Acta Crystallographica Section C
Structural Chemistry
ISSN 2053-2296

A structural study of 4-aminoantipyrine and six of its Schiff base derivatives

Malitsatsi J. Mnguni and Andreas Lemmerer*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, PO Wits 2050, South Africa
Correspondence e-mail: andreas.lemmerer@wits.ac.za

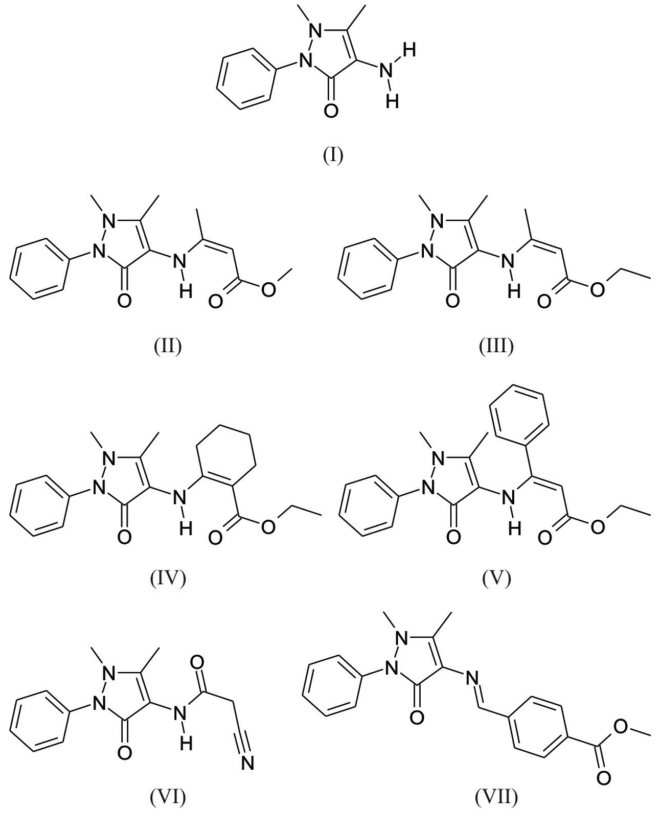
Received 12 November 2014
Accepted 12 December 2014

Six derivatives of 4-amino-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one (4-aminoantipyrine), $C_{11}H_{13}N_3O$, (I), have been synthesized and structurally characterized to investigate the changes in the observed hydrogen-bonding motifs compared to the original 4-aminoantipyrine. The derivatives were synthesized from the reactions of 4-aminoantipyrine with various aldehyde-, ketone- and ester-containing molecules, producing (*Z*)-methyl 3-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]but-2-enoate, $C_{16}H_{19}N_3O_3$, (II), (*Z*)-ethyl 3-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]but-2-enoate, $C_{17}H_{21}N_3O_3$, (III), ethyl 2-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]-cyclohex-1-enecarboxylate, $C_{20}H_{25}N_3O_3$, (IV), (*Z*)-ethyl 3-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-amino]-3-phenylacrylate, $C_{22}H_{23}N_3O_3$, (V), 2-cyano-*N*-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)acetamide, $C_{14}H_{14}N_4O_2$, (VI), and (*E*)-methyl 4-{[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]methyl}benzoate, $C_{20}H_{19}N_3O_3$, (VII). The asymmetric units of all these compounds have one molecule on a general position. The hydrogen bonding in (I) forms chains of molecules *via* intermolecular N—H···O hydrogen bonds around a crystallographic sixfold screw axis. In contrast, the formation of enamines for all derived compounds except (VII) favours the formation of a six-membered intramolecular N—H···O hydrogen-bonded ring in (II)–(V) and an intermolecular N—H···O hydrogen bond in (VI), whereas there is an intramolecular C—H···O hydrogen bond in the structure of imine (VII). All the reported compounds, except for (II), feature π–π interactions, while C—H···π interactions are observed in (II), C—H···O interactions are observed in (I), (III), (V) and (VI), and a C—O···π interaction is observed in (II).

Keywords: 4-aminoantipyrine; hydrogen bonding; crystal structure; π-bonding; anti-inflammatory agent; Schiff bases; biological activity.

1. Introduction

4-Aminoantipyrine (4-AAP), (I), is an anti-inflammatory agent which is used mainly as a reagent to detect phenols and peroxides (Adam, 2013). The use of 4-AAP as a nonsteroidal anti-inflammatory drug is rare because the drug causes agranulocytosis, *i.e.* a drop in the number of infection-fighting white blood cells (Adam, 2013). Some derivatives of 4-aminoantipyrines, such as dipyrone – an anti-inflammatory which is still in use – have medicinal properties (Li *et al.*, 2013, and references therein). 4-AAP can be modified easily by reacting it with either an aldehyde, ketone or ester functional group to form Schiff bases and the prepared derivatives then show increased biological activities, such as antitumor, fungicidal, bactericidal, antiviral, anti-inflammatory, antipyretic, analgesic, antiproliferative and antioxidant activities (Cunha *et al.*, 2005; Schilf *et al.*, 2013). Metal complexes of 4-AAP-derived Schiff bases have been prepared and tested for biological activity also (Leelavathy & Antony, 2013; El-Bindary *et al.*, 2013). Molecular salt complexes have also been prepared with quinol and picric acid (Adam, 2013). We synthesized six derivatives of 4-AAP, (II)–(VII) (see Scheme 1), and discuss the changes in molecular packing and



Scheme 1

hydrogen bonding compared to those of the parent 4-AAP, (I) (Scheme 1), and to related compounds in the Cambridge Structural Database (CSD, Version 5.34, with a May 2013 update; Groom & Allen, 2014). The derivatizations were carried out with the molecules shown in Scheme 2. This report is a continuation of structural studies looking at how the hydrogen bonding changes in a series of related structures by

Table 1
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	$C_{11}H_{13}N_3O$	$C_{16}H_{19}N_3O_3$	$C_{17}H_{21}N_3O_3$	$C_{20}H_{25}N_3O_3$
M_r	203.24	301.34	315.37	355.43
Crystal system, space group	Hexagonal, $P6_1$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
Temperature (K)	173	173	173	173
a, b, c (Å)	7.4519 (1), 7.4519 (1), 31.8705 (7)	11.2061 (14), 7.4638 (8), 19.044 (2)	13.427 (2), 10.1086 (14), 12.2801 (18)	7.3857 (2), 9.2159 (3), 13.7494 (4)
α, β, γ (°)	90, 90, 120	90, 106.655 (4), 90	90, 101.690 (5), 90	85.898 (1), 84.499 (1), 85.210 (1)
V (Å^3)	1532.69 (5)	1526.0 (3)	1632.2 (4)	926.40 (5)
Z	6	4	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	0.09	0.09	0.09
Crystal size (mm)	0.45 × 0.18 × 0.15	0.42 × 0.33 × 0.13	0.42 × 0.39 × 0.31	0.3 × 0.3 × 0.19
Data collection				
Diffractometer	Bruker D8 Venture Photon diffractometer	Bruker D8 Venture Photon diffractometer	Bruker D8 Venture Photon diffractometer	Bruker D8 Venture Photon diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.95, 0.96	0.96, 0.99	0.96, 0.97	0.95, 0.96
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13962, 2455, 2353	12126, 3670, 3114	20796, 3921, 3494	20559, 4466, 3628
R_{int}	0.031	0.018	0.021	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.660	0.660	0.661	0.660
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.083, 1.07	0.039, 0.108, 1.04	0.040, 0.115, 1.04	0.039, 0.107, 1.04
No. of reflections	2455	3670	3921	4466
No. of parameters	147	207	216	242
No. of restraints	1	0	0	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.15	0.32, −0.25	0.30, −0.26	0.24, −0.23

	(V)	(VI)	(VII)
Crystal data			
Chemical formula	$C_{22}H_{23}N_3O_3$	$C_{14}H_{14}N_4O_2$	$C_{20}H_{19}N_3O_3$
M_r	377.43	270.29	349.38
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$
Temperature (K)	173	173	173
a, b, c (Å)	8.4851 (7), 12.4253 (10), 18.0314 (18)	6.9996 (8), 12.3350 (16), 15.8345 (19)	32.7563 (10), 6.9258 (2), 16.4002 (5)
α, β, γ (°)	90, 92.282 (3), 90	90, 99.666 (4), 90	90, 106.032 (1), 90
V (Å^3)	1899.5 (3)	1347.7 (3)	3575.90 (19)
Z	4	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	0.09	0.09
Crystal size (mm)	0.44 × 0.34 × 0.11	0.67 × 0.16 × 0.11	0.68 × 0.24 × 0.09
Data collection			
Diffractometer	Bruker D8 Venture Photon diffractometer	Bruker D8 Venture Photon diffractometer	Bruker D8 Venture Photon diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.95, 0.96	0.98, 0.99	0.95, 0.99
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28673, 4570, 3838	19472, 3252, 2737	31732, 4312, 3539
R_{int}	0.025	0.023	0.040
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.660	0.660	0.660
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.095, 1.04	0.036, 0.097, 1.03	0.040, 0.110, 1.03
No. of reflections	4570	3252	4312
No. of parameters	260	187	238
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.19	0.27, −0.18	0.24, −0.30

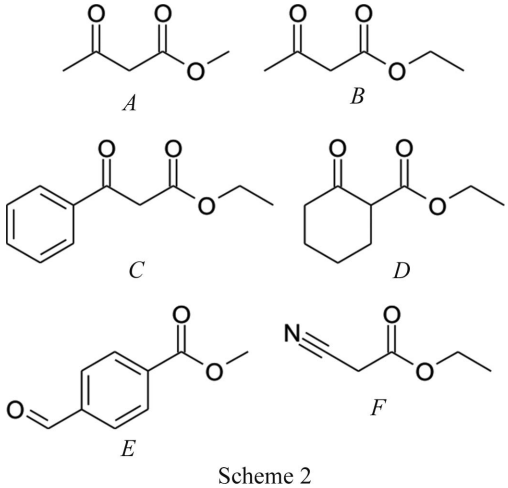
Computer programs: *APEX2* (Bruker, 2007), *SAINT-Plus* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 1999), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

varying the substituents on an organic backbone (Omondi *et al.*, 2009; Lemmerer & Michael, 2010*a*,*b*, 2011).

2. Experimental

2.1. Synthesis and crystallization

All chemicals were purchased from commercial sources and used as received. Crystals where grown by slow evaporation under ambient conditions of a methanol solution containing a 1:1 ratio of 4-aminoantipyrine and the aldehyde/ketone or ester reactant. The solutions were stirred and heated gently overnight to allow for complete reaction. Detailed masses and volumes are as follows: for (II), 4-AAP (0.100 g, 0.492 mmol) and methyl 3-oxobutanoate (see *A* in Scheme 2; 0.058 g, 0.500 mmol) in 8 ml methanol; for (III), 4-AAP (0.100 g, 0.492 mmol) and ethyl 3-oxobutanoate (*B*; 0.065 g, 0.500 mmol) in 8 ml methanol; for (IV), 4-AAP (0.100 g, 0.492 mmol) and ethyl 2-oxocyclohexanecarboxylate (*C*; 0.085 g, 0.500 mmol) in 8 ml methanol; for (V), 4-AAP (0.100 g, 0.492 mmol) and ethyl 3-oxo-3-phenylpropanoate (*D*; 0.096 g, 0.500 mmol) in 8 ml methanol; for (VI), 4-AAP (0.100 g, 0.492 mmol) and 4-formylbenzoate (*E*; 0.082 g, 0.500 mmol) in 8 ml methanol; for (VI), 4-AAP (0.100 g, 0.492 mmol) and ethyl cyanoacetate (*F*; 0.057 g, 0.500 mmol) in 8 ml methanol.



Scheme 2

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For all compounds, C-bound H atoms were placed geometrically [C—H = 0.95 (alkene and aromatic), 0.98 (methyl) or 0.99 Å (methylene)] and refined as riding, with U_{iso}(H) = 1.5U_{eq}(C) for methyl groups and 1.2U_{eq}(C) otherwise. H atoms on N atoms were located in difference maps and their coordinates and U_{iso}(H) values allowed to refine freely.

In (I), the absolute structure was chosen arbitrarily, and refinement of the absolute structure parameter (Flack & Bernardinelli, 2000) was not posible as molybdenum radiation was used. The Friedel pairs of reflections were thus merged prior to the final refinements. In addition, the crystals of (I) showed merohedral twinning, and the twin law ($\bar{1}$ 0 0 1 1 0 0 0 $\bar{1}$), with the minor twin fraction refining to 0.00232, resulted in a significant improvement of the refinement statistics. The Flack *x* absolute structure parameter [0.2 (10)] was determined using 1076 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013).

3. Results and discussion

The molecular structures and atomic numbering schemes of the asymmetric units of compounds (I)–(VII) are shown in Fig. 1, and the packing diagrams are shown in Figs. 2 and 3.

Recently, the room-temperature crystal structure of 4-AAP, (I), was reported (Li *et al.*, 2013; CCDC deposition number 801822). The crystallographic indicators show a poor-quality data set [R_{int} = 0.097 and *R*1 (all data) = 0.0992] with low redundancy. Crystals grown from propan-2-ol by us showed bipyramidal crystal habits, and were observed as twinned under polarized light microscopy. We collected a low-temperature data set with the same unit cell as reported previously, with higher redundancy, and after applying a twin law, a much improved set of crystallographic discrepancy factors was obtained. Comparable bond lengths and angles are observed. The asymmetric unit consists of one 4-AAP molecule on a general position in the hexagonal space group $P6_1$. The hydrogen bonding involves only one of the H atoms on the amine N3 atom (H3*A*). This forms a hydrogen bond to carbonyl atom O1^{i} of an adjacent molecule to form an infinite chain with graph set *C*(5) (Bernstein *et al.*, 1995) (see Table 2 for hydrogen-bond geometry and symmetry code). Ultimately, by virtue of the sixfold screw axis that defines the chain, a symmetrically pleasing helical form results down the crystallographic *c* axis (Fig. 2). Adjacent 4-AAP moleclues interact along the *b* axis by C8—H8···O1(x, $y+1$, z) hydrogen bonding [H···O = 3.378 (3) Å and C—H···O = 143°], and along the *a* axis, there is a π–π interaction between the benzene (atoms C6–C11) and pyrazole (atoms C1–N1) rings, with a centroid–centroid ($Cg\cdots Cg^{viii}$) distance of 3.9705 (15) Å [symmetry code: (viii) y, $-x+y+1$, $z-\frac{1}{6}$].

The reaction of the ketone group of methyl 3-oxobutanoate with the amine group of 4-AAP produced enamine (II). The formation of an enamine favours the formation of an intramolecular six-membered hydrogen-bonded ring with graph set *S*(6) (Etter, 1990) involving amine atom H3 and ester carbonyl atom O2 (Fig. 1; see Table 3 for hydrogen-bond geometry). The molecules pack in a head-to-tail fashion along the *a* axis, with two intermolecular interactions involving π systems (Fig. 3*a*). Firstly, atom C10 interacts with the centroid (*Cg*1) of the benzene ring through atom H10 [H10···*Cg*1^{ix} = 2.75 Å and

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···O1^{i}	0.86 (4)	2.15 (4)	2.999 (3)	170 (3)

Symmetry code: (i) $x-y$, $x-1$, $z+\frac{1}{6}$.

