)	−0.0040 (10)
C41	0.0826 (15)	0.0513 (11)	0.0542 (12)	−0.0012 (10)	0.0087 (11)	−0.0119 (9)
O41	0.1000 (12)	0.0851 (11)	0.0520 (8)	−0.0015 (9)	0.0233 (8)	−0.0131 (7)
O51	0.0639 (8)	0.0432 (7)	0.0748 (9)	−0.0105 (6)	0.0349 (7)	−0.0144 (6)
C51	0.0511 (10)	0.0438 (9)	0.0458 (9)	−0.0049 (8)	0.0155 (8)	−0.0075 (8)
C52	0.0542 (10)	0.0474 (10)	0.0496 (10)	−0.0046 (8)	0.0188 (8)	0.0022 (8)
C53	0.0523 (11)	0.0437 (10)	0.0582 (11)	−0.0008 (8)	0.0083 (9)	0.0008 (8)
C54	0.0418 (9)	0.0554 (11)	0.0486 (10)	0.0040 (8)	0.0074 (8)	−0.0060 (8)
C55	0.0486 (10)	0.0624 (12)	0.0547 (11)	−0.0048 (9)	0.0196 (9)	0.0025 (9)
C56	0.0583 (11)	0.0445 (10)	0.0603 (11)	−0.0086 (8)	0.0202 (9)	0.0012 (9)
N54	0.0526 (10)	0.0765 (13)	0.0705 (11)	0.0135 (9)	0.0111 (9)	−0.0097 (10)
O411	0.1183 (16)	0.0660 (12)	0.1644 (19)	0.0205 (11)	0.0609 (14)	−0.0166 (12)
O412	0.0690 (10)	0.1129 (14)	0.0875 (11)	0.0230 (9)	0.0358 (9)	0.0012 (10)

Geometric parameters (Å, º)

N1—C5	1.346 (2)	C31—H31A	0.9600
N1—N2	1.3792 (19)	C31—H31B	0.9600
N1—C11	1.425 (2)	C31—H31C	0.9600
N2—C3	1.318 (2)	C41—O41	1.205 (2)
C3—C4	1.412 (2)	C41—H41	0.9300
C3—C31	1.490 (3)	O51—C51	1.392 (2)
C4—C5	1.379 (2)	C51—C52	1.375 (2)
C4—C41	1.436 (3)	C51—C56	1.377 (2)
C5—O51	1.349 (2)	C52—C53	1.374 (2)
C11—C12	1.378 (2)	C52—H52	0.9300
C11—C16	1.383 (2)	C53—C54	1.374 (2)
C12—C13	1.382 (3)	C53—H53	0.9300
C12—H12	0.9300	C54—C55	1.373 (3)
C13—C14	1.371 (3)	C54—N54	1.464 (2)
C13—H13	0.9300	C55—C56	1.373 (2)
C14—C15	1.366 (3)	C55—H55	0.9300
C14—H14	0.9300	C56—H56	0.9300
C15—C16	1.379 (3)	N54—O411	1.208 (2)
C15—H15	0.9300	N54—O412	1.217 (2)
C16—H16	0.9300		
C5—N1—N2	110.74 (14)	C3—C31—H31A	109.5
C5—N1—C11	130.35 (14)	C3—C31—H31B	109.5
N2—N1—C11	118.85 (13)	H31A—C31—H31B	109.5
C3—N2—N1	104.96 (13)	C3—C31—H31C	109.5
N2—C3—C4	112.24 (16)	H31A—C31—H31C	109.5
N2—C3—C31	119.70 (16)	H31B—C31—H31C	109.5
C4—C3—C31	128.05 (17)	O41—C41—C4	126.9 (2)
C5—C4—C3	103.77 (15)	O41—C41—H41	116.5
C5—C4—C41	129.73 (17)	C4—C41—H41	116.5
C3—C4—C41	126.36 (18)	C5—O51—C51	118.98 (13)
N1—C5—O51	119.02 (15)	C52—C51—C56	122.32 (16)
N1—C5—C4	108.26 (15)	C52—C51—O51	122.25 (15)
O51—C5—C4	132.58 (15)	C56—C51—O51	115.38 (15)
C12—C11—C16	120.40 (17)	C53—C52—C51	118.61 (16)
C12—C11—N1	121.39 (15)	C53—C52—H52	120.7
C16—C11—N1	118.21 (16)	C51—C52—H52	120.7
C11—C12—C13	119.28 (19)	C52—C53—C54	118.99 (17)
C11—C12—H12	120.4	C52—C53—H53	120.5
C13—C12—H12	120.4	C54—C53—H53	120.5
C14—C13—C12	120.5 (2)	C55—C54—C53	122.36 (16)
C14—C13—H13	119.8	C55—C54—N54	118.60 (17)
C12—C13—H13	119.8	C53—C54—N54	119.02 (18)
C15—C14—C13	120.0 (2)	C54—C55—C56	118.77 (16)
C15—C14—H14	120.0	C54—C55—H55	120.6
C13—C14—H14	120.0	C56—C55—H55	120.6

C14—C15—C16	120.7 (2)	C55—C56—C51	118.85 (17)
C14—C15—H15	119.7	C55—C56—H56	120.6
C16—C15—H15	119.7	C51—C56—H56	120.6
C15—C16—C11	119.23 (19)	O411—N54—O412	123.20 (19)
C15—C16—H16	120.4	O411—N54—C54	118.24 (18)
C11—C16—H16	120.4	O412—N54—C54	118.56 (19)
C5—N1—N2—C3	−0.03 (18)	C13—C14—C15—C16	−0.2 (3)
C11—N1—N2—C3	177.50 (14)	C14—C15—C16—C11	0.0 (3)
N1—N2—C3—C4	0.99 (19)	C12—C11—C16—C15	0.7 (3)
N1—N2—C3—C31	−178.18 (15)	N1—C11—C16—C15	179.87 (17)
N2—C3—C4—C5	−1.54 (19)	C5—C4—C41—O41	−1.9 (3)
C31—C3—C4—C5	177.54 (18)	C3—C4—C41—O41	−176.9 (2)
N2—C3—C4—C41	174.50 (17)	N1—C5—O51—C51	−136.63 (16)
C31—C3—C4—C41	−6.4 (3)	C4—C5—O51—C51	48.3 (3)
N2—N1—C5—O51	−177.14 (14)	C5—O51—C51—C52	32.7 (3)
C11—N1—C5—O51	5.7 (3)	C5—O51—C51—C56	−149.82 (17)
N2—N1—C5—C4	−0.94 (19)	C56—C51—C52—C53	3.2 (3)
C11—N1—C5—C4	−178.10 (16)	O51—C51—C52—C53	−179.48 (16)
C3—C4—C5—N1	1.44 (18)	C51—C52—C53—C54	−0.7 (3)
C41—C4—C5—N1	−174.41 (18)	C52—C53—C54—C55	−2.0 (3)
C3—C4—C5—O51	176.93 (18)	C52—C53—C54—N54	176.39 (16)
C41—C4—C5—O51	1.1 (3)	C53—C54—C55—C56	2.2 (3)
C5—N1—C11—C12	−32.5 (3)	N54—C54—C55—C56	−176.22 (17)
N2—N1—C11—C12	150.56 (16)	C54—C55—C56—C51	0.3 (3)
C5—N1—C11—C16	148.36 (18)	C52—C51—C56—C55	−3.1 (3)
N2—N1—C11—C16	−28.6 (2)	O51—C51—C56—C55	179.48 (17)
C16—C11—C12—C13	−1.3 (3)	C55—C54—N54—O411	179.3 (2)
N1—C11—C12—C13	179.59 (17)	C53—C54—N54—O411	0.8 (3)
C11—C12—C13—C14	1.1 (3)	C55—C54—N54—O412	0.0 (3)
C12—C13—C14—C15	−0.4 (3)	C53—C54—N54—O412	−178.45 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···O412^{i}	0.93	2.57	3.330 (3)	139
C52—H52···O41^{ii}	0.93	2.53	3.456 (2)	174
C55—H55···O411^{iii}	0.93	2.50	3.259 (3)	139
C53—H53···*Cg*2^{iv}	0.93	2.84	3.564 (2)	135

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

3-Methyl-5-(naphthalen-2-yloxy)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (V)

Crystal data

$C_{21}H_{16}N_2O_2$
M_r = 328.36
Monoclinic, $P2_1/n$
a = 7.7302 (6) Å
b = 17.2550 (16) Å
c = 13.1989 (11) Å
β = 106.079 (2)°
V = 1691.7 (2) Å^3

$Z = 4$
$F(000) = 688$
$D_x = 1.289$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4456 reflections

$\theta = 2.0$–$29.0°$
$\mu = 0.08$ mm^{-1}
$T = 296$ K
Block, brown
0.20 × 0.16 × 0.14 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
Detector resolution: 0.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
$T_{min} = 0.954$, $T_{max} = 0.988$

34394 measured reflections
4311 independent reflections
2711 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 28.6°$, $\theta_{min} = 2.4°$
$h = -9 \rightarrow 10$
$k = -23 \rightarrow 23$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.130$
$S = 1.03$
4311 reflections
227 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.449P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.49965 (16)	0.38271 (8)	0.43857 (10)	0.0354 (3)
N2	0.32134 (17)	0.36741 (8)	0.38728 (10)	0.0415 (3)
C3	0.2601 (2)	0.32861 (10)	0.45616 (13)	0.0404 (4)
C4	0.3964 (2)	0.31630 (10)	0.55195 (13)	0.0393 (4)
C5	0.5463 (2)	0.35199 (9)	0.53568 (12)	0.0356 (3)
C11	0.60936 (19)	0.42022 (9)	0.38274 (11)	0.0328 (3)
C12	0.7251 (2)	0.47936 (9)	0.42849 (13)	0.0411 (4)
H12	0.7348	0.4949	0.4973	0.049*
C13	0.8265 (2)	0.51508 (11)	0.37058 (16)	0.0522 (5)
H13	0.9065	0.5544	0.4010	0.063*
C14	0.8099 (3)	0.49299 (12)	0.26867 (17)	0.0616 (6)
H14	0.8775	0.5176	0.2298	0.074*
C15	0.6933 (3)	0.43438 (12)	0.22374 (15)	0.0598 (5)
H15	0.6820	0.4197	0.1544	0.072*
C16	0.5936 (2)	0.39740 (10)	0.28053 (13)	0.0447 (4)
H16	0.5160	0.3573	0.2503	0.054*