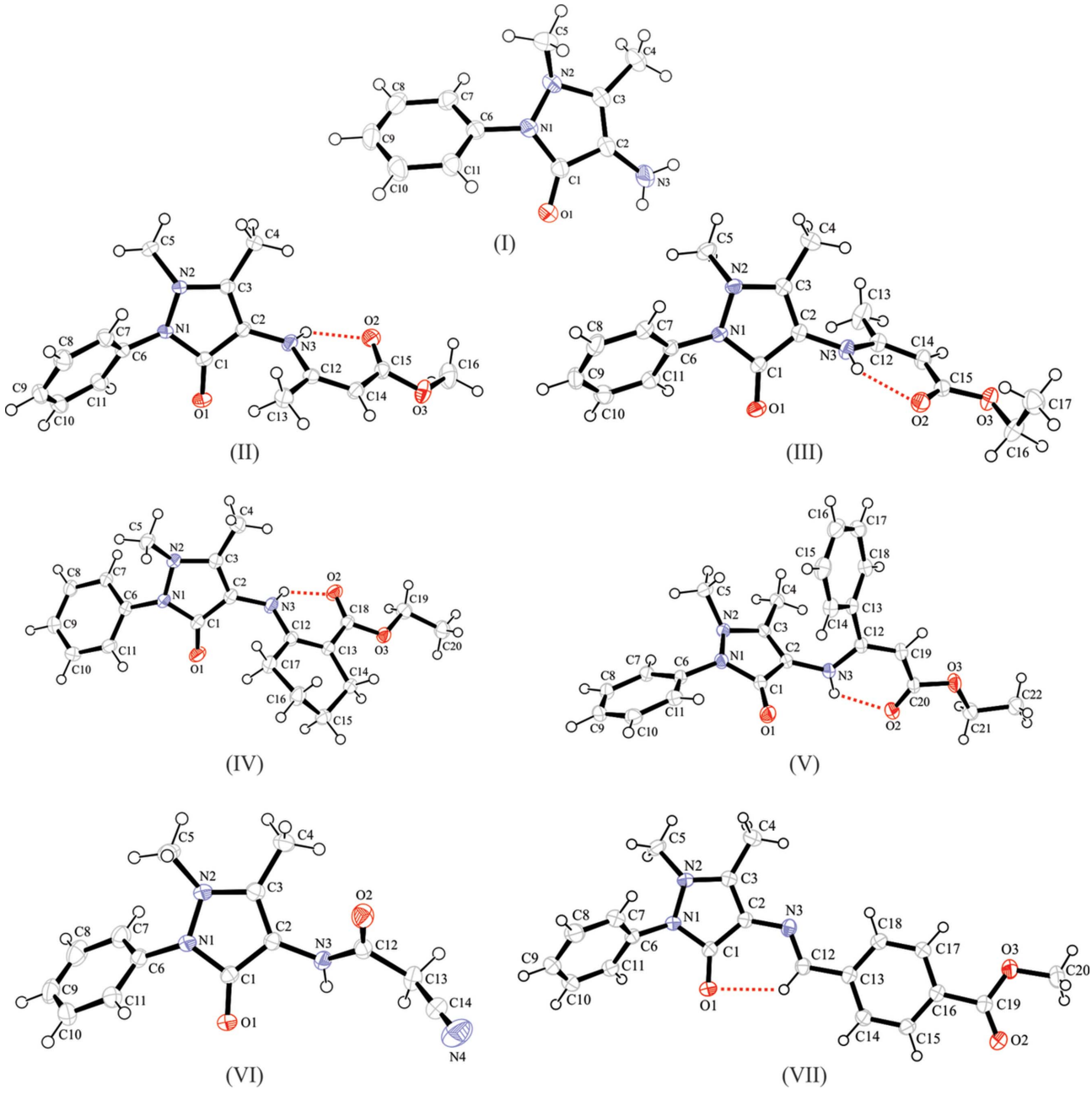


Figure 1
Perspective views of compounds (I)–(VII), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O2	0.865 (15)	2.048 (16)	2.7312 (13)	135 (1)

Table 4
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O2	0.886 (18)	2.009 (18)	2.7192 (12)	136 (1)
C11—H11···O1^{ii}	0.95	2.35	3.2829 (14)	167
C8—H8···O3^{iii}	0.95	2.7	3.6206 (15)	164

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

C10—H10···$Cg1^{ix}$ = 172°; symmetry code: (ix) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$]. Secondly, the five-membered pyrazole ring forms a close contact with the O1 ketone group of a neighbouring inversion-related molecule, such that the centroid of the pyrazole ring (*Cg*2) has an O1···$Cg2^{iv}$ distance of 3.7581 (12) Å [symmetry code: (iv) $-x+1, -y+1, -z+1$].

The reaction of the ketone group of ethyl 3-oxobutanoate with the amine group of 4-AAP produced enamine (III). Amine atom H3 forms an intramolecular hydrogen bond with

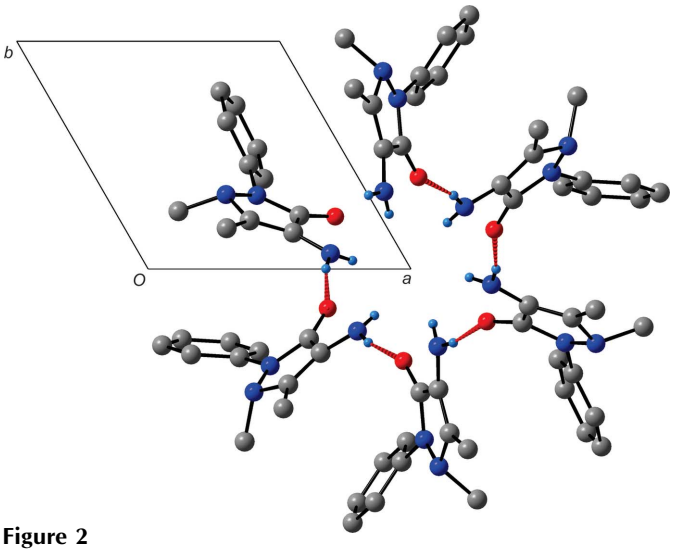


Figure 2
View of the one-dimensional hydrogen-bonded chain down the sixfold screw axis in (I). Note the lack of any hydrogen-bond interactions of the second amine H facing towards the centre of the helix. H atoms not involved in hydrogen-bonding interactions have been omitted for clarity. The N—H···O hydrogen-bond interactions are shown as dashed red lines.

Table 5
Hydrogen-bond geometry (Å, °) for (IV).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O2	0.896 (16)	1.934 (16)	2.6618 (13)	137 (1)

Table 6
Hydrogen-bond geometry (Å, °) for (V).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O2	0.867 (16)	2.224 (15)	2.8413 (13)	128 (1)
N3—H3···O2^{iv}	0.867 (16)	2.404 (16)	3.1590 (14)	146 (1)
C8—H8···O1^{v}	0.95	2.6	3.5462 (15)	176

Symmetry codes: (iv) $-x+1, -y+1, -z+1$; (v) $x+1, y, z$.

graph set $S(6)$ to ester carbonyl atom O2, similar to (II) (Fig. 1). However, it has additional C—H···O hydrogen-bond interactions, *viz.* C11—H11···O1^{ii}, forming an $R_2^2(12)$ hydrogen-bonded ring, and C8—H8···O3^{iii}, forming an $R_4^4(28)$ ring (Fig. 3*b*; see Table 4 for hydrogen-bond geometry and symmetry codes). Pairs of molecules are stabilized by centrosymmtric π–π interactions between adjacent pyrazole rings [$Cg\cdots Cg^{iv}$ = 3.9668 (9) Å]. Overall, the molecules pack antiparallel along the *c* axis.

The reaction of the ketone group of ethyl 2-oxocyclohexanecarboxylate with the amine group of 4-AAP produced enamine (IV). Amine atom H3 forms an intramolecular hydrogen bond with graph set $S(6)$ to ester carbonyl atom O2 (Fig. 1 and Table 5). Pairs of molecules form dimers stabilized again by centrosymmtric π–π interactions between adjacent pyrazole rings [$Cg\cdots Cg^{iv}$ = 4.3240 (7) Å] (Fig. 3*c*). The individual molecules pack antiparallel along the *c* axis.

The reaction of the ketone group of ethyl 3-oxo-3-phenylpropanoate with the amine group of 4-AAP produced

Table 7
Hydrogen-bond geometry (Å, °) for (VI).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1^{vi}	0.903 (15)	1.884 (15)	2.7835 (12)	174 (1)
C9—H9···O2^{vii}	0.95	2.55	3.4485 (16)	157

Symmetry codes: (vi) $-x+1, -y+1, -z$; (vii) $x, y-1, z$.

Table 8
Hydrogen-bond geometry (Å, °) for (VII).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···O1	0.95	2.37	3.0486 (17)	128

enamine (V). Amine atom H3 forms an intramolecular hydrogen bond with graph set $S(6)$ to ester carbonyl atom O2, similar to (II) (Fig. 1). However, it has an additional N3—H3···O2^{iv} hydrogen-bond interaction between neighbouring molecules, thus forming also an $R_2^2(4)$ hydrogen-bonded ring dimer (Fig. 3*d*; see Table 6 for hydrogen-bond geometry and symmetry codes). The dimers are connected *via* a weak C8—H8···O1^{v} hydrogen bond along the *a* axis. Pairs of molecules are again stabilized by centrosymmtric π–π interactions, this time between adjacent C6–C11 benzene rings [$Cg\cdots Cg^{x}$ = 4.3681 (8) Å; symmetry code: (x) $-x+2, -y, -z+1$].

The reaction of the ester group of ethyl cyanoacetate with the amine group of 4-AAP produced enamine (VI) (Fig. 1). Amine atom H3 forms an intermolecular N—H···O hydrogen bond to ring carbonyl atom O1^{vi} of a neighbouring molecule producing an $R_2^2(10)$ hydrogen-bonded ring dimer (Fig. 3*e*; see Table 7 for hydrogen-bond geometry and symmetry codes). In addition, there is an intermolecular C9—H9···O2^{vii} hydrogen bond between translationally related molecules along the *b* axis. A π–π interaction is observed between the pyrazole rings of isolated pairs of molecules [$Cg\cdots Cg^{xi}$ = 4.2438 (8) Å; symmetry code: (xi) $-x, -y+1, -z$] (Fig. 3*e*).

The reaction of the aldehyde group of methyl 4-formylbenzoate with the amine group of 4-AAP produced imine (VII), in contrast to the tautomerization to an enamine seen in the other compounds. Alkene atom H12 forms an intramolecular C—H···O hydrogen bond with graph set $S(6)$ to ring carbonyl atom O1 (Fig. 1), which is different to the intramolecular hydrogen bonds observed in all the other compounds. The packing diagram of (VII) (Fig. 3*f*; see Table 8 for hydrogen-bond geometry) shows the head-to-tail arrangement and the π–π interactions between the pyrazole and benzene rings of isolated pairs of molecules. The centroid of the pyrazole ring is 3.6772 (7) Å from the centroid of the benzene ring at $(-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1)$.

Comparatively, there are similarities and some variations in the hydrogen-bonding interactions that derivatives (II)–(VII) of 4-AAP show compared to those in parent compound (I). There is an intramolecular N—H···O hydrogen bond between the enamine N3 and ester carbonyl O2 atoms in (II) and (IV)–(VI). However, in (V), the pattern is slightly different due to the bifurcated nature of the H3···O2/O2^{iv} interaction. The bifurcation of the three-centred interaction was confirmed by

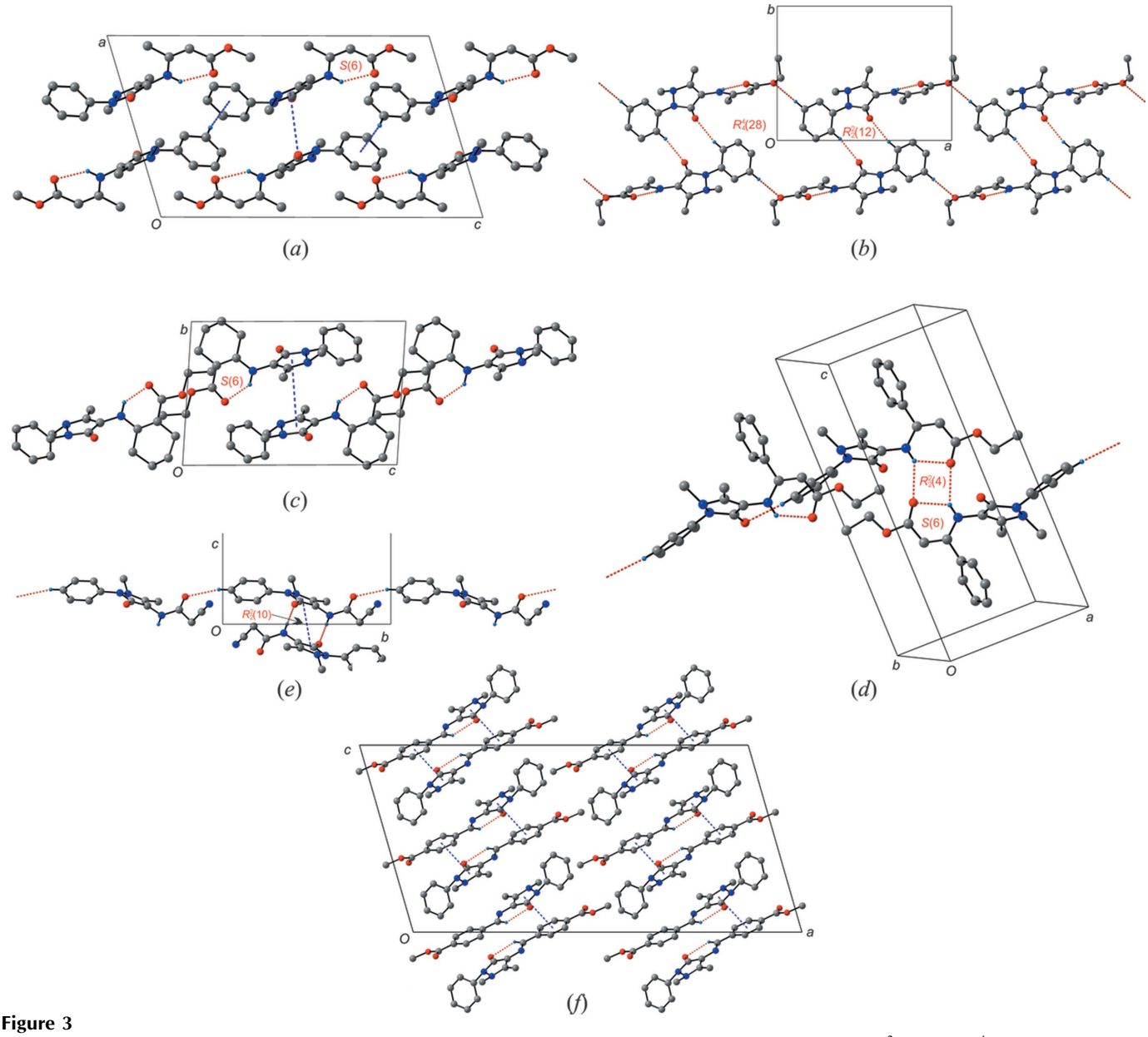


Figure 3
(*a*) Packing diagram of (II). (*b*) View of the intermolecular C—H···O hydrogen bonds forming a sequence of $R_2^2(12)$ and $R_4^4(28)$ rings in (III). (*c*) Packing diagram of (IV); note the absence of any intermolecular hydrogen-bond interactions. (*d*) View of the inter- and intramolecular N—H···O hydrogen bonds forming an $R_2^2(4)$ ring and an $S(6)$ ring in (V). (*e*) View of the intermolecular N—H···O hydrogen bonds forming an $R_2^2(10)$ ring and a chain of C—H···O hydrogen bonds in (VI). (*f*) Packing diagram of (VII); note the absence of any intermolecular hydrogen-bond interactions. H atoms not involved in hydrogen-bond interactions have been omitted for clarity. The N—H···O and C—H···O hydrogen-bond interactions are shown as dashed red lines, while interactions involving aromatic rings (π–π, O···π and H···π) are shown as dashed blue lines.

the sum of the angles around atom H3, *i.e.* 356 (1)°. In the one structure that does not form the enamine tautomer, but rather the imine tautomer, *i.e.* (VII), an intramolecular $S(6)$ hydrogen bond is formed, but this time a weaker C—H···O-type interaction is observed. The molecule in the crystal of (VII) is an imine because the formation of an enamine would have required the removal of the aromaticity of the benzene ring, which is unfavourable. Since the molecule is in the imine form, it does not possess the amine hydrogen-bond donor. The presence of two different aromatic-ring systems, *i.e.* pyrazole and benzene, in all the compounds results in numerous π–π interactions. In terms of significant intermolecular interactions involving weak hydrogen bonding, amongst the structures there are two C—H···O interactions and one C—H···π interaction in addition to the stronger N—H···O hydrogen bonds.

There are 146 (136 neither solvated nor hydrated) structures in the CSD with the 4-aminoantipyrine backbone that all crystallize in the imine form and only six that crystallize in the enamine form. Unsurprisingly, all 136 of the imine structures have the intramolecular C—H···O $S(6)$ hydrogen bond, as seen in (VII). Similarly, for the five unsolvated enamine structures of the original six in the CSD, all have the intramolecular N—H···O hydrogen bond seen in (II)–(VI).

However, if one adds the criterion of having a C=O carbonyl group three C atoms away from the N atom, as is seen for the derivatized compounds (II)–(VII), then the number of resulting compounds without any solvent that have the imine tautomeric form decreases to only one. The five enamines found in the literature all contain a carbonyl group at this position, indicating that the presence of a second carbonyl group favours the formation of an enamine over an imine.

This material is based upon work supported financially by the University of the Witwatersrand Friedel Sellschop Grant and the Molecular Sciences Institute. The National Research Foundation National Equipment Programme (UID: 78572) is thanked for financing the purchase of the single-crystal diffractometer. Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and therefore the NRF does not accept any liability in regard thereto.

References

Adam, A. M. A. (2013). *Spectrochim. Acta Part A*, **104**, 1–13.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **35**, 1555–1573.
Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2007). *APEX2* and *SAINT-Plus* (including *XPREP*). Bruker AXS Inc., Madison, Wisconsin, USA.
Cunha, S., Oliveira, S. M., Rodrigues, M. T. Jr, Bastos, R. M., Ferrari, J., de Oliveira, C. M. A., Kato, L., Napolitano, H. B., Vencato, I. & Lariucci, C. (2005). *J. Mol. Struct.* **752**, 32–39.
El-Bindary, A. A., El-Sonbati, A. Z., Diab, M. A. & El-Kadar, M. K. A. (2013). *J. Chem.*, article No. 682186.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Flack, H. D. & Bernardinelli, G. (2000). *J. Appl. Cryst.* **33**, 1143–1148.
Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
Leelavathy, C. & Antony, S. A. (2013). *Spectrochim. Acta Part A*, **113**, 346–355.
Lemmerer, A. & Michael, J. P. (2010*a*). *CrystEngComm*, **10**, 95–102.
Lemmerer, A. & Michael, J. P. (2010*b*). *S. Afr. J. Chem.* **63**, 186–191.
Lemmerer, A. & Michael, J. P. (2011). *Acta Cryst.* C**67**, o288–o293.
Li, Y., Liu, Y., Wang, H., Xiong, X., Wein, P. & Li, F. (2013). *Molecules*, **18**, 877–893.
Omondi, B., Lemmerer, A., Fernandes, M. A., Levendis, D. C. & Layh, M. (2009). *CrystEngComm*, **11**, 1658–1665.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Schilf, W., Kamieński, B., Szady-Chełmieniecka, A., Kołodziej, B., Grech, E., Zarzeczańska, D., Wcisło, A. & Ossowski, T. (2013). *Spectrochim. Acta Part A*, **109**, 47–54.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2015). C**71**, 103-109 [doi:10.1107/S2053229614027247]

A structural study of 4-aminoantipyrine and six of its Schiff base derivatives

Malitsatsi J. Mnguni and Andreas Lemmerer

Computing details

For all compounds, data collection: *APEX3* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus* (Bruker 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

(I) 4-Amino-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one

Crystal data

$C_{11}H_{13}N_3O$
M_r = 203.24
Hexagonal, $P6_1$
Hall symbol: P 61
a = 7.4519 (1) Å
c = 31.8705 (7) Å
V = 1532.69 (5) Å^3
Z = 6
$F(000)$ = 648
D_x = 1.321 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5670 reflections
θ = 3.2–25.2°
μ = 0.09 mm^{-1}
T = 173 K
Prism, colourless
0.45 × 0.18 × 0.15 mm

Data collection

Bruker D8 Venture Photon CMOS diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.95, T_{max} = 0.96
13962 measured reflections
2455 independent reflections
2353 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 28.0°, θ_{min} = 1.3°
h = −9→9
k = −9→9
l = −42→42

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.083
S = 1.07
2455 reflections
147 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.0558P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.026
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Absolute structure: Flack x determined using 1076 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013).
Absolute structure parameter: 0.2 (10)

Special details

Experimental. Absorption corrections were made using the program *SADABS* (Sheldrick, 1996)

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6930 (4)	0.2346 (4)	0.15103 (7)	0.0282 (5)
C2	0.6318 (4)	0.1598 (4)	0.19357 (8)	0.0305 (5)
C3	0.4930 (4)	0.2136 (4)	0.20641 (7)	0.0291 (5)
C4	0.3883 (4)	0.1794 (4)	0.24802 (8)	0.0384 (6)
H4A	0.4364	0.1081	0.2668	0.058*
H4B	0.2379	0.0944	0.2443	0.058*
H4C	0.4218	0.3133	0.2602	0.058*
C5	0.2424 (4)	0.2541 (4)	0.16340 (9)	0.0355 (5)
H5A	0.2387	0.3398	0.1405	0.053*
H5B	0.1676	0.2648	0.1877	0.053*
H5C	0.1768	0.1094	0.1542	0.053*
C6	0.6124 (4)	0.4585 (4)	0.10609 (7)	0.0271 (5)
C7	0.6249 (4)	0.6488 (4)	0.11171 (9)	0.0332 (5)
H7	0.6065	0.6903	0.1388	0.04*
C8	0.6649 (4)	0.7790 (4)	0.07719 (10)	0.0403 (6)
H8	0.6741	0.91	0.0808	0.048*
C9	0.6909 (4)	0.7174 (5)	0.03793 (9)	0.0437 (7)
H9	0.7174	0.8059	0.0145	0.052*
C10	0.6784 (4)	0.5272 (5)	0.03254 (8)	0.0395 (6)
H10	0.6986	0.4867	0.0055	0.047*
C11	0.6369 (4)	0.3960 (4)	0.06634 (7)	0.0319 (5)
H11	0.625	0.2641	0.0625	0.038*
N1	0.5751 (3)	0.3231 (3)	0.14030 (6)	0.0280 (4)
N2	0.4599 (3)	0.3271 (4)	0.17519 (6)	0.0291 (4)
N3	0.7274 (4)	0.0677 (5)	0.21505 (9)	0.0508 (7)
H3A	0.675 (5)	−0.001 (5)	0.2376 (11)	0.036 (8)*
H3B	0.797 (6)	0.040 (5)	0.2010 (11)	0.042 (9)*
O1	0.8267 (3)	0.2302 (3)	0.12882 (6)	0.0356 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0287 (11)	0.0295 (11)	0.0257 (10)	0.0140 (9)	0.0007 (9)	0.0023 (9)
C2	0.0296 (12)	0.0312 (11)	0.0265 (11)	0.0121 (10)	0.0026 (9)	0.0047 (9)
C3	0.0280 (10)	0.0294 (10)	0.0231 (10)	0.0093 (9)	0.0018 (9)	0.0005 (9)
C4	0.0437 (14)	0.0404 (14)	0.0260 (12)	0.0172 (11)	0.0086 (11)	0.0020 (11)
C5	0.0274 (12)	0.0381 (13)	0.0403 (12)	0.0159 (11)	0.0031 (10)	−0.0030 (12)
C6	0.0222 (10)	0.0326 (12)	0.0254 (10)	0.0130 (9)	−0.0011 (9)	0.0018 (9)

C7	0.0303 (11)	0.0365 (13)	0.0354 (12)	0.0187 (11)	−0.0018 (10)	0.0009 (10)
C8	0.0312 (12)	0.0366 (13)	0.0546 (16)	0.0181 (11)	−0.0011 (12)	0.0111 (13)
C9	0.0352 (13)	0.0501 (17)	0.0418 (14)	0.0184 (13)	−0.0011 (13)	0.0200 (13)
C10	0.0365 (14)	0.0532 (16)	0.0260 (11)	0.0203 (12)	−0.0026 (11)	0.0054 (12)
C11	0.0308 (11)	0.0364 (12)	0.0270 (11)	0.0156 (10)	−0.0032 (10)	0.0012 (10)
N1	0.0305 (10)	0.0345 (10)	0.0225 (8)	0.0189 (8)	0.0030 (7)	0.0025 (8)
N2	0.0288 (10)	0.0324 (11)	0.0249 (9)	0.0143 (8)	0.0047 (7)	0.0010 (8)
N3	0.0520 (15)	0.0734 (19)	0.0419 (14)	0.0425 (15)	0.0166 (13)	0.0307 (15)
O1	0.0382 (10)	0.0463 (10)	0.0307 (9)	0.0274 (8)	0.0096 (8)	0.0096 (8)

Geometric parameters (Å, º)

C1—O1	1.236 (3)	C6—C11	1.393 (3)
C1—N1	1.380 (3)	C6—N1	1.416 (3)
C1—C2	1.450 (3)	C7—C8	1.397 (4)
C2—C3	1.346 (3)	C7—H7	0.95
C2—N3	1.391 (4)	C8—C9	1.380 (5)
C3—N2	1.405 (3)	C8—H8	0.95
C3—C4	1.495 (3)	C9—C10	1.384 (5)
C4—H4A	0.98	C9—H9	0.95
C4—H4B	0.98	C10—C11	1.382 (4)
C4—H4C	0.98	C10—H10	0.95
C5—N2	1.477 (3)	C11—H11	0.95
C5—H5A	0.98	N1—N2	1.414 (3)
C5—H5B	0.98	N3—H3A	0.86 (4)
C5—H5C	0.98	N3—H3B	0.79 (4)
C6—C7	1.385 (4)		
O1—C1—N1	125.8 (2)	C6—C7—C8	119.4 (3)
O1—C1—C2	128.9 (2)	C6—C7—H7	120.3
N1—C1—C2	105.22 (19)	C8—C7—H7	120.3
C3—C2—N3	131.0 (2)	C9—C8—C7	120.0 (3)
C3—C2—C1	108.1 (2)	C9—C8—H8	120
N3—C2—C1	120.6 (2)	C7—C8—H8	120
C2—C3—N2	110.87 (19)	C8—C9—C10	120.3 (2)
C2—C3—C4	129.2 (2)	C8—C9—H9	119.8
N2—C3—C4	119.8 (2)	C10—C9—H9	119.8
C3—C4—H4A	109.5	C11—C10—C9	120.3 (3)
C3—C4—H4B	109.5	C11—C10—H10	119.9
H4A—C4—H4B	109.5	C9—C10—H10	119.9
C3—C4—H4C	109.5	C10—C11—C6	119.5 (2)
H4A—C4—H4C	109.5	C10—C11—H11	120.2
H4B—C4—H4C	109.5	C6—C11—H11	120.2
N2—C5—H5A	109.5	C1—N1—N2	110.69 (18)
N2—C5—H5B	109.5	C1—N1—C6	125.93 (19)
H5A—C5—H5B	109.5	N2—N1—C6	119.71 (19)
N2—C5—H5C	109.5	C3—N2—N1	104.66 (18)
H5A—C5—H5C	109.5	C3—N2—C5	116.7 (2)

H5B—C5—H5C	109.5	N1—N2—C5	110.97 (18)
C7—C6—C11	120.5 (2)	C2—N3—H3A	121 (2)
C7—C6—N1	121.2 (2)	C2—N3—H3B	115 (2)
C11—C6—N1	118.3 (2)	H3A—N3—H3B	119 (3)
O1—C1—C2—C3	174.7 (3)	O1—C1—N1—N2	−171.4 (2)
N1—C1—C2—C3	−2.7 (3)	C2—C1—N1—N2	6.1 (3)
O1—C1—C2—N3	−0.1 (4)	O1—C1—N1—C6	−13.3 (4)
N1—C1—C2—N3	−177.5 (2)	C2—C1—N1—C6	164.3 (2)
N3—C2—C3—N2	172.3 (3)	C7—C6—N1—C1	−127.3 (3)
C1—C2—C3—N2	−1.7 (3)	C11—C6—N1—C1	52.5 (3)
N3—C2—C3—C4	−3.7 (5)	C7—C6—N1—N2	29.0 (3)
C1—C2—C3—C4	−177.8 (3)	C11—C6—N1—N2	−151.1 (2)
C11—C6—C7—C8	−0.8 (4)	C2—C3—N2—N1	5.3 (3)
N1—C6—C7—C8	179.1 (2)	C4—C3—N2—N1	−178.2 (2)
C6—C7—C8—C9	0.2 (4)	C2—C3—N2—C5	128.4 (2)
C7—C8—C9—C10	−0.3 (4)	C4—C3—N2—C5	−55.1 (3)
C8—C9—C10—C11	0.9 (4)	C1—N1—N2—C3	−7.1 (3)
C9—C10—C11—C6	−1.5 (4)	C6—N1—N2—C3	−166.8 (2)
C7—C6—C11—C10	1.4 (4)	C1—N1—N2—C5	−133.8 (2)
N1—C6—C11—C10	−178.4 (2)	C6—N1—N2—C5	66.6 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···O1^{i}	0.86 (4)	2.15 (4)	2.999 (3)	170 (3)

Symmetry code: (i) *x*−*y*, *x*−1, *z*+1/6.

(II) (*Z*)-Methyl 3-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]but-2-enoate

Crystal data

$C_{16}H_{19}N_3O_3$
M_r = 301.34
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 11.2061 (14) Å
b = 7.4638 (8) Å
c = 19.044 (2) Å
β = 106.655 (4)°
V = 1526.0 (3) Å^3
Z = 4
$F(000)$ = 640
D_x = 1.312 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6999 reflections
θ = 3.3–28.3°
μ = 0.09 mm^{-1}
T = 173 K
Plate, colourless
0.42 × 0.33 × 0.13 mm

Data collection

Bruker D8 Venture Photon diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.96, T_{max} = 0.99
12126 measured reflections
3670 independent reflections
3114 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 28.0°, θ_{min} = 3.5°
h = −14→14
k = −9→8
l = −23→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.108$
$S = 1.04$
3670 reflections
207 parameters
0 restraints

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.4578P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Experimental. Absorption corrections were made using the program *SADABS* (Sheldrick, 1996)
Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.33084 (10)	0.54325 (15)	0.48152 (6)	0.0223 (2)
C2	0.27364 (10)	0.42379 (15)	0.42209 (6)	0.0222 (2)
C3	0.27806 (10)	0.25393 (15)	0.44904 (6)	0.0215 (2)
C4	0.23794 (12)	0.08445 (16)	0.40829 (7)	0.0300 (3)
H4A	0.1794	0.1114	0.3604	0.045*
H4B	0.1971	0.0077	0.4362	0.045*
H4C	0.3108	0.0224	0.4014	0.045*
C5	0.40900 (12)	0.11438 (15)	0.56482 (6)	0.0274 (3)
H5A	0.3791	−0.0026	0.5436	0.041*
H5B	0.4079	0.1176	0.6161	0.041*
H5C	0.4943	0.1336	0.5624	0.041*
C6	0.36757 (10)	0.49332 (14)	0.61445 (6)	0.0210 (2)
C7	0.28437 (11)	0.42183 (16)	0.64849 (6)	0.0258 (2)
H7	0.2311	0.3258	0.6264	0.031*
C8	0.27954 (12)	0.49164 (18)	0.71511 (7)	0.0310 (3)
H8	0.223	0.4426	0.7388	0.037*
C9	0.35629 (12)	0.63190 (17)	0.74739 (7)	0.0311 (3)
H9	0.3514	0.6807	0.7926	0.037*
C10	0.44014 (12)	0.70079 (17)	0.71360 (7)	0.0320 (3)
H10	0.4935	0.7964	0.736	0.038*
C11	0.44716 (11)	0.63159 (16)	0.64722 (7)	0.0271 (3)
H11	0.5057	0.6783	0.6245	0.032*
C12	0.11810 (10)	0.58614 (15)	0.32668 (6)	0.0229 (2)
C13	0.05629 (12)	0.64069 (17)	0.38326 (7)	0.0295 (3)
H13A	0.0234	0.5343	0.4014	0.044*
H13B	−0.0121	0.7235	0.3614	0.044*
H13C	0.1171	0.7	0.424	0.044*
C14	0.07240 (11)	0.64379 (16)	0.25596 (6)	0.0255 (2)
H14	0.0037	0.724	0.2444	0.031*