C31	0.0691 (2)	0.30215 (13)	0.42740 (16)	0.0597 (5)
H31A	0.0073	0.3213	0.3586	0.090*
H31B	0.0115	0.3216	0.4780	0.090*
H31C	0.0654	0.2465	0.4270	0.090*
C41	0.3834 (3)	0.27328 (11)	0.64338 (15)	0.0526 (5)
H41	0.4890	0.2654	0.6969	0.063*
O41	0.2458 (2)	0.24671 (9)	0.65573 (13)	0.0737 (5)
O51	0.72116 (14)	0.35620 (8)	0.59018 (8)	0.0467 (3)
C51	0.9302 (2)	0.33196 (9)	0.75230 (12)	0.0358 (3)
H51	0.9925	0.3013	0.7163	0.043*
C52	0.7727 (2)	0.36509 (9)	0.69996 (12)	0.0362 (4)
C53	0.6730 (2)	0.41139 (11)	0.75088 (14)	0.0492 (4)
H53	0.5655	0.4342	0.7130	0.059*
C54	0.7369 (2)	0.42215 (11)	0.85672 (14)	0.0522 (5)
H54	0.6702	0.4517	0.8914	0.063*
C54A	0.9017 (2)	0.38972 (10)	0.91541 (12)	0.0401 (4)
C55	0.9757 (3)	0.40256 (12)	1.02489 (14)	0.0530 (5)
H55	0.9116	0.4319	1.0614	0.064*
C56	1.1380 (3)	0.37294 (13)	1.07740 (14)	0.0588 (5)
H56	1.1842	0.3820	1.1493	0.071*
C57	1.2360 (3)	0.32887 (12)	1.02410 (15)	0.0577 (5)
H57	1.3483	0.3096	1.0605	0.069*
C58	1.1689 (2)	0.31377 (11)	0.91914 (14)	0.0486 (4)
H58	1.2346	0.2833	0.8849	0.058*
C58A	1.0003 (2)	0.34402 (9)	0.86189 (12)	0.0357 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0282 (7)	0.0455 (8)	0.0302 (7)	−0.0012 (5)	0.0041 (5)	0.0019 (6)
N2	0.0287 (7)	0.0557 (9)	0.0367 (7)	−0.0034 (6)	0.0036 (6)	−0.0029 (6)
C3	0.0342 (8)	0.0449 (9)	0.0429 (9)	−0.0035 (7)	0.0120 (7)	−0.0081 (7)
C4	0.0386 (9)	0.0423 (9)	0.0402 (9)	0.0018 (7)	0.0166 (7)	−0.0001 (7)
C5	0.0313 (8)	0.0443 (9)	0.0309 (8)	0.0048 (7)	0.0082 (6)	0.0022 (6)
C11	0.0296 (7)	0.0358 (8)	0.0318 (8)	0.0015 (6)	0.0068 (6)	0.0027 (6)
C12	0.0413 (9)	0.0420 (9)	0.0383 (9)	0.0001 (7)	0.0084 (7)	−0.0052 (7)
C13	0.0493 (10)	0.0455 (10)	0.0625 (12)	−0.0127 (8)	0.0166 (9)	−0.0026 (9)
C14	0.0722 (14)	0.0593 (12)	0.0655 (13)	−0.0135 (10)	0.0393 (11)	0.0030 (10)
C15	0.0767 (14)	0.0670 (13)	0.0451 (10)	−0.0114 (11)	0.0327 (10)	−0.0055 (9)
C16	0.0494 (10)	0.0473 (10)	0.0380 (9)	−0.0078 (8)	0.0131 (8)	−0.0056 (7)
C31	0.0395 (10)	0.0760 (14)	0.0642 (13)	−0.0148 (9)	0.0153 (9)	−0.0146 (11)
C41	0.0580 (11)	0.0540 (11)	0.0537 (11)	0.0038 (9)	0.0284 (9)	0.0080 (9)
O41	0.0737 (10)	0.0734 (10)	0.0916 (12)	−0.0013 (8)	0.0523 (9)	0.0165 (8)
O51	0.0296 (6)	0.0782 (9)	0.0297 (6)	0.0051 (5)	0.0039 (5)	0.0068 (5)
C51	0.0315 (8)	0.0417 (9)	0.0333 (8)	0.0025 (6)	0.0076 (6)	0.0016 (7)
C52	0.0329 (8)	0.0453 (9)	0.0291 (8)	0.0013 (7)	0.0061 (6)	0.0050 (7)
C53	0.0374 (9)	0.0583 (11)	0.0470 (10)	0.0154 (8)	0.0034 (8)	0.0015 (8)
C54	0.0450 (10)	0.0606 (12)	0.0514 (11)	0.0110 (8)	0.0139 (9)	−0.0113 (9)

C54A	0.0398 (9)	0.0454 (9)	0.0348 (8)	−0.0031 (7)	0.0098 (7)	−0.0009 (7)
C55	0.0565 (12)	0.0643 (12)	0.0392 (10)	−0.0084 (9)	0.0149 (9)	−0.0089 (9)
C56	0.0611 (12)	0.0744 (14)	0.0329 (9)	−0.0137 (10)	−0.0004 (9)	0.0020 (9)
C57	0.0466 (11)	0.0665 (13)	0.0476 (11)	0.0001 (9)	−0.0076 (9)	0.0077 (9)
C58	0.0409 (9)	0.0554 (11)	0.0432 (10)	0.0068 (8)	0.0009 (8)	0.0033 (8)
C58A	0.0326 (8)	0.0377 (8)	0.0350 (8)	−0.0019 (6)	0.0061 (7)	0.0056 (6)

Geometric parameters (Å, º)

N1—C5	1.3408 (19)	C31—H31C	0.9600
N1—N2	1.3824 (17)	C41—O41	1.210 (2)
N1—C11	1.4240 (19)	C41—H41	0.9300
N2—C3	1.318 (2)	O51—C52	1.4008 (18)
C3—C4	1.420 (2)	C51—C52	1.350 (2)
C3—C31	1.491 (2)	C51—C58A	1.412 (2)
C4—C5	1.381 (2)	C51—H51	0.9300
C4—C41	1.444 (2)	C52—C53	1.404 (2)
C5—O51	1.3455 (18)	C53—C54	1.359 (2)
C11—C16	1.378 (2)	C53—H53	0.9300
C11—C12	1.381 (2)	C54—C54A	1.411 (2)
C12—C13	1.382 (2)	C54—H54	0.9300
C12—H12	0.9300	C54A—C58A	1.414 (2)
C13—C14	1.370 (3)	C54A—C55	1.416 (2)
C13—H13	0.9300	C55—C56	1.354 (3)
C14—C15	1.375 (3)	C55—H55	0.9300
C14—H14	0.9300	C56—C57	1.394 (3)
C15—C16	1.373 (2)	C56—H56	0.9300
C15—H15	0.9300	C57—C58	1.363 (2)
C16—H16	0.9300	C57—H57	0.9300
C31—H31A	0.9600	C58—C58A	1.413 (2)
C31—H31B	0.9600	C58—H58	0.9300

C5—N1—N2	111.14 (12)	H31B—C31—H31C	109.5
C5—N1—C11	129.29 (12)	O41—C41—C4	125.07 (19)
N2—N1—C11	119.30 (12)	O41—C41—H41	117.5
C3—N2—N1	105.01 (13)	C4—C41—H41	117.5
N2—C3—C4	111.76 (14)	C5—O51—C52	120.97 (12)
N2—C3—C31	119.97 (16)	C52—C51—C58A	119.83 (14)
C4—C3—C31	128.26 (16)	C52—C51—H51	120.1
C5—C4—C3	104.03 (14)	C58A—C51—H51	120.1
C5—C4—C41	127.95 (16)	C51—C52—O51	116.15 (13)
C3—C4—C41	127.96 (16)	C51—C52—C53	122.23 (15)
N1—C5—O51	117.02 (13)	O51—C52—C53	121.41 (14)
N1—C5—C4	108.04 (13)	C54—C53—C52	118.57 (15)
O51—C5—C4	134.67 (14)	C54—C53—H53	120.7
C16—C11—C12	120.67 (14)	C52—C53—H53	120.7
C16—C11—N1	118.22 (14)	C53—C54—C54A	121.75 (16)
C12—C11—N1	121.09 (13)	C53—C54—H54	119.1

C11—C12—C13	119.06 (15)	C54A—C54—H54	119.1
C11—C12—H12	120.5	C54—C54A—C58A	118.46 (14)
C13—C12—H12	120.5	C54—C54A—C55	123.10 (16)
C14—C13—C12	120.38 (17)	C58A—C54A—C55	118.41 (15)
C14—C13—H13	119.8	C56—C55—C54A	121.20 (17)
C12—C13—H13	119.8	C56—C55—H55	119.4
C13—C14—C15	120.02 (17)	C54A—C55—H55	119.4
C13—C14—H14	120.0	C55—C56—C57	120.24 (17)
C15—C14—H14	120.0	C55—C56—H56	119.9
C16—C15—C14	120.44 (17)	C57—C56—H56	119.9
C16—C15—H15	119.8	C58—C57—C56	120.69 (18)
C14—C15—H15	119.8	C58—C57—H57	119.7
C15—C16—C11	119.40 (16)	C56—C57—H57	119.7
C15—C16—H16	120.3	C57—C58—C58A	120.52 (17)
C11—C16—H16	120.3	C57—C58—H58	119.7
C3—C31—H31A	109.5	C58A—C58—H58	119.7
C3—C31—H31B	109.5	C51—C58A—C58	121.90 (15)
H31A—C31—H31B	109.5	C51—C58A—C54A	119.14 (14)
C3—C31—H31C	109.5	C58—C58A—C54A	118.93 (15)
H31A—C31—H31C	109.5		