C15	0.12353 (11)	0.58856 (16)	0.19846 (6)	0.0263 (3)
C16	0.11845 (15)	0.6344 (2)	0.07489 (7)	0.0453 (4)
H16A	0.204	0.6798	0.0868	0.068*
H16B	0.0677	0.6926	0.0302	0.068*
H16C	0.1185	0.5046	0.0671	0.068*
N1	0.36827 (9)	0.43209 (12)	0.54355 (5)	0.0218 (2)
N2	0.32779 (9)	0.25576 (12)	0.52354 (5)	0.0216 (2)
N3	0.21884 (10)	0.47652 (13)	0.34857 (5)	0.0253 (2)
H3	0.2528 (14)	0.447 (2)	0.3147 (9)	0.035 (4)*
O1	0.34267 (8)	0.70732 (11)	0.48366 (5)	0.0302 (2)
O2	0.20659 (9)	0.47876 (12)	0.20326 (5)	0.0332 (2)
O3	0.06747 (9)	0.67266 (14)	0.13427 (5)	0.0355 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0243 (5)	0.0195 (5)	0.0241 (5)	0.0012 (4)	0.0086 (4)	0.0031 (4)
C2	0.0260 (5)	0.0209 (5)	0.0202 (5)	0.0036 (4)	0.0073 (4)	0.0026 (4)
C3	0.0229 (5)	0.0204 (5)	0.0212 (5)	0.0033 (4)	0.0063 (4)	0.0003 (4)
C4	0.0391 (7)	0.0209 (5)	0.0253 (6)	0.0030 (5)	0.0015 (5)	−0.0028 (4)
C5	0.0337 (6)	0.0195 (5)	0.0260 (6)	0.0054 (5)	0.0035 (5)	0.0041 (4)
C6	0.0216 (5)	0.0188 (5)	0.0203 (5)	0.0033 (4)	0.0026 (4)	0.0004 (4)
C7	0.0251 (5)	0.0259 (6)	0.0252 (6)	−0.0028 (4)	0.0054 (4)	−0.0021 (4)
C8	0.0312 (6)	0.0364 (7)	0.0273 (6)	0.0017 (5)	0.0111 (5)	0.0001 (5)
C9	0.0352 (6)	0.0337 (6)	0.0217 (6)	0.0075 (5)	0.0036 (5)	−0.0046 (5)
C10	0.0334 (6)	0.0281 (6)	0.0288 (6)	−0.0026 (5)	−0.0002 (5)	−0.0064 (5)
C11	0.0254 (6)	0.0255 (6)	0.0289 (6)	−0.0031 (4)	0.0056 (5)	−0.0014 (5)
C12	0.0247 (5)	0.0184 (5)	0.0248 (6)	−0.0021 (4)	0.0056 (4)	0.0002 (4)
C13	0.0282 (6)	0.0330 (6)	0.0280 (6)	0.0030 (5)	0.0094 (5)	−0.0002 (5)
C14	0.0245 (5)	0.0240 (5)	0.0256 (6)	0.0018 (4)	0.0037 (4)	0.0035 (4)
C15	0.0289 (6)	0.0250 (6)	0.0220 (6)	−0.0058 (5)	0.0026 (4)	0.0021 (4)
C16	0.0520 (9)	0.0604 (10)	0.0236 (6)	−0.0095 (7)	0.0108 (6)	0.0056 (6)
N1	0.0281 (5)	0.0153 (4)	0.0215 (5)	−0.0012 (4)	0.0065 (4)	−0.0003 (3)
N2	0.0292 (5)	0.0146 (4)	0.0198 (4)	0.0006 (4)	0.0048 (4)	0.0006 (3)
N3	0.0329 (5)	0.0249 (5)	0.0190 (5)	0.0084 (4)	0.0087 (4)	0.0040 (4)
O1	0.0402 (5)	0.0173 (4)	0.0325 (5)	−0.0024 (3)	0.0092 (4)	0.0034 (3)
O2	0.0425 (5)	0.0301 (5)	0.0275 (4)	0.0053 (4)	0.0111 (4)	−0.0002 (4)
O3	0.0349 (5)	0.0464 (6)	0.0231 (4)	−0.0012 (4)	0.0048 (4)	0.0098 (4)

Geometric parameters (Å, º)

C1—O1	1.2312 (14)	C9—C10	1.3812 (19)
C1—N1	1.4057 (14)	C9—H9	0.95
C1—C2	1.4390 (16)	C10—C11	1.3887 (18)
C2—C3	1.3633 (15)	C10—H10	0.95
C2—N3	1.4141 (14)	C11—H11	0.95
C3—N2	1.3677 (14)	C12—N3	1.3593 (15)
C3—C4	1.4848 (16)	C12—C14	1.3659 (16)

C4—H4A	0.98	C12—C13	1.4948 (16)
C4—H4B	0.98	C13—H13A	0.98
C4—H4C	0.98	C13—H13B	0.98
C5—N2	1.4662 (14)	C13—H13C	0.98
C5—H5A	0.98	C14—C15	1.4343 (17)
C5—H5B	0.98	C14—H14	0.95
C5—H5C	0.98	C15—O2	1.2237 (15)
C6—C7	1.3860 (16)	C15—O3	1.3575 (14)
C6—C11	1.3895 (16)	C16—O3	1.4343 (17)
C6—N1	1.4276 (14)	C16—H16A	0.98
C7—C8	1.3868 (17)	C16—H16B	0.98
C7—H7	0.95	C16—H16C	0.98
C8—C9	1.3822 (18)	N1—N2	1.4086 (12)
C8—H8	0.95	N3—H3	0.865 (15)

O1—C1—N1	123.77 (10)	C11—C10—H10	119.7
O1—C1—C2	131.43 (11)	C10—C11—C6	119.24 (11)
N1—C1—C2	104.70 (9)	C10—C11—H11	120.4
C3—C2—N3	126.17 (10)	C6—C11—H11	120.4
C3—C2—C1	108.67 (10)	N3—C12—C14	122.39 (11)
N3—C2—C1	125.13 (10)	N3—C12—C13	117.29 (10)
C2—C3—N2	109.96 (10)	C14—C12—C13	120.31 (11)
C2—C3—C4	128.51 (10)	C12—C13—H13A	109.5
N2—C3—C4	121.53 (10)	C12—C13—H13B	109.5
C3—C4—H4A	109.5	H13A—C13—H13B	109.5
C3—C4—H4B	109.5	C12—C13—H13C	109.5
H4A—C4—H4B	109.5	H13A—C13—H13C	109.5
C3—C4—H4C	109.5	H13B—C13—H13C	109.5
H4A—C4—H4C	109.5	C12—C14—C15	122.91 (11)
H4B—C4—H4C	109.5	C12—C14—H14	118.5
N2—C5—H5A	109.5	C15—C14—H14	118.5
N2—C5—H5B	109.5	O2—C15—O3	121.51 (11)
H5A—C5—H5B	109.5	O2—C15—C14	126.67 (11)
N2—C5—H5C	109.5	O3—C15—C14	111.82 (11)
H5A—C5—H5C	109.5	O3—C16—H16A	109.5
H5B—C5—H5C	109.5	O3—C16—H16B	109.5
C7—C6—C11	120.47 (11)	H16A—C16—H16B	109.5
C7—C6—N1	120.39 (10)	O3—C16—H16C	109.5
C11—C6—N1	119.06 (10)	H16A—C16—H16C	109.5
C6—C7—C8	119.41 (11)	H16B—C16—H16C	109.5
C6—C7—H7	120.3	C1—N1—N2	109.19 (8)
C8—C7—H7	120.3	C1—N1—C6	121.65 (9)
C9—C8—C7	120.59 (12)	N2—N1—C6	117.80 (9)
C9—C8—H8	119.7	C3—N2—N1	107.09 (8)
C7—C8—H8	119.7	C3—N2—C5	123.70 (9)
C10—C9—C8	119.64 (11)	N1—N2—C5	115.16 (9)
C10—C9—H9	120.2	C12—N3—C2	123.92 (10)
C8—C9—H9	120.2	C12—N3—H3	115.2 (10)

C9—C10—C11	120.61 (12)	C2—N3—H3	120.6 (10)
C9—C10—H10	119.7	C15—O3—C16	115.58 (11)
O1—C1—C2—C3	−176.21 (12)	C2—C1—N1—N2	−3.94 (11)
N1—C1—C2—C3	0.18 (12)	O1—C1—N1—C6	30.18 (16)
O1—C1—C2—N3	2.0 (2)	C2—C1—N1—C6	−146.57 (10)
N1—C1—C2—N3	178.38 (10)	C7—C6—N1—C1	112.10 (12)
N3—C2—C3—N2	−174.40 (10)	C11—C6—N1—C1	−64.76 (14)
C1—C2—C3—N2	3.78 (13)	C7—C6—N1—N2	−27.50 (14)
N3—C2—C3—C4	5.9 (2)	C11—C6—N1—N2	155.64 (10)
C1—C2—C3—C4	−175.94 (11)	C2—C3—N2—N1	−6.19 (12)
C11—C6—C7—C8	1.14 (17)	C4—C3—N2—N1	173.56 (10)
N1—C6—C7—C8	−175.67 (10)	C2—C3—N2—C5	−143.89 (11)
C6—C7—C8—C9	0.34 (18)	C4—C3—N2—C5	35.87 (16)
C7—C8—C9—C10	−1.23 (19)	C1—N1—N2—C3	6.29 (12)
C8—C9—C10—C11	0.63 (19)	C6—N1—N2—C3	150.55 (9)
C9—C10—C11—C6	0.83 (19)	C1—N1—N2—C5	148.07 (10)
C7—C6—C11—C10	−1.73 (17)	C6—N1—N2—C5	−67.67 (12)
N1—C6—C11—C10	175.13 (11)	C14—C12—N3—C2	175.65 (11)
N3—C12—C14—C15	2.42 (18)	C13—C12—N3—C2	−5.27 (17)
C13—C12—C14—C15	−176.63 (11)	C3—C2—N3—C12	115.01 (14)
C12—C14—C15—O2	4.5 (2)	C1—C2—N3—C12	−62.89 (16)
C12—C14—C15—O3	−176.07 (11)	O2—C15—O3—C16	−4.56 (17)
O1—C1—N1—N2	172.80 (10)	C14—C15—O3—C16	176.01 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O2	0.865 (15)	2.048 (16)	2.7312 (13)	135 (1)

(III) (*Z*)-Ethyl 3-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]but-2-enoate

Crystal data

$C_{17}H_{21}N_3O_3$
M_r = 315.37
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 13.427 (2) Å
b = 10.1086 (14) Å
c = 12.2801 (18) Å
β = 101.690 (5)°
V = 1632.2 (4) Å^3
Z = 4
F(000) = 672

D_x = 1.283 Mg m^{-3}
D_m = 0 Mg m^{-3}
D_m measured by ?
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9952 reflections
θ = 3.4–28.3°
μ = 0.09 mm^{-1}
T = 173 K
Block, brown
0.42 × 0.39 × 0.31 mm

Data collection

Bruker D8 Venture Photon diffractometer
ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.96, T_{max} = 0.97
20796 measured reflections

3921 independent reflections
3494 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 28.0°$, $\theta_{min} = 3.4°$
$h = -17 \rightarrow 17$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.115$
$S = 1.04$
3921 reflections
216 parameters
0 restraints
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.4416P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Experimental. Absorption corrections were made using the program *SADABS* (Sheldrick, 1996)

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.50682 (8)	0.24189 (10)	0.49565 (8)	0.0220 (2)
C2	0.56615 (8)	0.34047 (10)	0.45208 (8)	0.0224 (2)
C3	0.50318 (8)	0.41389 (10)	0.37465 (8)	0.0230 (2)
C4	0.52683 (9)	0.52616 (11)	0.30537 (10)	0.0307 (2)
H4A	0.5958	0.5584	0.3353	0.046*
H4B	0.4779	0.5978	0.3066	0.046*
H4C	0.5223	0.496	0.2287	0.046*
C5	0.33522 (9)	0.36253 (12)	0.25646 (9)	0.0298 (2)
H5A	0.3317	0.449	0.2197	0.045*
H5B	0.2673	0.3373	0.267	0.045*
H5C	0.3601	0.2962	0.2102	0.045*
C6	0.31891 (8)	0.20442 (10)	0.45872 (8)	0.0218 (2)
C7	0.24395 (8)	0.28769 (11)	0.48285 (9)	0.0262 (2)
H7	0.2516	0.381	0.48	0.031*
C8	0.15768 (9)	0.23323 (13)	0.51115 (10)	0.0326 (3)
H8	0.1057	0.2893	0.5273	0.039*
C9	0.14749 (9)	0.09698 (14)	0.51584 (10)	0.0357 (3)
H9	0.0889	0.0598	0.5361	0.043*
C10	0.22245 (10)	0.01499 (12)	0.49106 (10)	0.0342 (3)
H10	0.2146	−0.0783	0.4939	0.041*
C11	0.30883 (9)	0.06761 (11)	0.46209 (9)	0.0273 (2)
H11	0.3602	0.0113	0.4449	0.033*
C12	0.74722 (8)	0.34228 (10)	0.44013 (9)	0.0248 (2)
C13	0.72015 (10)	0.29611 (16)	0.32186 (11)	0.0412 (3)
H13A	0.6707	0.2239	0.3158	0.062*

H13B	0.7815	0.2646	0.2984	0.062*
H13C	0.6905	0.3697	0.2741	0.062*
C14	0.84661 (8)	0.36475 (11)	0.48936 (9)	0.0265 (2)
H14	0.8971	0.353	0.4461	0.032*
C15	0.87833 (8)	0.40522 (10)	0.60321 (9)	0.0235 (2)
C16	1.02030 (9)	0.46559 (14)	0.74458 (10)	0.0371 (3)
H16A	1.0937	0.4438	0.7636	0.044*
H16B	0.9857	0.4142	0.7947	0.044*
C17	1.00661 (11)	0.61014 (14)	0.76352 (12)	0.0419 (3)
H17A	1.0376	0.6615	0.7114	0.063*
H17B	1.0394	0.633	0.8399	0.063*
H17C	0.9339	0.6306	0.7517	0.063*
N1	0.40925 (7)	0.25677 (9)	0.43186 (7)	0.0237 (2)
N2	0.40470 (7)	0.37017 (9)	0.36466 (7)	0.0229 (2)
N3	0.67072 (7)	0.35975 (10)	0.49527 (8)	0.0250 (2)
H3	0.6905 (13)	0.3796 (17)	0.5667 (15)	0.049 (4)*
O1	0.53027 (6)	0.16475 (8)	0.57443 (6)	0.02857 (19)
O2	0.82303 (6)	0.41981 (8)	0.67041 (6)	0.02946 (19)
O3	0.97998 (6)	0.42703 (9)	0.63075 (7)	0.0325 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0195 (5)	0.0245 (5)	0.0215 (4)	0.0030 (4)	0.0030 (4)	−0.0016 (4)
C2	0.0207 (5)	0.0253 (5)	0.0215 (4)	0.0001 (4)	0.0048 (4)	−0.0035 (4)
C3	0.0244 (5)	0.0239 (5)	0.0214 (5)	0.0012 (4)	0.0066 (4)	−0.0027 (4)
C4	0.0361 (6)	0.0269 (5)	0.0300 (5)	−0.0004 (4)	0.0093 (5)	0.0033 (4)
C5	0.0282 (6)	0.0387 (6)	0.0201 (5)	0.0037 (4)	−0.0009 (4)	0.0012 (4)
C6	0.0187 (5)	0.0265 (5)	0.0191 (4)	0.0003 (4)	0.0011 (4)	0.0006 (4)
C7	0.0238 (5)	0.0271 (5)	0.0267 (5)	0.0033 (4)	0.0028 (4)	−0.0004 (4)
C8	0.0209 (5)	0.0469 (7)	0.0299 (6)	0.0038 (5)	0.0049 (4)	−0.0014 (5)
C9	0.0252 (6)	0.0515 (7)	0.0295 (6)	−0.0124 (5)	0.0030 (4)	0.0033 (5)
C10	0.0366 (6)	0.0303 (6)	0.0326 (6)	−0.0097 (5)	−0.0007 (5)	0.0026 (5)
C11	0.0275 (5)	0.0261 (5)	0.0264 (5)	0.0018 (4)	0.0011 (4)	−0.0011 (4)
C12	0.0247 (5)	0.0247 (5)	0.0256 (5)	0.0008 (4)	0.0062 (4)	−0.0040 (4)
C13	0.0280 (6)	0.0633 (9)	0.0321 (6)	0.0019 (6)	0.0058 (5)	−0.0218 (6)
C14	0.0222 (5)	0.0315 (5)	0.0268 (5)	0.0000 (4)	0.0074 (4)	−0.0044 (4)
C15	0.0217 (5)	0.0218 (5)	0.0264 (5)	0.0001 (4)	0.0033 (4)	0.0020 (4)
C16	0.0283 (6)	0.0457 (7)	0.0326 (6)	−0.0014 (5)	−0.0047 (5)	−0.0058 (5)
C17	0.0436 (7)	0.0443 (7)	0.0383 (7)	−0.0091 (6)	0.0095 (6)	−0.0053 (6)
N1	0.0194 (4)	0.0267 (4)	0.0242 (4)	0.0026 (3)	0.0025 (3)	0.0058 (3)
N2	0.0233 (4)	0.0255 (4)	0.0194 (4)	0.0023 (3)	0.0028 (3)	0.0034 (3)
N3	0.0198 (4)	0.0335 (5)	0.0215 (4)	−0.0023 (3)	0.0035 (3)	−0.0047 (3)
O1	0.0248 (4)	0.0322 (4)	0.0275 (4)	0.0056 (3)	0.0024 (3)	0.0074 (3)
O2	0.0265 (4)	0.0387 (5)	0.0237 (4)	−0.0019 (3)	0.0061 (3)	0.0003 (3)
O3	0.0213 (4)	0.0433 (5)	0.0315 (4)	−0.0017 (3)	0.0018 (3)	−0.0070 (3)

Geometric parameters (Å, º)