C5—N1—N2—C3	1.54 (17)	N1—C11—C16—C15	177.84 (16)
C11—N1—N2—C3	176.03 (13)	C5—C4—C41—O41	175.77 (19)
N1—N2—C3—C4	−1.31 (18)	C3—C4—C41—O41	−7.5 (3)
N1—N2—C3—C31	179.93 (15)	N1—C5—O51—C52	146.36 (14)
N2—C3—C4—C5	0.64 (19)	C4—C5—O51—C52	−40.5 (3)
C31—C3—C4—C5	179.27 (17)	C58A—C51—C52—O51	174.26 (13)
N2—C3—C4—C41	−176.73 (16)	C58A—C51—C52—C53	−0.5 (2)
C31—C3—C4—C41	1.9 (3)	C5—O51—C52—C51	148.23 (15)
N2—N1—C5—O51	173.68 (13)	C5—O51—C52—C53	−37.0 (2)
C11—N1—C5—O51	−0.1 (2)	C51—C52—C53—C54	−0.9 (3)
N2—N1—C5—C4	−1.17 (18)	O51—C52—C53—C54	−175.35 (16)
C11—N1—C5—C4	−174.96 (14)	C52—C53—C54—C54A	1.6 (3)
C3—C4—C5—N1	0.34 (17)	C53—C54—C54A—C58A	−0.9 (3)
C41—C4—C5—N1	177.71 (16)	C53—C54—C54A—C55	177.24 (18)
C3—C4—C5—O51	−173.21 (17)	C54—C54A—C55—C56	−177.22 (18)
C41—C4—C5—O51	4.2 (3)	C58A—C54A—C55—C56	0.9 (3)
C5—N1—C11—C16	131.39 (17)	C54A—C55—C56—C57	0.0 (3)
N2—N1—C11—C16	−42.0 (2)	C55—C56—C57—C58	−1.2 (3)
C5—N1—C11—C12	−50.3 (2)	C56—C57—C58—C58A	1.4 (3)
N2—N1—C11—C12	136.31 (15)	C52—C51—C58A—C58	−176.80 (16)
C16—C11—C12—C13	−0.5 (2)	C52—C51—C58A—C54A	1.1 (2)
N1—C11—C12—C13	−178.77 (15)	C57—C58—C58A—C51	177.50 (17)
C11—C12—C13—C14	1.1 (3)	C57—C58—C58A—C54A	−0.5 (3)
C12—C13—C14—C15	−0.7 (3)	C54—C54A—C58A—C51	−0.5 (2)
C13—C14—C15—C16	−0.3 (3)	C55—C54A—C58A—C51	−178.71 (15)
C14—C15—C16—C11	0.9 (3)	C54—C54A—C58A—C58	177.54 (16)
C12—C11—C16—C15	−0.4 (3)	C55—C54A—C58A—C58	−0.7 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C51—H51···O41^{i}	0.93	2.50	3.386 (2)	160
C12—H12···*Cg*1^{ii}	0.93	2.96	3.4804 (17)	117
C53—H53···*Cg*2^{ii}	0.93	2.78	3.6477 (19)	155

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+1, −*y*+1, −*z*+1.

3-Methyl-1-phenyl-5-(piperidin-1-yl)-1*H*-pyrazole-4-carbaldehyde (VI)

Crystal data

$C_{16}H_{19}N_3O$
M_r = 269.34
Monoclinic, $P2_1/n$
a = 8.9432 (7) Å
b = 16.0546 (14) Å
c = 10.1155 (8) Å
β = 97.777 (2)°
V = 1439.0 (2) Å^3
Z = 4
$F(000)$ = 576
D_x = 1.243 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3504 reflections
θ = 2.4–28.1°
μ = 0.08 mm^{-1}
T = 296 K
Block, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
Detector resolution: 0.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.950, T_{max} = 0.992
27358 measured reflections
3000 independent reflections
1869 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 26.6°, θ_{min} = 2.4°
h = −11→11
k = −20→20
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.141
S = 1.05
3000 reflections
183 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 0.4589P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.011 (2)

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}
N1	0.35185 (18)	0.62845 (10)	0.68452 (15)	0.0453 (4)
N2	0.39911 (19)	0.66723 (12)	0.57496 (17)	0.0531 (5)
C3	0.3664 (2)	0.61450 (15)	0.4763 (2)	0.0522 (5)
C4	0.3031 (2)	0.53927 (13)	0.51801 (18)	0.0479 (5)
C5	0.2954 (2)	0.55100 (12)	0.65407 (18)	0.0427 (5)
C11	0.3634 (2)	0.67370 (12)	0.80659 (19)	0.0448 (5)
C12	0.2377 (2)	0.68566 (13)	0.8697 (2)	0.0520 (5)
H12	0.1447	0.6644	0.8324	0.062*
C13	0.2501 (3)	0.72930 (14)	0.9883 (2)	0.0618 (6)
H13	0.1656	0.7373	1.0312	0.074*
C14	0.3876 (3)	0.76093 (15)	1.0431 (2)	0.0674 (7)
H14	0.3962	0.7897	1.1235	0.081*
C15	0.5118 (3)	0.75014 (15)	0.9793 (2)	0.0685 (7)
H15	0.6040	0.7727	1.0158	0.082*
C16	0.5011 (2)	0.70600 (14)	0.8610 (2)	0.0574 (6)
H16	0.5860	0.6981	0.8185	0.069*
C31	0.3991 (3)	0.63675 (19)	0.3393 (2)	0.0774 (8)
H31A	0.4450	0.6909	0.3412	0.116*
H31B	0.3067	0.6373	0.2787	0.116*
H31C	0.4666	0.5963	0.3100	0.116*
C41	0.2749 (3)	0.46445 (16)	0.4411 (2)	0.0646 (6)
H41	0.2456	0.4179	0.4859	0.078*
O41	0.2855 (2)	0.45590 (13)	0.32399 (16)	0.0913 (6)
N51	0.24068 (18)	0.50265 (10)	0.74926 (15)	0.0456 (4)
C52	0.1312 (3)	0.43642 (16)	0.7089 (2)	0.0616 (6)
H52A	0.1842	0.3857	0.6916	0.074*
H52B	0.0682	0.4524	0.6272	0.074*
C53	0.0347 (3)	0.42096 (16)	0.8158 (2)	0.0653 (6)
H53A	−0.0323	0.3745	0.7900	0.078*
H53B	−0.0269	0.4697	0.8254	0.078*
C54	0.1283 (3)	0.40178 (14)	0.9484 (2)	0.0596 (6)
H54A	0.1778	0.3483	0.9432	0.071*
H54B	0.0629	0.3982	1.0173	0.071*
C55	0.2464 (2)	0.46891 (15)	0.9851 (2)	0.0560 (6)
H55A	0.1969	0.5204	1.0045	0.067*
H55B	0.3124	0.4523	1.0648	0.067*
C56	0.3381 (2)	0.48331 (13)	0.87430 (19)	0.0489 (5)
H56A	0.4074	0.5291	0.8975	0.059*
H56B	0.3972	0.4339	0.8621	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0486 (9)	0.0487 (10)	0.0407 (9)	−0.0008 (8)	0.0135 (7)	0.0070 (7)
N2	0.0523 (10)	0.0596 (11)	0.0498 (10)	0.0034 (8)	0.0161 (8)	0.0169 (9)

C3	0.0477 (12)	0.0675 (14)	0.0430 (11)	0.0110 (10)	0.0123 (9)	0.0149 (11)
C4	0.0496 (12)	0.0587 (13)	0.0356 (10)	0.0092 (10)	0.0067 (8)	0.0054 (9)
C5	0.0402 (10)	0.0497 (12)	0.0383 (10)	0.0035 (9)	0.0059 (8)	0.0056 (8)
C11	0.0491 (12)	0.0418 (11)	0.0434 (11)	−0.0002 (9)	0.0055 (9)	0.0065 (9)
C12	0.0516 (12)	0.0548 (13)	0.0508 (12)	−0.0007 (10)	0.0110 (10)	0.0015 (10)
C13	0.0809 (17)	0.0562 (14)	0.0508 (13)	0.0075 (12)	0.0180 (12)	0.0024 (11)
C14	0.102 (2)	0.0501 (14)	0.0471 (13)	0.0009 (13)	−0.0025 (13)	0.0030 (10)
C15	0.0754 (17)	0.0559 (14)	0.0676 (16)	−0.0100 (13)	−0.0150 (13)	0.0043 (12)
C16	0.0505 (13)	0.0552 (14)	0.0655 (14)	−0.0028 (10)	0.0049 (10)	0.0091 (11)
C31	0.0787 (17)	0.108 (2)	0.0483 (14)	0.0014 (15)	0.0186 (12)	0.0238 (14)
C41	0.0819 (16)	0.0713 (16)	0.0397 (12)	0.0097 (13)	0.0041 (11)	−0.0009 (11)
O41	0.1297 (16)	0.1042 (15)	0.0387 (10)	0.0246 (12)	0.0068 (9)	−0.0075 (9)
N51	0.0496 (9)	0.0509 (10)	0.0355 (8)	−0.0103 (8)	0.0035 (7)	0.0041 (7)
C52	0.0649 (14)	0.0685 (15)	0.0503 (13)	−0.0166 (12)	0.0039 (11)	−0.0052 (11)
C53	0.0580 (13)	0.0693 (16)	0.0700 (15)	−0.0159 (12)	0.0142 (11)	−0.0012 (12)
C54	0.0655 (14)	0.0564 (14)	0.0611 (14)	−0.0045 (11)	0.0247 (11)	0.0074 (11)
C55	0.0619 (13)	0.0641 (14)	0.0427 (12)	−0.0004 (11)	0.0098 (10)	0.0079 (10)
C56	0.0515 (11)	0.0534 (12)	0.0414 (11)	−0.0026 (10)	0.0044 (9)	0.0101 (9)

Geometric parameters (Å, º)

N1—C5	1.361 (3)	C31—H31B	0.9600
N1—N2	1.386 (2)	C31—H31C	0.9600
N1—C11	1.424 (2)	C41—O41	1.209 (3)
N2—C3	1.311 (3)	C41—H41	0.9300
C3—C4	1.422 (3)	N51—C52	1.465 (3)
C3—C31	1.498 (3)	N51—C56	1.469 (2)
C4—C5	1.400 (3)	C52—C53	1.493 (3)
C4—C41	1.434 (3)	C52—H52A	0.9700
C5—N51	1.377 (2)	C52—H52B	0.9700
C11—C12	1.380 (3)	C53—C54	1.514 (3)
C11—C16	1.380 (3)	C53—H53A	0.9700
C12—C13	1.381 (3)	C53—H53B	0.9700
C12—H12	0.9300	C54—C55	1.519 (3)
C13—C14	1.375 (3)	C54—H54A	0.9700
C13—H13	0.9300	C54—H54B	0.9700
C14—C15	1.369 (4)	C55—C56	1.493 (3)
C14—H14	0.9300	C55—H55A	0.9700
C15—C16	1.383 (3)	C55—H55B	0.9700
C15—H15	0.9300	C56—H56A	0.9700
C16—H16	0.9300	C56—H56B	0.9700
C31—H31A	0.9600		

C5—N1—N2	111.91 (16)	O41—C41—C4	126.5 (2)
C5—N1—C11	130.03 (15)	O41—C41—H41	116.7
N2—N1—C11	118.02 (16)	C4—C41—H41	116.7
C3—N2—N1	104.94 (17)	C5—N51—C52	120.08 (16)
N2—C3—C4	112.29 (17)	C5—N51—C56	119.72 (15)

N2—C3—C31	119.9 (2)	C52—N51—C56	112.51 (16)
C4—C3—C31	127.8 (2)	N51—C52—C53	110.39 (18)
C5—C4—C3	104.59 (18)	N51—C52—H52A	109.6
C5—C4—C41	128.1 (2)	C53—C52—H52A	109.6
C3—C4—C41	126.73 (19)	N51—C52—H52B	109.6
N1—C5—N51	120.83 (16)	C53—C52—H52B	109.6
N1—C5—C4	106.22 (16)	H52A—C52—H52B	108.1
N51—C5—C4	132.91 (19)	C52—C53—C54	111.81 (19)
C12—C11—C16	120.2 (2)	C52—C53—H53A	109.3
C12—C11—N1	120.24 (18)	C54—C53—H53A	109.3
C16—C11—N1	119.60 (18)	C52—C53—H53B	109.3
C11—C12—C13	119.8 (2)	C54—C53—H53B	109.3
C11—C12—H12	120.1	H53A—C53—H53B	107.9
C13—C12—H12	120.1	C53—C54—C55	110.77 (18)
C14—C13—C12	120.0 (2)	C53—C54—H54A	109.5
C14—C13—H13	120.0	C55—C54—H54A	109.5
C12—C13—H13	120.0	C53—C54—H54B	109.5
C15—C14—C13	120.1 (2)	C55—C54—H54B	109.5
C15—C14—H14	119.9	H54A—C54—H54B	108.1
C13—C14—H14	119.9	C56—C55—C54	111.16 (18)
C14—C15—C16	120.5 (2)	C56—C55—H55A	109.4
C14—C15—H15	119.8	C54—C55—H55A	109.4
C16—C15—H15	119.8	C56—C55—H55B	109.4
C11—C16—C15	119.4 (2)	C54—C55—H55B	109.4
C11—C16—H16	120.3	H55A—C55—H55B	108.0
C15—C16—H16	120.3	N51—C56—C55	110.90 (17)
C3—C31—H31A	109.5	N51—C56—H56A	109.5
C3—C31—H31B	109.5	C55—C56—H56A	109.5
H31A—C31—H31B	109.5	N51—C56—H56B	109.5
C3—C31—H31C	109.5	C55—C56—H56B	109.5
H31A—C31—H31C	109.5	H56A—C56—H56B	108.0
H31B—C31—H31C	109.5		

C5—N1—N2—C3	2.2 (2)	N1—C11—C12—C13	179.70 (19)
C11—N1—N2—C3	−175.79 (16)	C11—C12—C13—C14	0.2 (3)
N1—N2—C3—C4	−2.3 (2)	C12—C13—C14—C15	0.8 (3)
N1—N2—C3—C31	178.66 (18)	C13—C14—C15—C16	−1.3 (4)
N2—C3—C4—C5	1.5 (2)	C12—C11—C16—C15	0.2 (3)
C31—C3—C4—C5	−179.5 (2)	N1—C11—C16—C15	179.78 (18)
N2—C3—C4—C41	−170.3 (2)	C14—C15—C16—C11	0.8 (3)
C31—C3—C4—C41	8.7 (3)	C5—C4—C41—O41	−178.4 (2)
N2—N1—C5—N51	−179.19 (16)	C3—C4—C41—O41	−8.4 (4)
C11—N1—C5—N51	−1.5 (3)	N1—C5—N51—C52	156.64 (19)
N2—N1—C5—C4	−1.3 (2)	C4—C5—N51—C52	−20.6 (3)
C11—N1—C5—C4	176.41 (18)	N1—C5—N51—C56	−56.2 (3)
C3—C4—C5—N1	−0.1 (2)	C4—C5—N51—C56	126.5 (2)
C41—C4—C5—N1	171.6 (2)	C5—N51—C52—C53	−152.67 (19)
C3—C4—C5—N51	177.5 (2)	C56—N51—C52—C53	58.0 (3)

C41—C4—C5—N51	−10.8 (4)	N51—C52—C53—C54	−55.2 (3)
C5—N1—C11—C12	−53.6 (3)	C52—C53—C54—C55	52.9 (3)
N2—N1—C11—C12	124.00 (19)	C53—C54—C55—C56	−52.5 (3)
C5—N1—C11—C16	126.9 (2)	C5—N51—C56—C55	152.27 (18)
N2—N1—C11—C16	−55.6 (2)	C52—N51—C56—C55	−58.3 (2)
C16—C11—C12—C13	−0.7 (3)	C54—C55—C56—N51	54.9 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···*Cg*1^{i}	0.93	2.97	3.848 (3)	159
C52—H52*A*···*Cg*2^{ii}	0.97	2.96	3.761 (3)	140

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

(3*RS*)-2-Acetyl-5-(4-azidophenyl)-5′-(2-chlorophenoxy)-3′-methyl-1′-phenyl-3,4-dihydro-1′*H*,2*H*-[3,4′-bipyrazole] (IX)

Crystal data

$C_{27}H_{22}ClN_7O_2$
M_r = 511.97
Triclinic, $P\overline{1}$
a = 10.8804 (4) Å
b = 11.3363 (4) Å
c = 11.5737 (4) Å
α = 97.294 (2)°
β = 90.050 (2)°
γ = 117.840 (2)°
V = 1249.15 (8) Å^3
Z = 2
F(000) = 532
D_x = 1.361 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 5359 reflections
θ = 2.1–26.9°
μ = 0.19 mm^{-1}
T = 296 K
Block, brown
0.19 × 0.17 × 0.14 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
Detector resolution: 0.3333 pixels mm^{-1}
φ and *ω* scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.930, T_{max} = 0.973
31603 measured reflections
5197 independent reflections
3299 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 26.6°, θ_{min} = 2.2°
h = −13→13
k = −14→14
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.126
S = 1.01
5197 reflections
336 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.5649P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 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}
N1	0.71807 (17)	0.56761 (16)	0.43542 (14)	0.0402 (4)
N2	0.76299 (18)	0.58772 (17)	0.55073 (15)	0.0440 (4)
C3	0.7240 (2)	0.6740 (2)	0.60408 (18)	0.0421 (5)
C4	0.6537 (2)	0.71218 (19)	0.52591 (17)	0.0389 (5)
C5	0.6526 (2)	0.64192 (19)	0.42071 (17)	0.0386 (5)
C11	0.7491 (2)	0.4825 (2)	0.35347 (19)	0.0440 (5)
C12	0.6618 (3)	0.4089 (3)	0.2551 (2)	0.0624 (7)
H12	0.5830	0.4175	0.2385	0.075*
C13	0.6939 (4)	0.3223 (3)	0.1819 (3)	0.0841 (9)
H13	0.6368	0.2732	0.1149	0.101*
C14	0.8090 (4)	0.3079 (3)	0.2070 (3)	0.0861 (10)
H14	0.8276	0.2468	0.1588	0.103*
C15	0.8964 (3)	0.3838 (3)	0.3033 (3)	0.0732 (8)
H15	0.9758	0.3759	0.3192	0.088*
C16	0.8672 (3)	0.4714 (2)	0.3765 (2)	0.0548 (6)
H16	0.9271	0.5232	0.4415	0.066*
C31	0.7568 (3)	0.7191 (3)	0.73259 (19)	0.0600 (7)
H31A	0.8224	0.6925	0.7594	0.090*
H31B	0.6729	0.6784	0.7726	0.090*
H31C	0.7962	0.8155	0.7483	0.090*
N41	0.61493 (18)	0.95120 (17)	0.40567 (16)	0.0445 (4)
N42	0.68480 (18)	0.93628 (16)	0.49793 (16)	0.0455 (4)
C43	0.5997 (2)	0.8120 (2)	0.55003 (19)	0.0438 (5)
H43	0.5992	0.8350	0.6345	0.053*
C44	0.4552 (2)	0.7677 (2)	0.4914 (2)	0.0470 (5)
H44A	0.4112	0.6733	0.4578	0.056*
H44B	0.3950	0.7826	0.5464	0.056*
C45	0.4878 (2)	0.8570 (2)	0.39832 (19)	0.0419 (5)
C421	0.8207 (2)	1.0215 (2)	0.5319 (2)	0.0518 (6)
O421	0.87539 (17)	1.00095 (17)	0.61378 (16)	0.0665 (5)
C422	0.8969 (3)	1.1362 (2)	0.4651 (3)	0.0672 (7)
H42A	0.9713	1.2091	0.5146	0.101*
H42B	0.8338	1.1661	0.4387	0.101*
H42C	0.9344	1.1074	0.3990	0.101*
C451	0.3863 (2)	0.8423 (2)	0.30793 (19)	0.0438 (5)
C452	0.4201 (2)	0.9316 (2)	0.2269 (2)	0.0548 (6)
H432	0.5096	1.0035	0.2303	0.066*
C453	0.3229 (3)	0.9152 (3)	0.1418 (2)	0.0618 (7)
H453	0.3470	0.9759	0.0883	0.074*