C1—O1	1.2328 (13)	C10—C11	1.3864 (17)
C1—N1	1.3916 (13)	C10—H10	0.95
C1—C2	1.4446 (14)	C11—H11	0.95
C2—C3	1.3579 (15)	C12—N3	1.3515 (14)
C2—N3	1.4102 (14)	C12—C14	1.3679 (16)
C3—N2	1.3759 (14)	C12—C13	1.4985 (15)
C3—C4	1.4906 (15)	C13—H13A	0.98
C4—H4A	0.98	C13—H13B	0.98
C4—H4B	0.98	C13—H13C	0.98
C4—H4C	0.98	C14—C15	1.4360 (15)
C5—N2	1.4627 (13)	C14—H14	0.95
C5—H5A	0.98	C15—O2	1.2258 (13)
C5—H5B	0.98	C15—O3	1.3559 (13)
C5—H5C	0.98	C16—O3	1.4464 (14)
C6—C7	1.3893 (15)	C16—C17	1.4967 (19)
C6—C11	1.3910 (15)	C16—H16A	0.99
C6—N1	1.4220 (13)	C16—H16B	0.99
C7—C8	1.3887 (16)	C17—H17A	0.98
C7—H7	0.95	C17—H17B	0.98
C8—C9	1.3864 (19)	C17—H17C	0.98
C8—H8	0.95	N1—N2	1.4066 (12)
C9—C10	1.3844 (19)	N3—H3	0.886 (18)
C9—H9	0.95		
O1—C1—N1	124.87 (10)	C6—C11—H11	120.6
O1—C1—C2	130.90 (10)	N3—C12—C14	121.96 (10)
N1—C1—C2	104.11 (9)	N3—C12—C13	117.81 (10)
C3—C2—N3	128.24 (10)	C14—C12—C13	120.22 (10)
C3—C2—C1	108.94 (9)	C12—C13—H13A	109.5
N3—C2—C1	122.53 (9)	C12—C13—H13B	109.5
C2—C3—N2	109.74 (9)	H13A—C13—H13B	109.5
C2—C3—C4	129.89 (10)	C12—C13—H13C	109.5
N2—C3—C4	120.37 (9)	H13A—C13—H13C	109.5
C3—C4—H4A	109.5	H13B—C13—H13C	109.5
C3—C4—H4B	109.5	C12—C14—C15	123.23 (10)
H4A—C4—H4B	109.5	C12—C14—H14	118.4
C3—C4—H4C	109.5	C15—C14—H14	118.4
H4A—C4—H4C	109.5	O2—C15—O3	121.93 (10)
H4B—C4—H4C	109.5	O2—C15—C14	126.09 (10)
N2—C5—H5A	109.5	O3—C15—C14	111.98 (9)
N2—C5—H5B	109.5	O3—C16—C17	112.31 (11)
H5A—C5—H5B	109.5	O3—C16—H16A	109.1
N2—C5—H5C	109.5	C17—C16—H16A	109.1
H5A—C5—H5C	109.5	O3—C16—H16B	109.1
H5B—C5—H5C	109.5	C17—C16—H16B	109.1
C7—C6—C11	121.12 (10)	H16A—C16—H16B	107.9

C7—C6—N1	120.86 (10)	C16—C17—H17A	109.5
C11—C6—N1	118.00 (9)	C16—C17—H17B	109.5
C8—C7—C6	119.36 (11)	H17A—C17—H17B	109.5
C8—C7—H7	120.3	C16—C17—H17C	109.5
C6—C7—H7	120.3	H17A—C17—H17C	109.5
C9—C8—C7	119.90 (11)	H17B—C17—H17C	109.5
C9—C8—H8	120	C1—N1—N2	110.02 (8)
C7—C8—H8	120	C1—N1—C6	125.40 (9)
C10—C9—C8	120.22 (11)	N2—N1—C6	120.11 (8)
C10—C9—H9	119.9	C3—N2—N1	106.42 (8)
C8—C9—H9	119.9	C3—N2—C5	121.50 (9)
C9—C10—C11	120.66 (11)	N1—N2—C5	115.71 (9)
C9—C10—H10	119.7	C12—N3—C2	126.39 (9)
C11—C10—H10	119.7	C12—N3—H3	114.8 (11)
C10—C11—C6	118.73 (10)	C2—N3—H3	118.6 (11)
C10—C11—H11	120.6	C15—O3—C16	116.46 (9)
O1—C1—C2—C3	−171.19 (11)	O1—C1—N1—C6	11.97 (17)
N1—C1—C2—C3	4.94 (11)	C2—C1—N1—C6	−164.46 (9)
O1—C1—C2—N3	3.12 (17)	C7—C6—N1—C1	114.34 (12)
N1—C1—C2—N3	179.25 (9)	C11—C6—N1—C1	−64.49 (14)
N3—C2—C3—N2	−173.49 (9)	C7—C6—N1—N2	−39.49 (14)
C1—C2—C3—N2	0.40 (11)	C11—C6—N1—N2	141.68 (10)
N3—C2—C3—C4	6.68 (18)	C2—C3—N2—N1	−5.57 (11)
C1—C2—C3—C4	−179.43 (10)	C4—C3—N2—N1	174.28 (9)
C11—C6—C7—C8	0.22 (16)	C2—C3—N2—C5	−140.90 (10)
N1—C6—C7—C8	−178.58 (9)	C4—C3—N2—C5	38.95 (14)
C6—C7—C8—C9	0.46 (17)	C1—N1—N2—C3	8.90 (11)
C7—C8—C9—C10	−0.80 (18)	C6—N1—N2—C3	166.40 (9)
C8—C9—C10—C11	0.47 (18)	C1—N1—N2—C5	147.19 (9)
C9—C10—C11—C6	0.20 (17)	C6—N1—N2—C5	−55.31 (12)
C7—C6—C11—C10	−0.54 (16)	C14—C12—N3—C2	179.44 (10)
N1—C6—C11—C10	178.29 (9)	C13—C12—N3—C2	−0.92 (17)
N3—C12—C14—C15	1.55 (18)	C3—C2—N3—C12	−69.82 (16)
C13—C12—C14—C15	−178.08 (11)	C1—C2—N3—C12	117.04 (12)
C12—C14—C15—O2	2.80 (18)	O2—C15—O3—C16	1.37 (16)
C12—C14—C15—O3	−177.10 (10)	C14—C15—O3—C16	−178.72 (10)
O1—C1—N1—N2	168.01 (10)	C17—C16—O3—C15	−81.62 (13)
C2—C1—N1—N2	−8.42 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O2	0.886 (18)	2.009 (18)	2.7192 (12)	136 (1)
C11—H11···O1^{i}	0.95	2.35	3.2829 (14)	167
C8—H8···O3^{ii}	0.95	2.7	3.6206 (15)	164

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

(IV) Ethyl 2-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]cyclohex-1-enecarboxylate

Crystal data

$C_{20}H_{25}N_3O_3$
$M_r = 355.43$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.3857$ (2) Å
$b = 9.2159$ (3) Å
$c = 13.7494$ (4) Å
$\alpha = 85.898$ (1)°
$\beta = 84.499$ (1)°
$\gamma = 85.210$ (1)°
$V = 926.40$ (5) Å^3
$Z = 2$
$F(000) = 380$
$D_x = 1.274$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8186 reflections
$\theta = 2.2$–$28.3°$
$\mu = 0.09$ mm^{-1}
$T = 173$ K
Plate, colourless
0.3 × 0.3 × 0.19 mm

Data collection

Bruker D8 Venture Photon diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.95$, $T_{max} = 0.96$
20559 measured reflections
4466 independent reflections
3628 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 28.0°$, $\theta_{min} = 1.5°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 11$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.107$
$S = 1.04$
4466 reflections
242 parameters
0 restraints
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.2134P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Experimental. Absorption corrections were made using the program *SADABS* (Sheldrick, 1996)
Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.69149 (16)	0.77040 (13)	0.44703 (8)	0.0257 (2)
C2	0.56088 (16)	0.70172 (13)	0.39711 (8)	0.0253 (2)
C3	0.41466 (16)	0.67442 (12)	0.46160 (8)	0.0252 (2)
C4	0.24182 (17)	0.61259 (14)	0.44459 (9)	0.0325 (3)
H4A	0.2502	0.5807	0.3777	0.049*
H4B	0.1402	0.6873	0.4535	0.049*
H4C	0.2211	0.529	0.4913	0.049*
C5	0.29521 (17)	0.78324 (14)	0.61675 (9)	0.0302 (3)
H5A	0.2666	0.8836	0.5909	0.045*

H5B	0.3322	0.7843	0.6833	0.045*
H5C	0.187	0.7281	0.6182	0.045*
C6	0.70009 (16)	0.81214 (13)	0.62319 (8)	0.0249 (2)
C7	0.69056 (18)	0.71728 (13)	0.70625 (8)	0.0292 (3)
H7	0.6208	0.6348	0.709	0.035*
C8	0.78386 (19)	0.74410 (14)	0.78510 (9)	0.0341 (3)
H8	0.7779	0.6797	0.8422	0.041*
C9	0.88554 (19)	0.86411 (15)	0.78110 (9)	0.0345 (3)
H9	0.9494	0.8818	0.8353	0.041*
C10	0.89427 (17)	0.95840 (14)	0.69818 (9)	0.0320 (3)
H10	0.9639	1.041	0.6957	0.038*
C11	0.80186 (17)	0.93284 (13)	0.61877 (9)	0.0285 (3)
H11	0.8081	0.9974	0.5617	0.034*
C12	0.63541 (15)	0.74644 (12)	0.22002 (8)	0.0239 (2)
C13	0.68815 (15)	0.69490 (12)	0.12974 (8)	0.0236 (2)
C14	0.73716 (17)	0.79641 (13)	0.04140 (8)	0.0268 (3)
H14A	0.6382	0.8023	−0.0028	0.032*
H14B	0.8499	0.7551	0.0053	0.032*
C15	0.7664 (2)	0.94900 (14)	0.06831 (9)	0.0339 (3)
H15A	0.8841	0.9481	0.0974	0.041*
H15B	0.7713	1.0159	0.0086	0.041*
C16	0.6127 (2)	1.00262 (14)	0.14074 (9)	0.0346 (3)
H16A	0.4944	0.9992	0.113	0.042*
H16B	0.6271	1.105	0.1539	0.042*
C17	0.61487 (18)	0.90701 (13)	0.23578 (8)	0.0292 (3)
H17A	0.7169	0.9316	0.2718	0.035*
H17B	0.4999	0.9291	0.2771	0.035*
C18	0.69463 (16)	0.54040 (13)	0.11583 (8)	0.0253 (2)
C19	0.74116 (19)	0.35824 (13)	0.00053 (9)	0.0318 (3)
H19A	0.6193	0.3218	0.0185	0.038*
H19B	0.8307	0.2988	0.0388	0.038*
C20	0.7937 (2)	0.34768 (15)	−0.10745 (10)	0.0365 (3)
H20A	0.7042	0.407	−0.1446	0.055*
H20B	0.7963	0.2457	−0.1238	0.055*
H20C	0.9148	0.3835	−0.1243	0.055*
N1	0.60598 (13)	0.78805 (11)	0.54063 (7)	0.0262 (2)
N2	0.44476 (13)	0.71398 (11)	0.55359 (7)	0.0256 (2)
N3	0.59282 (14)	0.65599 (12)	0.30077 (7)	0.0273 (2)
H3	0.608 (2)	0.5608 (18)	0.2902 (11)	0.043 (4)*
O1	0.84587 (12)	0.80604 (10)	0.41948 (6)	0.0331 (2)
O2	0.66354 (13)	0.44227 (9)	0.17906 (6)	0.0339 (2)
O3	0.73861 (12)	0.50993 (9)	0.02103 (6)	0.0285 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0294 (6)	0.0280 (6)	0.0186 (5)	−0.0005 (5)	−0.0004 (4)	0.0019 (4)
C2	0.0295 (6)	0.0264 (6)	0.0192 (5)	−0.0004 (5)	−0.0007 (4)	0.0004 (4)

C3	0.0281 (6)	0.0235 (5)	0.0235 (5)	0.0003 (5)	−0.0025 (4)	−0.0013 (4)
C4	0.0302 (7)	0.0350 (7)	0.0330 (6)	−0.0043 (5)	−0.0030 (5)	−0.0048 (5)
C5	0.0310 (6)	0.0336 (6)	0.0248 (6)	−0.0015 (5)	0.0049 (5)	−0.0048 (5)
C6	0.0273 (6)	0.0282 (6)	0.0191 (5)	−0.0024 (5)	0.0002 (4)	−0.0031 (4)
C7	0.0403 (7)	0.0270 (6)	0.0208 (5)	−0.0090 (5)	0.0002 (5)	−0.0023 (4)
C8	0.0487 (8)	0.0343 (7)	0.0200 (5)	−0.0080 (6)	−0.0041 (5)	0.0002 (5)
C9	0.0396 (7)	0.0406 (7)	0.0255 (6)	−0.0087 (6)	−0.0060 (5)	−0.0064 (5)
C10	0.0315 (7)	0.0335 (7)	0.0320 (6)	−0.0109 (5)	0.0017 (5)	−0.0048 (5)
C11	0.0306 (6)	0.0289 (6)	0.0252 (6)	−0.0048 (5)	0.0016 (5)	0.0022 (5)
C12	0.0230 (6)	0.0277 (6)	0.0207 (5)	−0.0016 (5)	−0.0029 (4)	0.0010 (4)
C13	0.0250 (6)	0.0259 (6)	0.0200 (5)	−0.0034 (4)	−0.0022 (4)	0.0000 (4)
C14	0.0329 (6)	0.0278 (6)	0.0197 (5)	−0.0048 (5)	−0.0017 (4)	−0.0002 (4)
C15	0.0485 (8)	0.0283 (6)	0.0249 (6)	−0.0096 (6)	−0.0002 (5)	0.0010 (5)
C16	0.0519 (8)	0.0255 (6)	0.0257 (6)	0.0014 (6)	−0.0043 (5)	−0.0001 (5)
C17	0.0378 (7)	0.0272 (6)	0.0219 (5)	0.0015 (5)	−0.0020 (5)	−0.0023 (4)
C18	0.0252 (6)	0.0288 (6)	0.0218 (5)	−0.0020 (5)	−0.0009 (4)	−0.0015 (4)
C19	0.0383 (7)	0.0245 (6)	0.0326 (6)	−0.0015 (5)	−0.0018 (5)	−0.0051 (5)
C20	0.0421 (8)	0.0344 (7)	0.0333 (7)	−0.0002 (6)	−0.0021 (6)	−0.0097 (5)
N1	0.0273 (5)	0.0334 (5)	0.0181 (4)	−0.0078 (4)	0.0008 (4)	−0.0008 (4)
N2	0.0250 (5)	0.0302 (5)	0.0215 (5)	−0.0047 (4)	0.0020 (4)	−0.0032 (4)
N3	0.0367 (6)	0.0263 (5)	0.0181 (5)	−0.0020 (4)	0.0005 (4)	−0.0010 (4)
O1	0.0283 (5)	0.0460 (5)	0.0241 (4)	−0.0077 (4)	0.0016 (3)	0.0034 (4)
O2	0.0481 (6)	0.0267 (4)	0.0258 (4)	−0.0057 (4)	0.0022 (4)	0.0016 (3)
O3	0.0378 (5)	0.0250 (4)	0.0225 (4)	−0.0034 (4)	0.0010 (3)	−0.0040 (3)

Geometric parameters (Å, º)

C1—O1	1.2302 (14)	C12—C13	1.3707 (15)
C1—N1	1.3924 (14)	C12—C17	1.5040 (16)
C1—C2	1.4468 (17)	C13—C18	1.4464 (16)
C2—C3	1.3586 (17)	C13—C14	1.5137 (15)
C2—N3	1.4110 (14)	C14—C15	1.5171 (17)
C3—N2	1.3840 (14)	C14—H14A	0.99
C3—C4	1.4856 (17)	C14—H14B	0.99
C4—H4A	0.98	C15—C16	1.5115 (19)
C4—H4B	0.98	C15—H15A	0.99
C4—H4C	0.98	C15—H15B	0.99
C5—N2	1.4694 (15)	C16—C17	1.5235 (16)
C5—H5A	0.98	C16—H16A	0.99
C5—H5B	0.98	C16—H16B	0.99
C5—H5C	0.98	C17—H17A	0.99
C6—C7	1.3876 (16)	C17—H17B	0.99
C6—C11	1.3882 (16)	C18—O2	1.2289 (14)
C6—N1	1.4261 (14)	C18—O3	1.3562 (13)
C7—C8	1.3862 (17)	C19—O3	1.4439 (14)
C7—H7	0.95	C19—C20	1.5061 (18)
C8—C9	1.3828 (18)	C19—H19A	0.99
C8—H8	0.95	C19—H19B	0.99

C9—C10	1.3830 (18)	C20—H20A	0.98
C9—H9	0.95	C20—H20B	0.98
C10—C11	1.3856 (17)	C20—H20C	0.98
C10—H10	0.95	N1—N2	1.4118 (13)
C11—H11	0.95	N3—H3	0.896 (16)
C12—N3	1.3679 (15)		