C454	0.1896 (2)	0.8088 (3)	0.1354 (2)	0.0547 (6)
C455	0.1541 (3)	0.7189 (3)	0.2142 (2)	0.0601 (7)
H455	0.0645	0.6470	0.2100	0.072*
C456	0.2518 (2)	0.7356 (2)	0.2994 (2)	0.0550 (6)
H456	0.2271	0.6742	0.3522	0.066*
O51	0.59236 (14)	0.63452 (14)	0.31443 (12)	0.0439 (4)
C51	0.6722 (2)	0.7221 (2)	0.23830 (17)	0.0385 (5)
C52	0.6039 (2)	0.7120 (2)	0.13389 (18)	0.0456 (5)
Cl52	0.43183 (6)	0.59396 (7)	0.10230 (5)	0.0642 (2)
C53	0.6747 (3)	0.7974 (3)	0.0551 (2)	0.0687 (8)
H53	0.6296	0.7910	−0.0155	0.082*
C54	0.8119 (3)	0.8921 (3)	0.0802 (2)	0.0785 (9)
H54	0.8589	0.9505	0.0271	0.094*
C55	0.8794 (3)	0.9006 (3)	0.1834 (2)	0.0636 (7)
H55	0.9724	0.9644	0.1998	0.076*
C56	0.8105 (2)	0.8153 (2)	0.26297 (19)	0.0480 (5)
H56	0.8567	0.8205	0.3326	0.058*
N451	0.0955 (3)	0.8005 (3)	0.0454 (2)	0.0742 (7)
N452	−0.0178 (3)	0.6960 (3)	0.0307 (2)	0.0877 (8)
N453	−0.1227 (4)	0.6080 (4)	0.0081 (3)	0.1355 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0418 (10)	0.0384 (9)	0.0397 (10)	0.0174 (8)	−0.0021 (7)	0.0100 (7)
N2	0.0451 (10)	0.0426 (10)	0.0416 (10)	0.0167 (8)	−0.0031 (8)	0.0136 (8)
C3	0.0400 (12)	0.0384 (11)	0.0407 (12)	0.0109 (10)	0.0001 (9)	0.0119 (9)
C4	0.0391 (11)	0.0337 (10)	0.0387 (11)	0.0115 (9)	0.0015 (9)	0.0109 (9)
C5	0.0357 (11)	0.0347 (11)	0.0403 (11)	0.0109 (9)	−0.0020 (9)	0.0117 (9)
C11	0.0487 (13)	0.0374 (11)	0.0463 (12)	0.0182 (10)	0.0078 (10)	0.0158 (10)
C12	0.0735 (17)	0.0608 (15)	0.0554 (15)	0.0354 (14)	−0.0052 (13)	0.0016 (12)
C13	0.121 (3)	0.079 (2)	0.0584 (18)	0.057 (2)	−0.0056 (17)	−0.0079 (15)
C14	0.130 (3)	0.086 (2)	0.072 (2)	0.074 (2)	0.030 (2)	0.0143 (17)
C15	0.082 (2)	0.0752 (19)	0.087 (2)	0.0523 (17)	0.0281 (17)	0.0313 (17)
C16	0.0554 (15)	0.0517 (14)	0.0643 (15)	0.0287 (12)	0.0084 (12)	0.0175 (12)
C31	0.0672 (16)	0.0641 (16)	0.0424 (13)	0.0250 (13)	−0.0017 (11)	0.0104 (11)
N41	0.0434 (10)	0.0365 (9)	0.0544 (11)	0.0186 (8)	0.0051 (8)	0.0110 (8)
N42	0.0397 (10)	0.0341 (9)	0.0574 (12)	0.0118 (8)	0.0002 (8)	0.0116 (8)
C43	0.0445 (12)	0.0377 (11)	0.0463 (12)	0.0159 (10)	0.0050 (10)	0.0103 (9)
C44	0.0413 (12)	0.0416 (12)	0.0575 (14)	0.0171 (10)	0.0074 (10)	0.0155 (10)
C45	0.0401 (12)	0.0333 (11)	0.0527 (13)	0.0174 (10)	0.0078 (10)	0.0072 (9)
C421	0.0443 (13)	0.0400 (12)	0.0657 (16)	0.0166 (11)	0.0009 (12)	0.0034 (11)
O421	0.0530 (10)	0.0554 (10)	0.0780 (12)	0.0154 (9)	−0.0141 (9)	0.0071 (9)
C422	0.0487 (14)	0.0424 (13)	0.097 (2)	0.0082 (11)	0.0075 (13)	0.0173 (13)
C451	0.0418 (12)	0.0371 (11)	0.0530 (13)	0.0189 (10)	0.0057 (10)	0.0068 (10)
C452	0.0473 (13)	0.0476 (13)	0.0644 (16)	0.0159 (11)	0.0038 (11)	0.0170 (12)
C453	0.0617 (16)	0.0609 (16)	0.0640 (16)	0.0263 (14)	0.0049 (13)	0.0235 (13)
C454	0.0501 (14)	0.0638 (15)	0.0510 (14)	0.0278 (13)	0.0019 (11)	0.0073 (12)

C455	0.0433 (13)	0.0607 (15)	0.0644 (16)	0.0140 (12)	0.0027 (12)	0.0121 (13)
C456	0.0470 (14)	0.0545 (14)	0.0593 (15)	0.0179 (12)	0.0062 (11)	0.0184 (11)
O51	0.0410 (8)	0.0437 (8)	0.0401 (8)	0.0123 (7)	−0.0050 (6)	0.0148 (6)
C51	0.0421 (12)	0.0388 (11)	0.0356 (11)	0.0190 (10)	0.0035 (9)	0.0094 (9)
C52	0.0457 (12)	0.0528 (13)	0.0386 (12)	0.0229 (11)	−0.0004 (9)	0.0087 (10)
Cl52	0.0497 (4)	0.0759 (4)	0.0539 (4)	0.0191 (3)	−0.0120 (3)	0.0076 (3)
C53	0.0667 (17)	0.090 (2)	0.0464 (14)	0.0300 (16)	−0.0002 (12)	0.0273 (14)
C54	0.0714 (19)	0.086 (2)	0.0658 (18)	0.0193 (16)	0.0135 (15)	0.0425 (16)
C55	0.0487 (14)	0.0633 (16)	0.0617 (16)	0.0098 (12)	0.0057 (12)	0.0189 (13)
C56	0.0449 (13)	0.0504 (13)	0.0438 (12)	0.0178 (11)	−0.0009 (10)	0.0090 (10)
N451	0.0607 (15)	0.0910 (18)	0.0658 (15)	0.0306 (14)	−0.0037 (12)	0.0147 (13)
N452	0.0718 (18)	0.105 (2)	0.0770 (18)	0.0341 (18)	−0.0142 (14)	0.0112 (15)
N453	0.084 (2)	0.129 (3)	0.141 (3)	0.009 (2)	−0.044 (2)	0.014 (2)

Geometric parameters (Å, º)

N1—C5	1.358 (3)	C45—C451	1.457 (3)
N1—N2	1.375 (2)	C421—O421	1.221 (3)
N1—C11	1.420 (3)	C421—C422	1.492 (3)
N2—C3	1.324 (3)	C422—H42A	0.9600
C3—C4	1.413 (3)	C422—H42B	0.9600
C3—C31	1.496 (3)	C422—H42C	0.9600
C4—C5	1.364 (3)	C451—C456	1.390 (3)
C4—C43	1.498 (3)	C451—C452	1.391 (3)
C5—O51	1.368 (2)	C452—C453	1.375 (3)
C11—C16	1.377 (3)	C452—H432	0.9300
C11—C12	1.382 (3)	C453—C454	1.381 (3)
C12—C13	1.383 (4)	C453—H453	0.9300
C12—H12	0.9300	C454—C455	1.374 (3)
C13—C14	1.371 (4)	C454—N451	1.423 (3)
C13—H13	0.9300	C455—C456	1.378 (3)
C14—C15	1.370 (4)	C455—H455	0.9300
C14—H14	0.9300	C456—H456	0.9300
C15—C16	1.374 (3)	O51—C51	1.391 (2)
C15—H15	0.9300	C51—C56	1.378 (3)
C16—H16	0.9300	C51—C52	1.382 (3)
C31—H31A	0.9600	C52—C53	1.376 (3)
C31—H31B	0.9600	C52—Cl52	1.721 (2)
C31—H31C	0.9600	C53—C54	1.374 (4)
N41—C45	1.288 (3)	C53—H53	0.9300
N41—N42	1.382 (2)	C54—C55	1.371 (4)
N42—C421	1.357 (3)	C54—H54	0.9300
N42—C43	1.485 (3)	C55—C56	1.377 (3)
C43—C44	1.536 (3)	C55—H55	0.9300
C43—H43	0.9800	C56—H56	0.9300
C44—C45	1.500 (3)	N451—N452	1.239 (3)
C44—H44A	0.9700	N452—N453	1.112 (4)
C44—H44B	0.9700		

C5—N1—N2	109.94 (17)	H44A—C44—H44B	109.1
C5—N1—C11	131.03 (17)	N41—C45—C451	121.9 (2)
N2—N1—C11	118.97 (17)	N41—C45—C44	114.0 (2)
C3—N2—N1	105.22 (16)	C451—C45—C44	124.14 (18)
N2—C3—C4	112.06 (18)	O421—C421—N42	119.4 (2)
N2—C3—C31	119.7 (2)	O421—C421—C422	123.0 (2)
C4—C3—C31	128.3 (2)	N42—C421—C422	117.5 (2)
C5—C4—C3	103.77 (19)	C421—C422—H42A	109.5
C5—C4—C43	127.47 (19)	C421—C422—H42B	109.5
C3—C4—C43	128.67 (19)	H42A—C422—H42B	109.5
N1—C5—C4	109.00 (18)	C421—C422—H42C	109.5
N1—C5—O51	121.29 (18)	H42A—C422—H42C	109.5
C4—C5—O51	129.63 (19)	H42B—C422—H42C	109.5
C16—C11—C12	120.3 (2)	C456—C451—C452	117.9 (2)
C16—C11—N1	118.1 (2)	C456—C451—C45	120.2 (2)
C12—C11—N1	121.5 (2)	C452—C451—C45	121.93 (19)
C11—C12—C13	118.8 (3)	C453—C452—C451	120.9 (2)
C11—C12—H12	120.6	C453—C452—H432	119.5
C13—C12—H12	120.6	C451—C452—H432	119.5
C14—C13—C12	120.8 (3)	C452—C453—C454	120.2 (2)
C14—C13—H13	119.6	C452—C453—H453	119.9
C12—C13—H13	119.6	C454—C453—H453	119.9
C15—C14—C13	119.8 (3)	C455—C454—C453	119.9 (2)
C15—C14—H14	120.1	C455—C454—N451	123.8 (2)
C13—C14—H14	120.1	C453—C454—N451	116.3 (2)
C14—C15—C16	120.3 (3)	C454—C455—C456	119.8 (2)
C14—C15—H15	119.9	C454—C455—H455	120.1
C16—C15—H15	119.9	C456—C455—H455	120.1
C15—C16—C11	119.9 (3)	C455—C456—C451	121.4 (2)
C15—C16—H16	120.0	C455—C456—H456	119.3
C11—C16—H16	120.0	C451—C456—H456	119.3
C3—C31—H31A	109.5	C5—O51—C51	118.76 (15)
C3—C31—H31B	109.5	C56—C51—C52	120.60 (19)
H31A—C31—H31B	109.5	C56—C51—O51	123.61 (18)
C3—C31—H31C	109.5	C52—C51—O51	115.78 (17)
H31A—C31—H31C	109.5	C53—C52—C51	119.3 (2)
H31B—C31—H31C	109.5	C53—C52—Cl52	120.11 (18)
C45—N41—N42	107.91 (17)	C51—C52—Cl52	120.55 (16)
C421—N42—N41	123.31 (18)	C54—C53—C52	120.3 (2)
C421—N42—C43	123.29 (19)	C54—C53—H53	119.9
N41—N42—C43	113.24 (16)	C52—C53—H53	119.9
N42—C43—C4	111.51 (17)	C55—C54—C53	120.1 (2)
N42—C43—C44	100.58 (16)	C55—C54—H54	120.0
C4—C43—C44	115.07 (17)	C53—C54—H54	120.0
N42—C43—H43	109.8	C54—C55—C56	120.5 (2)
C4—C43—H43	109.8	C54—C55—H55	119.8
C44—C43—H43	109.8	C56—C55—H55	119.8

C45—C44—C43	102.78 (17)	C55—C56—C51	119.2 (2)
C45—C44—H44A	111.2	C55—C56—H56	120.4
C43—C44—H44A	111.2	C51—C56—H56	120.4
C45—C44—H44B	111.2	N452—N451—C454	115.9 (2)
C43—C44—H44B	111.2	N453—N452—N451	172.5 (4)
C5—N1—N2—C3	0.0 (2)	N42—N41—C45—C451	−178.72 (18)
C11—N1—N2—C3	177.67 (17)	N42—N41—C45—C44	2.3 (2)
N1—N2—C3—C4	−0.1 (2)	C43—C44—C45—N41	−9.3 (2)
N1—N2—C3—C31	−179.89 (18)	C43—C44—C45—C451	171.76 (19)
N2—C3—C4—C5	0.2 (2)	N41—N42—C421—O421	−179.4 (2)
C31—C3—C4—C5	179.9 (2)	C43—N42—C421—O421	−4.4 (3)
N2—C3—C4—C43	−176.68 (18)	N41—N42—C421—C422	−0.1 (3)
C31—C3—C4—C43	3.1 (3)	C43—N42—C421—C422	174.9 (2)
N2—N1—C5—C4	0.1 (2)	N41—C45—C451—C456	177.0 (2)
C11—N1—C5—C4	−177.18 (19)	C44—C45—C451—C456	−4.2 (3)
N2—N1—C5—O51	−176.85 (16)	N41—C45—C451—C452	−2.0 (3)
C11—N1—C5—O51	5.8 (3)	C44—C45—C451—C452	176.9 (2)
C3—C4—C5—N1	−0.2 (2)	C456—C451—C452—C453	0.5 (4)
C43—C4—C5—N1	176.73 (18)	C45—C451—C452—C453	179.5 (2)
C3—C4—C5—O51	176.47 (19)	C451—C452—C453—C454	−0.2 (4)
C43—C4—C5—O51	−6.6 (3)	C452—C453—C454—C455	−0.2 (4)
C5—N1—C11—C16	149.1 (2)	C452—C453—C454—N451	179.3 (2)
N2—N1—C11—C16	−28.0 (3)	C453—C454—C455—C456	0.2 (4)
C5—N1—C11—C12	−33.1 (3)	N451—C454—C455—C456	−179.3 (2)
N2—N1—C11—C12	149.8 (2)	C454—C455—C456—C451	0.2 (4)
C16—C11—C12—C13	1.3 (4)	C452—C451—C456—C455	−0.6 (3)
N1—C11—C12—C13	−176.5 (2)	C45—C451—C456—C455	−179.5 (2)
C11—C12—C13—C14	0.9 (4)	N1—C5—O51—C51	−90.0 (2)
C12—C13—C14—C15	−2.5 (5)	C4—C5—O51—C51	93.7 (2)
C13—C14—C15—C16	1.8 (5)	C5—O51—C51—C56	1.2 (3)
C14—C15—C16—C11	0.4 (4)	C5—O51—C51—C52	−178.15 (19)
C12—C11—C16—C15	−2.0 (3)	C56—C51—C52—C53	−0.9 (3)
N1—C11—C16—C15	175.9 (2)	O51—C51—C52—C53	178.4 (2)
C45—N41—N42—C421	−178.2 (2)	C56—C51—C52—Cl52	179.07 (17)
C45—N41—N42—C43	6.3 (2)	O51—C51—C52—Cl52	−1.6 (3)
C421—N42—C43—C4	−64.4 (3)	C51—C52—C53—C54	−0.2 (4)
N41—N42—C43—C4	111.03 (19)	Cl52—C52—C53—C54	179.7 (2)
C421—N42—C43—C44	173.1 (2)	C52—C53—C54—C55	0.9 (5)
N41—N42—C43—C44	−11.4 (2)	C53—C54—C55—C56	−0.5 (5)
C5—C4—C43—N42	−67.9 (3)	C54—C55—C56—C51	−0.7 (4)
C3—C4—C43—N42	108.3 (2)	C52—C51—C56—C55	1.4 (3)
C5—C4—C43—C44	45.8 (3)	O51—C51—C56—C55	−177.9 (2)
C3—C4—C43—C44	−138.0 (2)	C455—C454—N451—N452	−9.4 (4)
N42—C43—C44—C45	11.3 (2)	C453—C454—N451—N452	171.1 (3)
C4—C43—C44—C45	−108.61 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···N451^{i}	0.93	2.58	3.378 (5)	144
C55—H55···O421^{ii}	0.93	2.59	3.228 (4)	126

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

(3*RS*)-2-Acetyl-5-(4-azidophenyl)-3′-methyl-5′-(naphthalen-2-yloxy)-1′-phenyl-3,4-dihydro-1′*H*,2*H*-[3,4′-bipyrazole] (X)

Crystal data

$C_{31}H_{25}N_7O_2$
$M_r = 527.58$
Triclinic, $P\overline{1}$
$a = 10.4911$ (11) Å
$b = 11.2048$ (12) Å
$c = 13.5943$ (17) Å
$\alpha = 105.323$ (3)°
$\beta = 93.505$ (3)°
$\gamma = 117.460$ (3)°
$V = 1335.9$ (3) Å^3
$Z = 2$
$F(000) = 552$
$D_x = 1.312$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5566 reflections
$\theta = 2.2$–27.0°
$\mu = 0.09$ mm^{-1}
$T = 296$ K
Block, orange
0.15 × 0.13 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine focus sealed tube
Graphite monochromator
Detector resolution: 0.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
$T_{min} = 0.926$, $T_{max} = 0.990$
16901 measured reflections
5470 independent reflections
2883 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 26.6°$, $\theta_{min} = 2.2°$
$h = -12 \rightarrow 13$
$k = -13 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.178$
$S = 1.01$
5470 reflections
363 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0878P)^2 + 0.1031P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ 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}
N1	0.6651 (2)	0.45791 (19)	0.57177 (15)	0.0416 (5)