O1—C1—N1	124.35 (11)	C15—C14—H14A	109
O1—C1—C2	131.25 (11)	C13—C14—H14B	109
N1—C1—C2	104.39 (10)	C15—C14—H14B	109
C3—C2—N3	126.34 (11)	H14A—C14—H14B	107.8
C3—C2—C1	108.72 (10)	C16—C15—C14	110.09 (11)
N3—C2—C1	124.54 (10)	C16—C15—H15A	109.6
C2—C3—N2	109.92 (10)	C14—C15—H15A	109.6
C2—C3—C4	129.23 (11)	C16—C15—H15B	109.6
N2—C3—C4	120.85 (10)	C14—C15—H15B	109.6
C3—C4—H4A	109.5	H15A—C15—H15B	108.2
C3—C4—H4B	109.5	C15—C16—C17	109.66 (11)
H4A—C4—H4B	109.5	C15—C16—H16A	109.7
C3—C4—H4C	109.5	C17—C16—H16A	109.7
H4A—C4—H4C	109.5	C15—C16—H16B	109.7
H4B—C4—H4C	109.5	C17—C16—H16B	109.7
N2—C5—H5A	109.5	H16A—C16—H16B	108.2
N2—C5—H5B	109.5	C12—C17—C16	113.24 (10)
H5A—C5—H5B	109.5	C12—C17—H17A	108.9
N2—C5—H5C	109.5	C16—C17—H17A	108.9
H5A—C5—H5C	109.5	C12—C17—H17B	108.9
H5B—C5—H5C	109.5	C16—C17—H17B	108.9
C7—C6—C11	120.54 (11)	H17A—C17—H17B	107.7
C7—C6—N1	120.92 (10)	O2—C18—O3	120.68 (10)
C11—C6—N1	118.55 (10)	O2—C18—C13	126.86 (10)
C8—C7—C6	119.34 (11)	O3—C18—C13	112.46 (9)
C8—C7—H7	120.3	O3—C19—C20	107.49 (10)
C6—C7—H7	120.3	O3—C19—H19A	110.2
C9—C8—C7	120.38 (11)	C20—C19—H19A	110.2
C9—C8—H8	119.8	O3—C19—H19B	110.2
C7—C8—H8	119.8	C20—C19—H19B	110.2
C8—C9—C10	120.01 (11)	H19A—C19—H19B	108.5
C8—C9—H9	120	C19—C20—H20A	109.5
C10—C9—H9	120	C19—C20—H20B	109.5
C9—C10—C11	120.22 (11)	H20A—C20—H20B	109.5
C9—C10—H10	119.9	C19—C20—H20C	109.5
C11—C10—H10	119.9	H20A—C20—H20C	109.5
C10—C11—C6	119.51 (11)	H20B—C20—H20C	109.5
C10—C11—H11	120.2	C1—N1—N2	109.98 (9)
C6—C11—H11	120.2	C1—N1—C6	123.86 (10)
N3—C12—C13	122.39 (10)	N2—N1—C6	120.08 (9)
N3—C12—C17	115.68 (10)	C3—N2—N1	105.89 (9)

C13—C12—C17	121.90 (10)	C3—N2—C5	120.39 (10)
C12—C13—C18	120.43 (10)	N1—N2—C5	115.15 (9)
C12—C13—C14	121.70 (10)	C12—N3—C2	124.33 (10)
C18—C13—C14	117.85 (10)	C12—N3—H3	114.4 (10)
C13—C14—C15	112.91 (9)	C2—N3—H3	120.3 (10)
C13—C14—H14A	109	C18—O3—C19	115.81 (9)
O1—C1—C2—C3	175.21 (12)	C12—C13—C18—O2	−3.08 (19)
N1—C1—C2—C3	−3.53 (13)	C14—C13—C18—O2	178.25 (11)
O1—C1—C2—N3	2.1 (2)	C12—C13—C18—O3	176.17 (10)
N1—C1—C2—N3	−176.63 (10)	C14—C13—C18—O3	−2.50 (15)
N3—C2—C3—N2	169.71 (11)	O1—C1—N1—N2	−169.93 (11)
C1—C2—C3—N2	−3.24 (13)	C2—C1—N1—N2	8.92 (12)
N3—C2—C3—C4	−10.5 (2)	O1—C1—N1—C6	−17.55 (18)
C1—C2—C3—C4	176.55 (12)	C2—C1—N1—C6	161.30 (10)
C11—C6—C7—C8	0.00 (19)	C7—C6—N1—C1	−121.50 (13)
N1—C6—C7—C8	179.98 (11)	C11—C6—N1—C1	58.49 (16)
C6—C7—C8—C9	0.0 (2)	C7—C6—N1—N2	28.28 (16)
C7—C8—C9—C10	0.1 (2)	C11—C6—N1—N2	−151.74 (11)
C8—C9—C10—C11	−0.2 (2)	C2—C3—N2—N1	8.61 (13)
C9—C10—C11—C6	0.18 (19)	C4—C3—N2—N1	−171.21 (10)
C7—C6—C11—C10	−0.07 (19)	C2—C3—N2—C5	141.38 (11)
N1—C6—C11—C10	179.95 (11)	C4—C3—N2—C5	−38.44 (16)
N3—C12—C13—C18	2.18 (17)	C1—N1—N2—C3	−11.00 (12)
C17—C12—C13—C18	−175.80 (11)	C6—N1—N2—C3	−164.59 (10)
N3—C12—C13—C14	−179.20 (10)	C1—N1—N2—C5	−146.61 (10)
C17—C12—C13—C14	2.82 (17)	C6—N1—N2—C5	59.80 (14)
C12—C13—C14—C15	14.10 (16)	C13—C12—N3—C2	171.45 (11)
C18—C13—C14—C15	−167.24 (11)	C17—C12—N3—C2	−10.46 (16)
C13—C14—C15—C16	−47.09 (14)	C3—C2—N3—C12	129.14 (13)
C14—C15—C16—C17	63.96 (14)	C1—C2—N3—C12	−58.97 (17)
N3—C12—C17—C16	−164.18 (11)	O2—C18—O3—C19	1.53 (16)
C13—C12—C17—C16	13.92 (17)	C13—C18—O3—C19	−177.77 (10)
C15—C16—C17—C12	−46.68 (15)	C20—C19—O3—C18	−179.63 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O2	0.896 (16)	1.934 (16)	2.6618 (13)	137 (1)

(V) (*Z*)-Ethyl 3-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]-3-phenylacrylate

Crystal data

$C_{22}H_{23}N_3O_3$
M_r = 377.43
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 8.4851 (7) Å
b = 12.4253 (10) Å
c = 18.0314 (18) Å
β = 92.282 (3)°
V = 1899.5 (3) Å^3
Z = 4
$F(000)$ = 800
D_x = 1.32 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9961 reflections
θ = 3.2–28.2°
μ = 0.09 mm^{-1}
T = 173 K
Plate, yellow
0.44 × 0.34 × 0.11 mm

Data collection

Bruker D8 Venture Photon diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.95, T_{max} = 0.96
28673 measured reflections
4570 independent reflections
3838 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 28.0°, θ_{min} = 3.3°
h = −10→11
k = −16→16
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.095
S = 1.04
4570 reflections
260 parameters
0 restraints
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.6436P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Special details

Experimental. Absorption corrections were made using the program *SADABS* (Sheldrick, 1996)
Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.73101 (12)	0.24095 (9)	0.38575 (6)	0.0235 (2)
C2	0.68561 (12)	0.34800 (9)	0.36110 (6)	0.0228 (2)
C3	0.79944 (12)	0.38855 (9)	0.31873 (6)	0.0220 (2)
C4	0.80437 (14)	0.49224 (9)	0.27788 (7)	0.0277 (2)
H4A	0.7825	0.4793	0.2248	0.042*
H4B	0.9091	0.5247	0.2852	0.042*
H4C	0.7247	0.5412	0.2967	0.042*
C5	0.98523 (15)	0.29227 (10)	0.24187 (6)	0.0289 (3)
H5A	0.9037	0.2555	0.2113	0.043*
H5B	1.0782	0.2458	0.2478	0.043*
H5C	1.0147	0.3595	0.2176	0.043*
C6	0.99274 (12)	0.14792 (9)	0.37750 (6)	0.0210 (2)
C7	1.15038 (13)	0.17856 (9)	0.38681 (6)	0.0238 (2)
H7	1.1819	0.2497	0.3751	0.029*
C8	1.26092 (13)	0.10407 (10)	0.41337 (6)	0.0285 (2)
H8	1.3687	0.1242	0.4194	0.034*
C9	1.21484 (15)	0.00056 (10)	0.43107 (6)	0.0305 (3)
H9	1.2902	−0.0496	0.4505	0.037*

C10	1.05869 (15)	−0.02949 (9)	0.42031 (6)	0.0289 (3)
H10	1.0275	−0.1008	0.4319	0.035*
C11	0.94718 (13)	0.04313 (9)	0.39279 (6)	0.0250 (2)
H11	0.8406	0.0215	0.3844	0.03*
C12	0.42177 (12)	0.41268 (8)	0.32552 (6)	0.0226 (2)
C13	0.43943 (12)	0.36614 (9)	0.25002 (6)	0.0235 (2)
C14	0.46922 (13)	0.25684 (10)	0.23929 (7)	0.0287 (2)
H14	0.48	0.21	0.2808	0.034*
C15	0.48312 (14)	0.21660 (10)	0.16805 (8)	0.0343 (3)
H15	0.5039	0.1422	0.1612	0.041*
C16	0.46709 (14)	0.28360 (11)	0.10689 (7)	0.0356 (3)
H16	0.4784	0.2556	0.0584	0.043*
C17	0.43452 (14)	0.39154 (11)	0.11684 (7)	0.0323 (3)
H17	0.421	0.4376	0.075	0.039*
C18	0.42150 (13)	0.43263 (10)	0.18807 (7)	0.0275 (2)
H18	0.4001	0.507	0.1946	0.033*
C19	0.28782 (13)	0.46926 (9)	0.33825 (6)	0.0256 (2)
H19	0.2096	0.4728	0.2991	0.031*
C20	0.25582 (12)	0.52413 (9)	0.40659 (6)	0.0249 (2)
C21	0.06614 (15)	0.63645 (11)	0.46383 (7)	0.0336 (3)
H21A	0.1338	0.701	0.4698	0.04*
H21B	0.0747	0.5937	0.5102	0.04*
C22	−0.10227 (15)	0.66841 (12)	0.44690 (7)	0.0376 (3)
H22A	−0.1097	0.7066	0.3993	0.056*
H22B	−0.1384	0.7156	0.4863	0.056*
H22C	−0.1685	0.6038	0.444	0.056*
N1	0.87573 (10)	0.22321 (7)	0.35321 (5)	0.0233 (2)
N2	0.92385 (10)	0.31639 (7)	0.31523 (5)	0.02214 (19)
N3	0.54052 (11)	0.39661 (8)	0.37760 (6)	0.0269 (2)
H3	0.5283 (17)	0.4200 (12)	0.4223 (9)	0.036 (4)*
O1	0.66500 (9)	0.17733 (7)	0.42638 (5)	0.0320 (2)
O2	0.34206 (10)	0.52933 (8)	0.46196 (5)	0.0347 (2)
O3	0.11324 (10)	0.57275 (7)	0.40133 (5)	0.0329 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0181 (5)	0.0287 (6)	0.0236 (5)	0.0013 (4)	−0.0002 (4)	0.0024 (4)
C2	0.0199 (5)	0.0268 (5)	0.0215 (5)	0.0039 (4)	−0.0006 (4)	0.0012 (4)
C3	0.0213 (5)	0.0244 (5)	0.0199 (5)	0.0033 (4)	−0.0027 (4)	0.0004 (4)
C4	0.0283 (6)	0.0258 (6)	0.0292 (6)	0.0036 (5)	0.0016 (4)	0.0055 (5)
C5	0.0313 (6)	0.0319 (6)	0.0240 (6)	0.0048 (5)	0.0058 (4)	0.0021 (5)
C6	0.0208 (5)	0.0234 (5)	0.0188 (5)	0.0044 (4)	0.0009 (4)	−0.0001 (4)
C7	0.0224 (5)	0.0250 (5)	0.0239 (5)	0.0017 (4)	0.0014 (4)	−0.0008 (4)
C8	0.0213 (5)	0.0389 (6)	0.0252 (5)	0.0063 (5)	0.0000 (4)	−0.0011 (5)
C9	0.0328 (6)	0.0344 (6)	0.0245 (5)	0.0153 (5)	0.0026 (5)	0.0029 (5)
C10	0.0396 (6)	0.0223 (5)	0.0251 (5)	0.0055 (5)	0.0057 (5)	0.0025 (4)
C11	0.0266 (5)	0.0249 (5)	0.0236 (5)	−0.0003 (4)	0.0020 (4)	−0.0001 (4)

C12	0.0192 (5)	0.0197 (5)	0.0290 (6)	−0.0008 (4)	0.0012 (4)	0.0028 (4)
C13	0.0155 (5)	0.0251 (5)	0.0296 (6)	−0.0002 (4)	−0.0004 (4)	−0.0016 (4)
C14	0.0235 (5)	0.0247 (6)	0.0378 (6)	0.0002 (4)	0.0012 (5)	0.0006 (5)
C15	0.0272 (6)	0.0277 (6)	0.0482 (8)	0.0001 (5)	0.0039 (5)	−0.0099 (5)
C16	0.0265 (6)	0.0462 (8)	0.0341 (7)	−0.0036 (5)	0.0026 (5)	−0.0121 (6)
C17	0.0257 (6)	0.0413 (7)	0.0296 (6)	−0.0025 (5)	−0.0026 (5)	0.0020 (5)
C18	0.0220 (5)	0.0264 (6)	0.0337 (6)	0.0008 (4)	−0.0027 (4)	−0.0002 (5)
C19	0.0194 (5)	0.0260 (5)	0.0310 (6)	0.0020 (4)	−0.0027 (4)	−0.0022 (4)
C20	0.0190 (5)	0.0249 (5)	0.0307 (6)	0.0019 (4)	0.0000 (4)	0.0025 (4)
C21	0.0328 (6)	0.0391 (7)	0.0286 (6)	0.0108 (5)	−0.0015 (5)	−0.0093 (5)
C22	0.0329 (7)	0.0473 (8)	0.0328 (7)	0.0130 (6)	0.0033 (5)	−0.0082 (6)
N1	0.0193 (4)	0.0233 (5)	0.0275 (5)	0.0018 (4)	0.0025 (3)	0.0065 (4)
N2	0.0212 (4)	0.0226 (4)	0.0228 (4)	0.0023 (4)	0.0028 (3)	0.0048 (3)
N3	0.0224 (5)	0.0351 (5)	0.0231 (5)	0.0094 (4)	0.0017 (4)	0.0018 (4)
O1	0.0240 (4)	0.0344 (5)	0.0380 (5)	0.0014 (3)	0.0071 (3)	0.0121 (4)
O2	0.0266 (4)	0.0490 (5)	0.0282 (4)	0.0089 (4)	−0.0028 (3)	−0.0001 (4)
O3	0.0251 (4)	0.0415 (5)	0.0317 (4)	0.0127 (4)	−0.0039 (3)	−0.0110 (4)

Geometric parameters (Å, º)

C1—O1	1.2280 (14)	C12—N3	1.3645 (14)
C1—N1	1.3994 (14)	C12—C13	1.4920 (16)
C1—C2	1.4497 (15)	C13—C18	1.3929 (16)
C2—C3	1.3526 (15)	C13—C14	1.3963 (16)
C2—N3	1.4135 (14)	C14—C15	1.3878 (18)
C3—N2	1.3884 (14)	C14—H14	0.95
C3—C4	1.4855 (15)	C15—C16	1.384 (2)
C4—H4A	0.98	C15—H15	0.95
C4—H4B	0.98	C16—C17	1.3825 (19)
C4—H4C	0.98	C16—H16	0.95
C5—N2	1.4716 (14)	C17—C18	1.3905 (17)
C5—H5A	0.98	C17—H17	0.95
C5—H5B	0.98	C18—H18	0.95
C5—H5C	0.98	C19—C20	1.4435 (16)
C6—C11	1.3890 (15)	C19—H19	0.95
C6—C7	1.3945 (15)	C20—O2	1.2159 (14)
C6—N1	1.4206 (13)	C20—O3	1.3522 (13)
C7—C8	1.3892 (16)	C21—O3	1.4465 (14)
C7—H7	0.95	C21—C22	1.5027 (17)
C8—C9	1.3852 (18)	C21—H21A	0.99
C8—H8	0.95	C21—H21B	0.99
C9—C10	1.3828 (18)	C22—H22A	0.98
C9—H9	0.95	C22—H22B	0.98
C10—C11	1.3850 (16)	C22—H22C	0.98
C10—H10	0.95	N1—N2	1.4136 (12)
C11—H11	0.95	N3—H3	0.867 (16)
C12—C19	1.3637 (15)		