N2	0.6648 (2)	0.41194 (19)	0.46756 (15)	0.0432 (5)
C3	0.5257 (3)	0.3161 (2)	0.42124 (18)	0.0409 (6)
C4	0.4331 (2)	0.2966 (2)	0.49356 (17)	0.0391 (5)
C5	0.5259 (2)	0.3892 (2)	0.58743 (18)	0.0392 (5)
C11	0.8015 (3)	0.5485 (2)	0.64502 (19)	0.0457 (6)
C12	0.8116 (3)	0.6256 (4)	0.7444 (3)	0.0944 (12)
H12	0.7279	0.6222	0.7660	0.113*
C13	0.9477 (4)	0.7090 (4)	0.8131 (3)	0.1192 (15)
H13	0.9540	0.7593	0.8814	0.143*
C14	1.0715 (3)	0.7182 (4)	0.7824 (3)	0.0908 (11)
H14	1.1624	0.7765	0.8285	0.109*
C15	1.0613 (3)	0.6411 (3)	0.6831 (3)	0.0735 (9)
H15	1.1455	0.6460	0.6615	0.088*
C16	0.9265 (3)	0.5558 (3)	0.6146 (2)	0.0579 (7)
H16	0.9203	0.5029	0.5473	0.069*
C31	0.4869 (3)	0.2469 (3)	0.30552 (18)	0.0582 (7)
H31A	0.4656	0.3036	0.2728	0.087*
H31B	0.4021	0.1537	0.2869	0.087*
H31C	0.5681	0.2387	0.2824	0.087*
N41	0.1695 (2)	0.06485 (19)	0.59131 (15)	0.0437 (5)
N42	0.2441 (2)	0.07050 (19)	0.51032 (15)	0.0441 (5)
C43	0.2714 (2)	0.1920 (2)	0.47299 (19)	0.0436 (6)
H43	0.2298	0.1557	0.3979	0.052*
C44	0.1791 (3)	0.2468 (3)	0.5328 (2)	0.0494 (6)
H44A	0.2369	0.3483	0.5702	0.059*
H44B	0.0936	0.2279	0.4858	0.059*
C45	0.1347 (2)	0.1634 (2)	0.60715 (18)	0.0409 (6)
C421	0.2925 (3)	−0.0227 (2)	0.4726 (2)	0.0473 (6)
O421	0.3548 (2)	−0.01416 (18)	0.39939 (15)	0.0622 (5)
C422	0.2662 (3)	−0.1327 (3)	0.5239 (2)	0.0611 (7)
H42A	0.1856	−0.2230	0.4805	0.092*
H42B	0.2432	−0.1049	0.5904	0.092*
H42C	0.3531	−0.1407	0.5336	0.092*
C451	0.0576 (2)	0.1863 (2)	0.68995 (19)	0.0451 (6)
C452	0.0181 (3)	0.1030 (3)	0.7542 (2)	0.0547 (7)
H452	0.0400	0.0297	0.7442	0.066*
C453	−0.0529 (3)	0.1269 (3)	0.8323 (2)	0.0611 (7)
H453	−0.0790	0.0695	0.8743	0.073*
C454	−0.0857 (3)	0.2361 (3)	0.8491 (2)	0.0565 (7)
C455	−0.0469 (3)	0.3205 (3)	0.7863 (2)	0.0595 (7)
H455	−0.0689	0.3938	0.7969	0.071*
C456	0.0244 (3)	0.2966 (3)	0.7078 (2)	0.0532 (7)
H456	0.0507	0.3545	0.6662	0.064*
N451	−0.1584 (3)	0.2531 (3)	0.9322 (2)	0.0777 (7)
N452	−0.1799 (3)	0.3563 (4)	0.9520 (2)	0.0815 (8)
N453	−0.2067 (3)	0.4447 (4)	0.9772 (3)	0.1105 (12)
O51	0.49499 (18)	0.42237 (16)	0.68363 (12)	0.0487 (4)
C51	0.4200 (2)	0.3517 (2)	0.82738 (17)	0.0442 (6)

H51	0.3925	0.4213	0.8433	0.053*
C52	0.4813 (2)	0.3339 (2)	0.74396 (17)	0.0406 (6)
C53	0.5294 (2)	0.2343 (2)	0.71852 (17)	0.0453 (6)
H53	0.5742	0.2262	0.6621	0.054*
C54	0.5090 (3)	0.1493 (3)	0.77839 (18)	0.0469 (6)
H54	0.5402	0.0825	0.7621	0.056*
C54A	0.4420 (3)	0.1604 (2)	0.86413 (18)	0.0438 (6)
C55	0.4151 (3)	0.0699 (3)	0.9256 (2)	0.0589 (7)
H55	0.4434	0.0009	0.9095	0.071*
C56	0.3490 (3)	0.0824 (3)	1.0070 (2)	0.0694 (8)
H56	0.3323	0.0221	1.0463	0.083*
C57	0.3056 (3)	0.1853 (3)	1.0325 (2)	0.0702 (8)
H57	0.2597	0.1926	1.0884	0.084*
C58	0.3298 (3)	0.2748 (3)	0.9765 (2)	0.0605 (7)
H58	0.3013	0.3436	0.9950	0.073*
C58A	0.3978 (2)	0.2648 (2)	0.89043 (17)	0.0426 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0408 (12)	0.0393 (11)	0.0473 (12)	0.0199 (10)	0.0116 (9)	0.0174 (9)
N2	0.0464 (12)	0.0413 (11)	0.0473 (12)	0.0217 (10)	0.0164 (10)	0.0215 (9)
C3	0.0443 (14)	0.0364 (13)	0.0481 (14)	0.0203 (12)	0.0117 (12)	0.0218 (11)
C4	0.0415 (13)	0.0334 (12)	0.0476 (14)	0.0194 (11)	0.0115 (11)	0.0190 (11)
C5	0.0441 (14)	0.0385 (13)	0.0449 (14)	0.0239 (12)	0.0173 (11)	0.0205 (11)
C11	0.0410 (14)	0.0374 (13)	0.0563 (16)	0.0173 (11)	0.0081 (12)	0.0164 (12)
C12	0.0551 (19)	0.102 (3)	0.084 (2)	0.0367 (19)	−0.0005 (17)	−0.026 (2)
C13	0.070 (2)	0.120 (3)	0.099 (3)	0.037 (2)	−0.015 (2)	−0.040 (2)
C14	0.051 (2)	0.079 (2)	0.095 (3)	0.0118 (17)	−0.0135 (18)	0.002 (2)
C15	0.0410 (16)	0.077 (2)	0.092 (2)	0.0178 (15)	0.0115 (16)	0.0335 (19)
C16	0.0437 (16)	0.0615 (17)	0.0608 (17)	0.0181 (14)	0.0144 (13)	0.0230 (14)
C31	0.0644 (17)	0.0618 (17)	0.0491 (16)	0.0312 (15)	0.0116 (13)	0.0198 (13)
N41	0.0374 (11)	0.0353 (11)	0.0577 (13)	0.0146 (9)	0.0101 (9)	0.0208 (9)
N42	0.0424 (11)	0.0344 (11)	0.0598 (13)	0.0186 (9)	0.0162 (10)	0.0216 (9)
C43	0.0391 (13)	0.0401 (13)	0.0548 (15)	0.0179 (11)	0.0114 (11)	0.0236 (11)
C44	0.0419 (14)	0.0420 (14)	0.0704 (17)	0.0205 (12)	0.0146 (12)	0.0274 (13)
C45	0.0324 (12)	0.0305 (12)	0.0541 (15)	0.0103 (10)	0.0050 (11)	0.0167 (11)
C421	0.0350 (13)	0.0373 (14)	0.0636 (17)	0.0156 (11)	0.0085 (12)	0.0130 (12)
O421	0.0629 (12)	0.0537 (11)	0.0772 (13)	0.0328 (10)	0.0268 (11)	0.0227 (10)
C422	0.0575 (16)	0.0433 (15)	0.089 (2)	0.0266 (13)	0.0149 (15)	0.0283 (14)
C451	0.0370 (13)	0.0407 (14)	0.0529 (15)	0.0163 (11)	0.0062 (11)	0.0148 (12)
C452	0.0532 (16)	0.0551 (16)	0.0636 (18)	0.0280 (14)	0.0171 (14)	0.0280 (14)
C453	0.0571 (17)	0.0638 (18)	0.0662 (19)	0.0262 (15)	0.0187 (14)	0.0328 (15)
C454	0.0471 (15)	0.0652 (18)	0.0528 (16)	0.0263 (14)	0.0129 (13)	0.0154 (14)
C455	0.0566 (17)	0.0575 (17)	0.0649 (18)	0.0320 (15)	0.0132 (14)	0.0139 (15)
C456	0.0529 (16)	0.0476 (15)	0.0609 (17)	0.0255 (13)	0.0135 (13)	0.0196 (13)
N451	0.0809 (18)	0.091 (2)	0.0712 (17)	0.0503 (17)	0.0300 (14)	0.0251 (15)
N452	0.0605 (16)	0.088 (2)	0.0682 (18)	0.0283 (16)	0.0139 (13)	0.0004 (16)

N453	0.097 (2)	0.097 (2)	0.111 (3)	0.051 (2)	0.0219 (18)	−0.0110 (19)
O51	0.0650 (11)	0.0464 (10)	0.0478 (10)	0.0340 (9)	0.0224 (8)	0.0206 (8)
C51	0.0475 (14)	0.0432 (14)	0.0431 (14)	0.0258 (12)	0.0098 (11)	0.0096 (11)
C52	0.0415 (13)	0.0411 (13)	0.0382 (13)	0.0201 (11)	0.0072 (11)	0.0129 (11)
C53	0.0489 (14)	0.0511 (15)	0.0420 (14)	0.0294 (13)	0.0130 (11)	0.0150 (12)
C54	0.0547 (15)	0.0474 (15)	0.0464 (15)	0.0325 (13)	0.0093 (12)	0.0137 (12)
C54A	0.0446 (14)	0.0444 (14)	0.0388 (13)	0.0206 (12)	0.0056 (11)	0.0118 (11)
C55	0.0701 (18)	0.0610 (17)	0.0538 (17)	0.0349 (15)	0.0145 (14)	0.0263 (14)
C56	0.082 (2)	0.080 (2)	0.0593 (18)	0.0407 (18)	0.0253 (16)	0.0394 (16)
C57	0.078 (2)	0.091 (2)	0.0538 (17)	0.0450 (19)	0.0273 (15)	0.0314 (17)
C58	0.0674 (18)	0.0701 (19)	0.0484 (16)	0.0382 (16)	0.0194 (14)	0.0169 (14)
C58A	0.0408 (13)	0.0448 (14)	0.0363 (13)	0.0187 (11)	0.0053 (11)	0.0099 (11)

Geometric parameters (Å, º)

N1—C5	1.363 (3)	C422—H42A	0.9600
N1—N2	1.373 (2)	C422—H42B	0.9600
N1—C11	1.422 (3)	C422—H42C	0.9600
N2—C3	1.328 (3)	C451—C452	1.387 (3)
C3—C4	1.411 (3)	C451—C456	1.399 (3)
C3—C31	1.493 (3)	C452—C453	1.373 (3)
C4—C5	1.368 (3)	C452—H452	0.9300
C4—C43	1.505 (3)	C453—C454	1.384 (4)
C5—O51	1.364 (2)	C453—H453	0.9300
C11—C12	1.366 (4)	C454—C455	1.380 (4)
C11—C16	1.372 (3)	C454—N451	1.422 (3)
C12—C13	1.389 (4)	C455—C456	1.378 (3)
C12—H12	0.9300	C455—H455	0.9300
C13—C14	1.356 (5)	C456—H456	0.9300
C13—H13	0.9300	N451—N452	1.243 (4)
C14—C15	1.365 (4)	N452—N453	1.125 (4)
C14—H14	0.9300	O51—C52	1.411 (3)
C15—C16	1.379 (4)	C51—C52	1.352 (3)
C15—H15	0.9300	C51—C58A	1.411 (3)
C16—H16	0.9300	C51—H51	0.9300
C31—H31A	0.9600	C52—C53	1.398 (3)
C31—H31B	0.9600	C53—C54	1.363 (3)
C31—H31C	0.9600	C53—H53	0.9300
N41—C45	1.286 (3)	C54—C54A	1.404 (3)
N41—N42	1.387 (3)	C54—H54	0.9300
N42—C421	1.360 (3)	C54A—C58A	1.419 (3)
N42—C43	1.488 (3)	C54A—C55	1.420 (3)
C43—C44	1.535 (3)	C55—C56	1.352 (3)
C43—H43	0.9800	C55—H55	0.9300
C44—C45	1.506 (3)	C56—C57	1.396 (4)
C44—H44A	0.9700	C56—H56	0.9300
C44—H44B	0.9700	C57—C58	1.357 (4)
C45—C451	1.462 (3)	C57—H57	0.9300

C421—O421	1.224 (3)	C58—C58A	1.413 (3)
C421—C422	1.499 (4)	C58—H58	0.9300
C5—N1—N2	109.79 (18)	N42—C421—C422	117.4 (2)
C5—N1—C11	130.2 (2)	C421—C422—H42A	109.5
N2—N1—C11	119.39 (18)	C421—C422—H42B	109.5
C3—N2—N1	105.52 (18)	H42A—C422—H42B	109.5
N2—C3—C4	111.9 (2)	C421—C422—H42C	109.5
N2—C3—C31	119.0 (2)	H42A—C422—H42C	109.5
C4—C3—C31	129.1 (2)	H42B—C422—H42C	109.5
C5—C4—C3	104.0 (2)	C452—C451—C456	118.0 (2)
C5—C4—C43	128.0 (2)	C452—C451—C45	121.9 (2)
C3—C4—C43	128.0 (2)	C456—C451—C45	120.1 (2)
N1—C5—O51	121.4 (2)	C453—C452—C451	121.1 (2)
N1—C5—C4	108.9 (2)	C453—C452—H452	119.4
O51—C5—C4	129.7 (2)	C451—C452—H452	119.4
C12—C11—C16	119.3 (2)	C452—C453—C454	120.4 (3)
C12—C11—N1	122.4 (2)	C452—C453—H453	119.8
C16—C11—N1	118.3 (2)	C454—C453—H453	119.8
C11—C12—C13	119.5 (3)	C455—C454—C453	119.4 (2)
C11—C12—H12	120.2	C455—C454—N451	124.3 (3)
C13—C12—H12	120.2	C453—C454—N451	116.3 (3)
C14—C13—C12	121.1 (3)	C456—C455—C454	120.2 (2)
C14—C13—H13	119.4	C456—C455—H455	119.9
C12—C13—H13	119.4	C454—C455—H455	119.9
C13—C14—C15	119.3 (3)	C455—C456—C451	120.8 (3)
C13—C14—H14	120.4	C455—C456—H456	119.6
C15—C14—H14	120.4	C451—C456—H456	119.6
C14—C15—C16	120.2 (3)	N452—N451—C454	116.6 (3)
C14—C15—H15	119.9	N453—N452—N451	173.0 (4)
C16—C15—H15	119.9	C5—O51—C52	118.44 (16)
C11—C16—C15	120.6 (3)	C52—C51—C58A	120.1 (2)
C11—C16—H16	119.7	C52—C51—H51	119.9
C15—C16—H16	119.7	C58A—C51—H51	119.9
C3—C31—H31A	109.5	C51—C52—C53	122.4 (2)
C3—C31—H31B	109.5	C51—C52—O51	116.1 (2)
H31A—C31—H31B	109.5	C53—C52—O51	121.5 (2)
C3—C31—H31C	109.5	C54—C53—C52	118.4 (2)
H31A—C31—H31C	109.5	C54—C53—H53	120.8
H31B—C31—H31C	109.5	C52—C53—H53	120.8
C45—N41—N42	108.22 (19)	C53—C54—C54A	121.6 (2)
C421—N42—N41	122.79 (19)	C53—C54—H54	119.2
C421—N42—C43	123.8 (2)	C54A—C54—H54	119.2
N41—N42—C43	113.33 (17)	C54—C54A—C58A	119.1 (2)
N42—C43—C4	111.61 (17)	C54—C54A—C55	122.6 (2)
N42—C43—C44	100.55 (18)	C58A—C54A—C55	118.3 (2)
C4—C43—C44	116.11 (19)	C56—C55—C54A	121.2 (3)
N42—C43—H43	109.4	C56—C55—H55	119.4

C4—C43—H43	109.4	C54A—C55—H55	119.4
C44—C43—H43	109.4	C55—C56—C57	120.3 (3)
C45—C44—C43	103.33 (18)	C55—C56—H56	119.8
C45—C44—H44A	111.1	C57—C56—H56	119.8
C43—C44—H44A	111.1	C58—C57—C56	120.7 (3)
C45—C44—H44B	111.1	C58—C57—H57	119.7
C43—C44—H44B	111.1	C56—C57—H57	119.7
H44A—C44—H44B	109.1	C57—C58—C58A	120.8 (3)
N41—C45—C451	121.0 (2)	C57—C58—H58	119.6
N41—C45—C44	113.7 (2)	C58A—C58—H58	119.6
C451—C45—C44	125.3 (2)	C51—C58A—C58	122.9 (2)
O421—C421—N42	119.7 (2)	C51—C58A—C54A	118.3 (2)
O421—C421—C422	122.9 (2)	C58—C58A—C54A	118.8 (2)

C5—N1—N2—C3	0.0 (2)	N41—N42—C421—O421	178.4 (2)
C11—N1—N2—C3	172.04 (18)	C43—N42—C421—O421	−4.6 (3)
N1—N2—C3—C4	−0.5 (2)	N41—N42—C421—C422	−1.6 (3)
N1—N2—C3—C31	178.74 (18)	C43—N42—C421—C422	175.4 (2)
N2—C3—C4—C5	0.8 (2)	N41—C45—C451—C452	−0.4 (3)
C31—C3—C4—C5	−178.4 (2)	C44—C45—C451—C452	178.8 (2)
N2—C3—C4—C43	−175.98 (19)	N41—C45—C451—C456	178.2 (2)
C31—C3—C4—C43	4.9 (4)	C44—C45—C451—C456	−2.6 (3)
N2—N1—C5—O51	−175.81 (17)	C456—C451—C452—C453	0.6 (4)
C11—N1—C5—O51	13.3 (3)	C45—C451—C452—C453	179.3 (2)
N2—N1—C5—C4	0.5 (2)	C451—C452—C453—C454	−0.4 (4)
C11—N1—C5—C4	−170.4 (2)	C452—C453—C454—C455	0.2 (4)
C3—C4—C5—N1	−0.7 (2)	C452—C453—C454—N451	−179.6 (2)
C43—C4—C5—N1	176.04 (19)	C453—C454—C455—C456	−0.2 (4)
C3—C4—C5—O51	175.1 (2)	N451—C454—C455—C456	179.6 (2)
C43—C4—C5—O51	−8.1 (4)	C454—C455—C456—C451	0.4 (4)
C5—N1—C11—C12	−26.2 (4)	C452—C451—C456—C455	−0.7 (4)
N2—N1—C11—C12	163.7 (3)	C45—C451—C456—C455	−179.3 (2)
C5—N1—C11—C16	152.5 (2)	C455—C454—N451—N452	−4.2 (4)
N2—N1—C11—C16	−17.6 (3)	C453—C454—N451—N452	175.6 (2)
C16—C11—C12—C13	−0.5 (5)	N1—C5—O51—C52	−100.0 (2)
N1—C11—C12—C13	178.2 (3)	C4—C5—O51—C52	84.6 (3)
C11—C12—C13—C14	1.8 (7)	C58A—C51—C52—C53	−2.2 (3)
C12—C13—C14—C15	−1.8 (7)	C58A—C51—C52—O51	178.06 (19)
C13—C14—C15—C16	0.6 (5)	C5—O51—C52—C51	−166.12 (19)
C12—C11—C16—C15	−0.7 (4)	C5—O51—C52—C53	14.2 (3)
N1—C11—C16—C15	−179.4 (2)	C51—C52—C53—C54	2.2 (3)
C14—C15—C16—C11	0.6 (5)	O51—C52—C53—C54	−178.1 (2)
C45—N41—N42—C421	−178.16 (19)	C52—C53—C54—C54A	−0.2 (3)
C45—N41—N42—C43	4.6 (2)	C53—C54—C54A—C58A	−1.6 (3)
C421—N42—C43—C4	−62.2 (3)	C53—C54—C54A—C55	177.8 (2)
N41—N42—C43—C4	115.0 (2)	C54—C54A—C55—C56	−179.3 (2)
C421—N42—C43—C44	174.0 (2)	C58A—C54A—C55—C56	0.1 (4)
N41—N42—C43—C44	−8.7 (2)	C54A—C55—C56—C57	0.0 (4)

C5—C4—C43—N42	−71.3 (3)	C55—C56—C57—C58	−0.4 (4)
C3—C4—C43—N42	104.7 (2)	C56—C57—C58—C58A	0.8 (4)
C5—C4—C43—C44	43.1 (3)	C52—C51—C58A—C58	−177.8 (2)
C3—C4—C43—C44	−140.9 (2)	C52—C51—C58A—C54A	0.3 (3)
N42—C43—C44—C45	8.9 (2)	C57—C58—C58A—C51	177.4 (2)
C4—C43—C44—C45	−111.7 (2)	C57—C58—C58A—C54A	−0.7 (4)
N42—N41—C45—C451	−178.57 (18)	C54—C54A—C58A—C51	1.5 (3)
N42—N41—C45—C44	2.2 (2)	C55—C54A—C58A—C51	−177.9 (2)
C43—C44—C45—N41	−7.5 (2)	C54—C54A—C58A—C58	179.7 (2)
C43—C44—C45—C451	173.2 (2)	C55—C54A—C58A—C58	0.3 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C44—H44*A*···N2^{i}	0.97	2.60	3.397 (4)	139

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