O1—C1—N1	125.27 (10)	C14—C13—C12	121.92 (10)
O1—C1—C2	130.66 (10)	C15—C14—C13	120.08 (12)
N1—C1—C2	104.05 (9)	C15—C14—H14	120
C3—C2—N3	127.39 (10)	C13—C14—H14	120
C3—C2—C1	109.14 (9)	C16—C15—C14	120.76 (12)
N3—C2—C1	123.41 (10)	C16—C15—H15	119.6
C2—C3—N2	110.27 (10)	C14—C15—H15	119.6
C2—C3—C4	129.64 (10)	C17—C16—C15	119.60 (12)
N2—C3—C4	120.08 (10)	C17—C16—H16	120.2
C3—C4—H4A	109.5	C15—C16—H16	120.2
C3—C4—H4B	109.5	C16—C17—C18	119.98 (12)
H4A—C4—H4B	109.5	C16—C17—H17	120
C3—C4—H4C	109.5	C18—C17—H17	120
H4A—C4—H4C	109.5	C17—C18—C13	120.86 (11)
H4B—C4—H4C	109.5	C17—C18—H18	119.6
N2—C5—H5A	109.5	C13—C18—H18	119.6
N2—C5—H5B	109.5	C12—C19—C20	125.00 (10)
H5A—C5—H5B	109.5	C12—C19—H19	117.5
N2—C5—H5C	109.5	C20—C19—H19	117.5
H5A—C5—H5C	109.5	O2—C20—O3	122.78 (11)
H5B—C5—H5C	109.5	O2—C20—C19	126.77 (10)
C11—C6—C7	120.35 (10)	O3—C20—C19	110.44 (9)
C11—C6—N1	118.81 (10)	O3—C21—C22	106.03 (10)
C7—C6—N1	120.84 (10)	O3—C21—H21A	110.5
C8—C7—C6	119.40 (11)	C22—C21—H21A	110.5
C8—C7—H7	120.3	O3—C21—H21B	110.5
C6—C7—H7	120.3	C22—C21—H21B	110.5
C9—C8—C7	120.34 (11)	H21A—C21—H21B	108.7
C9—C8—H8	119.8	C21—C22—H22A	109.5
C7—C8—H8	119.8	C21—C22—H22B	109.5
C10—C9—C8	119.74 (11)	H22A—C22—H22B	109.5
C10—C9—H9	120.1	C21—C22—H22C	109.5
C8—C9—H9	120.1	H22A—C22—H22C	109.5
C9—C10—C11	120.76 (11)	H22B—C22—H22C	109.5
C9—C10—H10	119.6	C1—N1—N2	110.45 (8)
C11—C10—H10	119.6	C1—N1—C6	126.06 (9)
C10—C11—C6	119.36 (11)	N2—N1—C6	118.48 (8)
C10—C11—H11	120.3	C3—N2—N1	105.79 (8)
C6—C11—H11	120.3	C3—N2—C5	117.99 (9)
C19—C12—N3	123.86 (11)	N1—N2—C5	112.84 (9)
C19—C12—C13	117.91 (10)	C12—N3—C2	122.90 (10)
N3—C12—C13	118.23 (9)	C12—N3—H3	118.6 (10)
C18—C13—C14	118.70 (11)	C2—N3—H3	118.4 (10)
C18—C13—C12	119.35 (10)	C20—O3—C21	117.64 (9)

O1—C1—C2—C3	177.76 (12)	N3—C12—C19—C20	3.14 (18)
N1—C1—C2—C3	−1.23 (12)	C13—C12—C19—C20	−176.56 (10)
O1—C1—C2—N3	−4.83 (19)	C12—C19—C20—O2	0.8 (2)

N1—C1—C2—N3	176.18 (10)	C12—C19—C20—O3	179.86 (11)
N3—C2—C3—N2	−179.52 (10)	O1—C1—N1—N2	−174.85 (11)
C1—C2—C3—N2	−2.24 (13)	C2—C1—N1—N2	4.21 (11)
N3—C2—C3—C4	−0.6 (2)	O1—C1—N1—C6	−20.54 (18)
C1—C2—C3—C4	176.65 (11)	C2—C1—N1—C6	158.52 (10)
C11—C6—C7—C8	−1.65 (16)	C11—C6—N1—C1	47.88 (15)
N1—C6—C7—C8	177.53 (10)	C7—C6—N1—C1	−131.33 (12)
C6—C7—C8—C9	−0.57 (17)	C11—C6—N1—N2	−159.65 (10)
C7—C8—C9—C10	1.77 (17)	C7—C6—N1—N2	21.15 (15)
C8—C9—C10—C11	−0.75 (17)	C2—C3—N2—N1	4.75 (12)
C9—C10—C11—C6	−1.46 (17)	C4—C3—N2—N1	−174.26 (9)
C7—C6—C11—C10	2.66 (16)	C2—C3—N2—C5	132.13 (10)
N1—C6—C11—C10	−176.55 (10)	C4—C3—N2—C5	−46.89 (14)
C19—C12—C13—C18	52.83 (14)	C1—N1—N2—C3	−5.60 (11)
N3—C12—C13—C18	−126.89 (11)	C6—N1—N2—C3	−162.10 (9)
C19—C12—C13—C14	−125.36 (12)	C1—N1—N2—C5	−136.01 (9)
N3—C12—C13—C14	54.92 (15)	C6—N1—N2—C5	67.49 (12)
C18—C13—C14—C15	1.09 (16)	C19—C12—N3—C2	−172.86 (11)
C12—C13—C14—C15	179.29 (10)	C13—C12—N3—C2	6.85 (16)
C13—C14—C15—C16	−0.29 (18)	C3—C2—N3—C12	68.10 (17)
C14—C15—C16—C17	−0.97 (18)	C1—C2—N3—C12	−108.82 (13)
C15—C16—C17—C18	1.41 (18)	O2—C20—O3—C21	2.31 (17)
C16—C17—C18—C13	−0.60 (17)	C19—C20—O3—C21	−176.77 (10)
C14—C13—C18—C17	−0.65 (16)	C22—C21—O3—C20	−173.01 (11)
C12—C13—C18—C17	−178.90 (10)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O2	0.867 (16)	2.224 (15)	2.8413 (13)	128 (1)
N3—H3···O2^{i}	0.867 (16)	2.404 (16)	3.1590 (14)	146 (1)
C8—H8···O1^{ii}	0.95	2.6	3.5462 (15)	176

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

(VI) 2-Cyano-*N*-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)acetamide

Crystal data

$C_{14}H_{14}N_4O_2$
M_r = 270.29
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 6.9996 (8) Å
b = 12.3350 (16) Å
c = 15.8345 (19) Å
β = 99.666 (4)°
V = 1347.7 (3) Å^3
Z = 4
$F(000)$ = 568
D_x = 1.332 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9915 reflections
θ = 3.1–28.3°
μ = 0.09 mm^{-1}
T = 173 K
Needle, colourless
0.67 × 0.16 × 0.11 mm

Data collection

Bruker D8 Venture Photon diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.98, T_{max} = 0.99
19472 measured reflections
3252 independent reflections
2737 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 28.0°, θ_{min} = 3.4°
h = −9→8
k = −16→16
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.097
S = 1.03
3252 reflections
187 parameters
0 restraints
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.3708P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Special details

Experimental. Absorption corrections were made using the program *SADABS* (Sheldrick, 1996)
Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.34738 (14)	0.45507 (8)	0.10778 (6)	0.0226 (2)
C2	0.23701 (14)	0.55169 (8)	0.08681 (7)	0.0231 (2)
C3	0.05925 (15)	0.53893 (8)	0.11050 (7)	0.0246 (2)
C4	−0.10439 (16)	0.61652 (10)	0.10627 (8)	0.0327 (3)
H4A	−0.1001	0.6511	0.1623	0.049*
H4B	−0.2273	0.5776	0.0907	0.049*
H4C	−0.0937	0.6721	0.0631	0.049*
C5	−0.05781 (17)	0.41025 (11)	0.21283 (8)	0.0349 (3)
H5A	0.012	0.4399	0.2667	0.052*
H5B	−0.068	0.3313	0.2178	0.052*
H5C	−0.188	0.4419	0.2007	0.052*
C6	0.25170 (15)	0.27381 (9)	0.15402 (7)	0.0251 (2)
C7	0.11104 (18)	0.20547 (10)	0.11078 (8)	0.0346 (3)
H7	−0.0041	0.2344	0.0783	0.041*
C8	0.1407 (2)	0.09414 (11)	0.11558 (9)	0.0438 (3)
H8	0.044	0.0465	0.0873	0.053*
C9	0.3095 (2)	0.05252 (10)	0.16110 (9)	0.0436 (3)
H9	0.3303	−0.0236	0.1631	0.052*
C10	0.4488 (2)	0.12139 (11)	0.20388 (9)	0.0408 (3)
H10	0.5653	0.0923	0.2351	0.049*
C11	0.42005 (17)	0.23284 (10)	0.20169 (7)	0.0311 (2)
H11	0.5142	0.2801	0.2324	0.037*

C12	0.32054 (15)	0.74122 (9)	0.06778 (7)	0.0258 (2)
C13	0.41768 (18)	0.81538 (9)	0.00944 (8)	0.0327 (3)
H13A	0.4643	0.7711	−0.0351	0.039*
H13B	0.3212	0.8677	−0.0197	0.039*
C14	0.58016 (17)	0.87440 (10)	0.05817 (8)	0.0339 (3)
N1	0.22982 (12)	0.38856 (7)	0.14719 (6)	0.0247 (2)
N2	0.04759 (12)	0.43659 (7)	0.14307 (6)	0.0255 (2)
N3	0.30922 (13)	0.63698 (7)	0.04169 (6)	0.0252 (2)
H3	0.375 (2)	0.6174 (12)	−0.0003 (9)	0.036 (4)*
N4	0.70659 (18)	0.92148 (12)	0.09499 (9)	0.0551 (3)
O1	0.51052 (10)	0.42821 (6)	0.09377 (5)	0.02694 (18)
O2	0.25709 (13)	0.77685 (7)	0.12907 (5)	0.0345 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0215 (5)	0.0229 (5)	0.0232 (5)	−0.0034 (4)	0.0033 (4)	−0.0020 (4)
C2	0.0218 (5)	0.0207 (5)	0.0265 (5)	−0.0024 (4)	0.0037 (4)	−0.0016 (4)
C3	0.0224 (5)	0.0242 (5)	0.0267 (5)	−0.0022 (4)	0.0024 (4)	−0.0028 (4)
C4	0.0240 (5)	0.0304 (6)	0.0441 (7)	0.0030 (4)	0.0075 (5)	−0.0004 (5)
C5	0.0271 (5)	0.0451 (7)	0.0349 (6)	0.0021 (5)	0.0127 (5)	0.0062 (5)
C6	0.0273 (5)	0.0230 (5)	0.0262 (5)	−0.0017 (4)	0.0080 (4)	0.0028 (4)
C7	0.0336 (6)	0.0318 (6)	0.0374 (6)	−0.0078 (5)	0.0034 (5)	0.0018 (5)
C8	0.0554 (8)	0.0291 (6)	0.0493 (8)	−0.0148 (6)	0.0162 (6)	−0.0043 (5)
C9	0.0616 (9)	0.0229 (5)	0.0538 (8)	0.0021 (6)	0.0315 (7)	0.0066 (5)
C10	0.0448 (7)	0.0367 (7)	0.0438 (7)	0.0114 (5)	0.0159 (6)	0.0160 (6)
C11	0.0307 (5)	0.0324 (6)	0.0299 (6)	0.0007 (5)	0.0048 (4)	0.0054 (5)
C12	0.0241 (5)	0.0230 (5)	0.0288 (5)	−0.0017 (4)	0.0000 (4)	0.0009 (4)
C13	0.0382 (6)	0.0260 (5)	0.0332 (6)	−0.0068 (5)	0.0039 (5)	0.0036 (5)
C14	0.0301 (6)	0.0305 (6)	0.0424 (7)	−0.0026 (5)	0.0104 (5)	0.0031 (5)
N1	0.0193 (4)	0.0234 (4)	0.0321 (5)	−0.0004 (3)	0.0065 (3)	0.0018 (4)
N2	0.0189 (4)	0.0263 (4)	0.0323 (5)	−0.0001 (3)	0.0069 (3)	0.0017 (4)
N3	0.0258 (4)	0.0214 (4)	0.0295 (5)	−0.0026 (3)	0.0078 (4)	0.0001 (4)
N4	0.0384 (6)	0.0614 (8)	0.0645 (8)	−0.0176 (6)	0.0056 (6)	−0.0012 (7)
O1	0.0205 (3)	0.0281 (4)	0.0333 (4)	0.0005 (3)	0.0078 (3)	0.0015 (3)
O2	0.0416 (5)	0.0268 (4)	0.0365 (4)	−0.0031 (3)	0.0109 (4)	−0.0052 (3)

Geometric parameters (Å, º)

C1—O1	1.2442 (12)	C7—H7	0.95
C1—N1	1.3828 (13)	C8—C9	1.376 (2)
C1—C2	1.4288 (15)	C8—H8	0.95
C2—C3	1.3676 (14)	C9—C10	1.382 (2)
C2—N3	1.4120 (13)	C9—H9	0.95
C3—N2	1.3713 (14)	C10—C11	1.3889 (18)
C3—C4	1.4855 (15)	C10—H10	0.95
C4—H4A	0.98	C11—H11	0.95
C4—H4B	0.98	C12—O2	1.2153 (14)

C4—H4C	0.98	C12—N3	1.3489 (14)
C5—N2	1.4641 (14)	C12—C13	1.5373 (15)
C5—H5A	0.98	C13—C14	1.4575 (17)
C5—H5B	0.98	C13—H13A	0.99
C5—H5C	0.98	C13—H13B	0.99
C6—C11	1.3839 (16)	C14—N4	1.1345 (17)
C6—C7	1.3865 (16)	N1—N2	1.3980 (12)
C6—N1	1.4258 (14)	N3—H3	0.903 (15)
C7—C8	1.3890 (18)		

O1—C1—N1	123.78 (9)	C7—C8—H8	119.8
O1—C1—C2	131.09 (10)	C8—C9—C10	120.05 (12)
N1—C1—C2	105.09 (8)	C8—C9—H9	120
C3—C2—N3	130.09 (10)	C10—C9—H9	120
C3—C2—C1	108.75 (9)	C9—C10—C11	120.57 (12)
N3—C2—C1	120.90 (9)	C9—C10—H10	119.7
C2—C3—N2	108.87 (9)	C11—C10—H10	119.7
C2—C3—C4	130.06 (10)	C6—C11—C10	118.80 (12)
N2—C3—C4	121.06 (9)	C6—C11—H11	120.6
C3—C4—H4A	109.5	C10—C11—H11	120.6
C3—C4—H4B	109.5	O2—C12—N3	125.37 (10)
H4A—C4—H4B	109.5	O2—C12—C13	121.50 (10)
C3—C4—H4C	109.5	N3—C12—C13	113.10 (10)
H4A—C4—H4C	109.5	C14—C13—C12	111.32 (10)
H4B—C4—H4C	109.5	C14—C13—H13A	109.4
N2—C5—H5A	109.5	C12—C13—H13A	109.4
N2—C5—H5B	109.5	C14—C13—H13B	109.4
H5A—C5—H5B	109.5	C12—C13—H13B	109.4
N2—C5—H5C	109.5	H13A—C13—H13B	108
H5A—C5—H5C	109.5	N4—C14—C13	178.86 (14)
H5B—C5—H5C	109.5	C1—N1—N2	109.57 (8)
C11—C6—C7	121.09 (11)	C1—N1—C6	123.96 (9)
C11—C6—N1	118.34 (10)	N2—N1—C6	120.65 (8)
C7—C6—N1	120.52 (10)	C3—N2—N1	107.23 (8)
C6—C7—C8	119.13 (12)	C3—N2—C5	123.88 (9)
C6—C7—H7	120.4	N1—N2—C5	116.24 (9)
C8—C7—H7	120.4	C12—N3—C2	124.25 (9)
C9—C8—C7	120.33 (13)	C12—N3—H3	118.1 (9)
C9—C8—H8	119.8	C2—N3—H3	116.3 (9)

O1—C1—C2—C3	175.50 (11)	C2—C1—N1—N2	5.83 (11)
N1—C1—C2—C3	−2.28 (11)	O1—C1—N1—C6	−19.06 (16)
O1—C1—C2—N3	0.73 (17)	C2—C1—N1—C6	158.93 (9)
N1—C1—C2—N3	−177.05 (9)	C11—C6—N1—C1	64.08 (14)
N3—C2—C3—N2	171.96 (10)	C7—C6—N1—C1	−113.18 (12)
C1—C2—C3—N2	−2.17 (12)	C11—C6—N1—N2	−145.63 (10)
N3—C2—C3—C4	−8.91 (19)	C7—C6—N1—N2	37.12 (15)
C1—C2—C3—C4	176.96 (11)	C2—C3—N2—N1	5.73 (11)

C11—C6—C7—C8	−0.10 (18)	C4—C3—N2—N1	−173.49 (10)
N1—C6—C7—C8	177.09 (11)	C2—C3—N2—C5	145.71 (10)
C6—C7—C8—C9	−1.4 (2)	C4—C3—N2—C5	−33.51 (15)
C7—C8—C9—C10	1.4 (2)	C1—N1—N2—C3	−7.30 (11)
C8—C9—C10—C11	0.21 (19)	C6—N1—N2—C3	−161.43 (9)
C7—C6—C11—C10	1.66 (17)	C1—N1—N2—C5	−150.77 (10)
N1—C6—C11—C10	−175.58 (10)	C6—N1—N2—C5	55.10 (13)
C9—C10—C11—C6	−1.72 (18)	O2—C12—N3—C2	−6.09 (17)
O2—C12—C13—C14	56.70 (15)	C13—C12—N3—C2	176.09 (9)
N3—C12—C13—C14	−125.39 (11)	C3—C2—N3—C12	58.82 (16)
O1—C1—N1—N2	−172.16 (9)	C1—C2—N3—C12	−127.66 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1^{i}	0.903 (15)	1.884 (15)	2.7835 (12)	174 (1)
C9—H9···O2^{ii}	0.95	2.55	3.4485 (16)	157

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

(VII) Methyl 4-{[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]methyl}benzoate

Crystal data

$C_{20}H_{19}N_3O_3$
M_r = 349.38
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 32.7563 (10) Å
b = 6.9258 (2) Å
c = 16.4002 (5) Å
β = 106.032 (1)°
V = 3575.90 (19) Å^3
Z = 8
F(000) = 1472
D_x = 1.298 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 8137 reflections
θ = 2.6–28.0°
μ = 0.09 mm^{-1}
T = 173 K
Plate, yellow
0.68 × 0.24 × 0.09 mm

Data collection

Bruker D8 Venture Photon diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.95, T_{max} = 0.99
31732 measured reflections
4312 independent reflections
3539 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 28.0°, θ_{min} = 2.6°
h = −41→43
k = −9→8
l = −21→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.110
S = 1.03
4312 reflections
238 parameters
0 restraints
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 2.065P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Special details

Experimental. Absorption corrections were made using the program *SADABS* (Sheldrick, 1996)

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.31423 (4)	0.32838 (17)	0.65668 (7)	0.0249 (2)
C2	0.27746 (4)	0.20497 (17)	0.64224 (7)	0.0241 (2)
C3	0.28930 (4)	0.03859 (17)	0.68905 (7)	0.0249 (2)
C4	0.26341 (4)	−0.13591 (19)	0.69093 (8)	0.0347 (3)
H4A	0.2742	−0.2437	0.6642	0.052*
H4B	0.2338	−0.1104	0.6599	0.052*
H4C	0.2652	−0.169	0.7499	0.052*
C5	0.35913 (4)	−0.11026 (18)	0.76603 (8)	0.0323 (3)
H5A	0.3425	−0.2272	0.7677	0.048*
H5B	0.3771	−0.0814	0.8232	0.048*
H5C	0.3771	−0.1307	0.7279	0.048*
C6	0.38177 (4)	0.31383 (17)	0.77103 (7)	0.0256 (2)
C7	0.38420 (4)	0.31516 (19)	0.85699 (8)	0.0315 (3)
H7	0.3631	0.2521	0.8771	0.038*
C8	0.41769 (5)	0.4094 (2)	0.91302 (8)	0.0371 (3)
H8	0.4198	0.4095	0.972	0.045*
C9	0.44812 (4)	0.5036 (2)	0.88369 (9)	0.0390 (3)
H9	0.471	0.5679	0.9224	0.047*
C10	0.44513 (4)	0.5039 (2)	0.79796 (9)	0.0368 (3)
H10	0.4658	0.5701	0.7779	0.044*
C11	0.41205 (4)	0.40798 (18)	0.74104 (8)	0.0307 (3)
H11	0.4102	0.4069	0.6822	0.037*
C12	0.22522 (4)	0.39995 (18)	0.55655 (7)	0.0265 (2)
H12	0.2467	0.4883	0.5522	0.032*
C13	0.18049 (4)	0.44398 (18)	0.51512 (7)	0.0256 (2)
C14	0.16980 (4)	0.62384 (18)	0.47654 (7)	0.0277 (3)
H14	0.1915	0.7145	0.4764	0.033*
C15	0.12782 (4)	0.67091 (18)	0.43851 (7)	0.0278 (3)
H15	0.1208	0.7938	0.4127	0.033*
C16	0.09584 (4)	0.53855 (18)	0.43809 (7)	0.0264 (2)
C17	0.10635 (4)	0.35766 (18)	0.47584 (8)	0.0293 (3)
H17	0.0846	0.2664	0.4753	0.035*
C18	0.14830 (4)	0.31137 (18)	0.51399 (7)	0.0294 (3)
H18	0.1553	0.1883	0.5396	0.035*
C19	0.05106 (4)	0.59546 (19)	0.39791 (8)	0.0309 (3)
C20	−0.02046 (5)	0.4949 (3)	0.35914 (14)	0.0618 (5)
H20A	−0.0302	0.581	0.3974	0.093*
H20B	−0.037	0.3753	0.3512	0.093*

H20C	−0.0243	0.5587	0.3042	0.093*
N1	0.34734 (3)	0.22117 (14)	0.71114 (6)	0.0262 (2)
N2	0.33035 (3)	0.05151 (14)	0.73522 (6)	0.0269 (2)
N3	0.23550 (3)	0.24258 (15)	0.59866 (6)	0.0261 (2)
O1	0.31896 (3)	0.49344 (13)	0.63305 (6)	0.0333 (2)
O2	0.03997 (3)	0.75497 (15)	0.37135 (7)	0.0445 (3)
O3	0.02396 (3)	0.45057 (14)	0.39547 (8)	0.0489 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0240 (6)	0.0246 (6)	0.0258 (5)	0.0030 (5)	0.0063 (4)	0.0011 (4)
C2	0.0237 (5)	0.0249 (6)	0.0247 (5)	0.0010 (5)	0.0084 (4)	−0.0007 (4)
C3	0.0268 (6)	0.0254 (6)	0.0241 (5)	−0.0001 (5)	0.0093 (4)	−0.0010 (4)
C4	0.0355 (7)	0.0312 (7)	0.0373 (6)	−0.0060 (6)	0.0100 (5)	0.0037 (5)
C5	0.0374 (7)	0.0244 (6)	0.0314 (6)	0.0058 (5)	0.0033 (5)	0.0048 (5)
C6	0.0231 (6)	0.0208 (6)	0.0312 (6)	0.0034 (4)	0.0044 (4)	0.0020 (4)
C7	0.0334 (6)	0.0282 (6)	0.0336 (6)	−0.0021 (5)	0.0102 (5)	0.0001 (5)
C8	0.0457 (8)	0.0318 (7)	0.0307 (6)	−0.0027 (6)	0.0051 (5)	−0.0016 (5)
C9	0.0376 (7)	0.0289 (7)	0.0427 (7)	−0.0064 (6)	−0.0019 (6)	−0.0001 (5)
C10	0.0303 (6)	0.0319 (7)	0.0465 (7)	−0.0051 (6)	0.0080 (5)	0.0058 (6)
C11	0.0296 (6)	0.0291 (6)	0.0331 (6)	0.0010 (5)	0.0080 (5)	0.0044 (5)
C12	0.0244 (6)	0.0292 (6)	0.0266 (5)	0.0008 (5)	0.0081 (4)	−0.0007 (4)
C13	0.0245 (6)	0.0297 (6)	0.0232 (5)	0.0029 (5)	0.0073 (4)	−0.0007 (4)
C14	0.0262 (6)	0.0294 (6)	0.0287 (5)	−0.0010 (5)	0.0095 (4)	0.0021 (5)
C15	0.0288 (6)	0.0269 (6)	0.0277 (5)	0.0026 (5)	0.0080 (5)	0.0036 (4)
C16	0.0255 (6)	0.0285 (6)	0.0246 (5)	0.0025 (5)	0.0062 (4)	0.0003 (4)
C17	0.0264 (6)	0.0269 (6)	0.0339 (6)	−0.0015 (5)	0.0075 (5)	0.0022 (5)
C18	0.0285 (6)	0.0272 (6)	0.0319 (6)	0.0024 (5)	0.0076 (5)	0.0042 (5)
C19	0.0270 (6)	0.0308 (7)	0.0323 (6)	0.0001 (5)	0.0040 (5)	0.0010 (5)
C20	0.0250 (7)	0.0426 (9)	0.1037 (14)	−0.0035 (7)	−0.0057 (8)	0.0077 (9)
N1	0.0250 (5)	0.0212 (5)	0.0305 (5)	−0.0009 (4)	0.0046 (4)	0.0045 (4)
N2	0.0279 (5)	0.0199 (5)	0.0312 (5)	−0.0002 (4)	0.0055 (4)	0.0041 (4)
N3	0.0231 (5)	0.0304 (5)	0.0248 (4)	0.0028 (4)	0.0066 (4)	−0.0009 (4)
O1	0.0306 (5)	0.0244 (5)	0.0417 (5)	−0.0001 (4)	0.0044 (4)	0.0087 (4)
O2	0.0296 (5)	0.0381 (6)	0.0599 (6)	0.0034 (4)	0.0024 (4)	0.0176 (5)
O3	0.0251 (5)	0.0311 (6)	0.0800 (8)	−0.0017 (4)	−0.0030 (5)	0.0054 (5)

Geometric parameters (Å, º)

C1—O1	1.2305 (14)	C10—H10	0.95
C1—N1	1.4109 (14)	C11—H11	0.95
C1—C2	1.4421 (16)	C12—N3	1.2844 (16)
C2—C3	1.3795 (16)	C12—C13	1.4670 (16)
C2—N3	1.3875 (14)	C12—H12	0.95
C3—N2	1.3518 (15)	C13—C18	1.3946 (17)
C3—C4	1.4815 (17)	C13—C14	1.3972 (17)
C4—H4A	0.98	C14—C15	1.3831 (16)

C4—H4B	0.98	C14—H14	0.95
C4—H4C	0.98	C15—C16	1.3904 (17)
C5—N2	1.4614 (15)	C15—H15	0.95
C5—H5A	0.98	C16—C17	1.3977 (17)
C5—H5B	0.98	C16—C19	1.4857 (16)
C5—H5C	0.98	C17—C18	1.3810 (17)
C6—C11	1.3859 (17)	C17—H17	0.95
C6—C7	1.3898 (17)	C18—H18	0.95
C6—N1	1.4271 (15)	C19—O2	1.2062 (16)
C7—C8	1.3846 (19)	C19—O3	1.3330 (16)
C7—H7	0.95	C20—O3	1.4449 (17)
C8—C9	1.384 (2)	C20—H20A	0.98
C8—H8	0.95	C20—H20B	0.98
C9—C10	1.382 (2)	C20—H20C	0.98
C9—H9	0.95	N1—N2	1.4028 (14)
C10—C11	1.3884 (18)		

O1—C1—N1	123.13 (11)	N3—C12—C13	120.35 (11)
O1—C1—C2	132.14 (11)	N3—C12—H12	119.8
N1—C1—C2	104.67 (10)	C13—C12—H12	119.8
C3—C2—N3	121.99 (11)	C18—C13—C14	119.15 (11)
C3—C2—C1	108.06 (10)	C18—C13—C12	121.61 (11)
N3—C2—C1	129.56 (11)	C14—C13—C12	119.23 (11)
N2—C3—C2	109.86 (10)	C15—C14—C13	120.52 (11)
N2—C3—C4	121.93 (11)	C15—C14—H14	119.7
C2—C3—C4	128.20 (11)	C13—C14—H14	119.7
C3—C4—H4A	109.5	C14—C15—C16	120.04 (11)
C3—C4—H4B	109.5	C14—C15—H15	120
H4A—C4—H4B	109.5	C16—C15—H15	120
C3—C4—H4C	109.5	C15—C16—C17	119.72 (11)
H4A—C4—H4C	109.5	C15—C16—C19	118.51 (11)
H4B—C4—H4C	109.5	C17—C16—C19	121.77 (11)
N2—C5—H5A	109.5	C18—C17—C16	120.08 (11)
N2—C5—H5B	109.5	C18—C17—H17	120
H5A—C5—H5B	109.5	C16—C17—H17	120
N2—C5—H5C	109.5	C17—C18—C13	120.47 (12)
H5A—C5—H5C	109.5	C17—C18—H18	119.8
H5B—C5—H5C	109.5	C13—C18—H18	119.8
C11—C6—C7	120.72 (11)	O2—C19—O3	123.15 (11)
C11—C6—N1	118.31 (10)	O2—C19—C16	124.43 (12)
C7—C6—N1	120.94 (11)	O3—C19—C16	112.42 (11)
C8—C7—C6	119.29 (12)	O3—C20—H20A	109.5
C8—C7—H7	120.4	O3—C20—H20B	109.5
C6—C7—H7	120.4	H20A—C20—H20B	109.5
C9—C8—C7	120.40 (12)	O3—C20—H20C	109.5
C9—C8—H8	119.8	H20A—C20—H20C	109.5
C7—C8—H8	119.8	H20B—C20—H20C	109.5
C10—C9—C8	119.92 (12)	N2—N1—C1	108.88 (9)

C10—C9—H9	120	N2—N1—C6	118.85 (9)
C8—C9—H9	120	C1—N1—C6	121.49 (10)
C9—C10—C11	120.42 (12)	C3—N2—N1	107.96 (9)
C9—C10—H10	119.8	C3—N2—C5	126.14 (10)
C11—C10—H10	119.8	N1—N2—C5	118.12 (9)
C6—C11—C10	119.24 (12)	C12—N3—C2	120.76 (10)
C6—C11—H11	120.4	C19—O3—C20	116.02 (11)
C10—C11—H11	120.4		

O1—C1—C2—C3	−175.46 (12)	C12—C13—C18—C17	178.86 (11)
N1—C1—C2—C3	1.93 (12)	C15—C16—C19—O2	−6.30 (19)
O1—C1—C2—N3	−2.7 (2)	C17—C16—C19—O2	173.01 (13)
N1—C1—C2—N3	174.70 (11)	C15—C16—C19—O3	174.72 (11)
N3—C2—C3—N2	−170.52 (10)	C17—C16—C19—O3	−5.97 (17)
C1—C2—C3—N2	2.91 (13)	O1—C1—N1—N2	171.78 (11)
N3—C2—C3—C4	10.72 (18)	C2—C1—N1—N2	−5.91 (12)
C1—C2—C3—C4	−175.85 (11)	O1—C1—N1—C6	27.94 (16)
C11—C6—C7—C8	−0.97 (19)	C2—C1—N1—C6	−149.75 (10)
N1—C6—C7—C8	−178.87 (12)	C11—C6—N1—N2	146.60 (11)
C6—C7—C8—C9	0.9 (2)	C7—C6—N1—N2	−35.45 (16)
C7—C8—C9—C10	0.1 (2)	C11—C6—N1—C1	−72.99 (14)
C8—C9—C10—C11	−0.9 (2)	C7—C6—N1—C1	104.96 (13)
C7—C6—C11—C10	0.17 (19)	C2—C3—N2—N1	−6.64 (12)
N1—C6—C11—C10	178.13 (11)	C4—C3—N2—N1	172.21 (10)
C9—C10—C11—C6	0.8 (2)	C2—C3—N2—C5	−154.88 (11)
N3—C12—C13—C18	−5.38 (17)	C4—C3—N2—C5	23.98 (17)
N3—C12—C13—C14	174.01 (10)	C1—N1—N2—C3	7.89 (12)
C18—C13—C14—C15	0.73 (17)	C6—N1—N2—C3	152.83 (10)
C12—C13—C14—C15	−178.67 (10)	C1—N1—N2—C5	159.07 (10)
C13—C14—C15—C16	−0.31 (17)	C6—N1—N2—C5	−55.98 (14)
C14—C15—C16—C17	−0.33 (17)	C13—C12—N3—C2	−176.14 (10)
C14—C15—C16—C19	178.99 (11)	C3—C2—N3—C12	178.95 (11)
C15—C16—C17—C18	0.54 (18)	C1—C2—N3—C12	7.07 (18)
C19—C16—C17—C18	−178.76 (11)	O2—C19—O3—C20	−0.4 (2)
C16—C17—C18—C13	−0.10 (18)	C16—C19—O3—C20	178.58 (13)
C14—C13—C18—C17	−0.53 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···O1	0.95	2.37	3.0486 (17)	128