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Ethyl 3-methyl-1-phenyl-5-(*p*-tolyl)-1*H*-pyrazole-4-carboxylate

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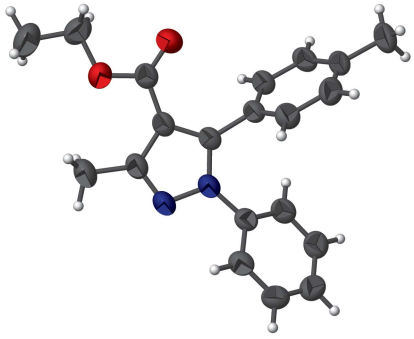
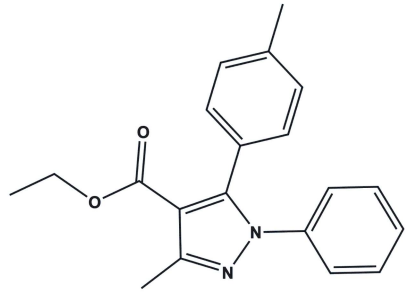
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{20}H_{20}N_2O_2$, the pyrazole ring makes dihedral angles of 39.74 (8) and 60.35 (8)° with the phenyl and toluene rings, respectively. The dihedral angle between the phenyl and toluene rings is 62.01 (7)°.

3D view



Chemical scheme



Structure description

Pyrazoles are an important class of five-membered nitrogen heterocycles, which are very widely used as synthetic scaffolds for the construction of bioactive molecules (Ajay *et al.*, 2015). Apart from their synthetic utilities, pyrazole derivatives themselves exhibit a broad spectrum of biological activities (Farghaly *et al.*, 2012). As part of our studies in this area, we herein report on the crystal structure of the title compound.

The molecular structure of the title compound is shown in Fig. 1. The pyrazole ring (N1/N2/C1–C3) makes dihedral angles of 39.74 (8) and 60.35 (8)° with the phenyl (C8–C13) and the toluene (C14–C19) rings, respectively. The dihedral angle between the phenyl and toluene rings is 62.01 (7)°.

In the crystal, molecules are linked by C—H···π interactions, forming chains propagating along the *a* axis (Table 1 and Fig. 2).

Synthesis and crystallization

To a solution of (*E*)-ethyl 2-(4-methylbenzylidene)-3-oxobutanoate (0.01 mol), which was obtained by our earlier reported procedure (Naveen *et al.*, 2016), and phenylhydrazine hydrochloride (0.01 mol) in ethyl alcohol (20 ml), 3–4 drops of piperidine were

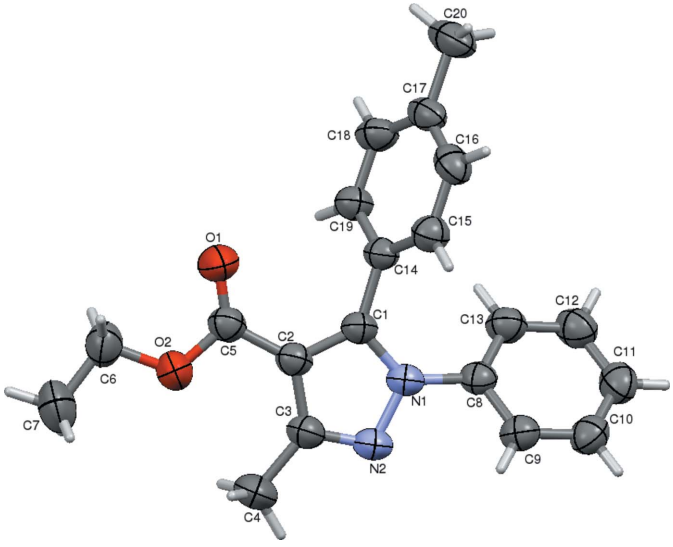


Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

added. The mixture was refluxed on a water bath for 3 h. The progress of the reaction was monitored by TLC. After completion, the mixture was poured into ice-cold water and the solid separated was filtered, and washed with ice-cold water to obtain the crude title product. The solid obtained was crystallized from methanol by slow evaporation giving pale-yellow rectangular-shaped crystals (90% yield; m.p. 358–359 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

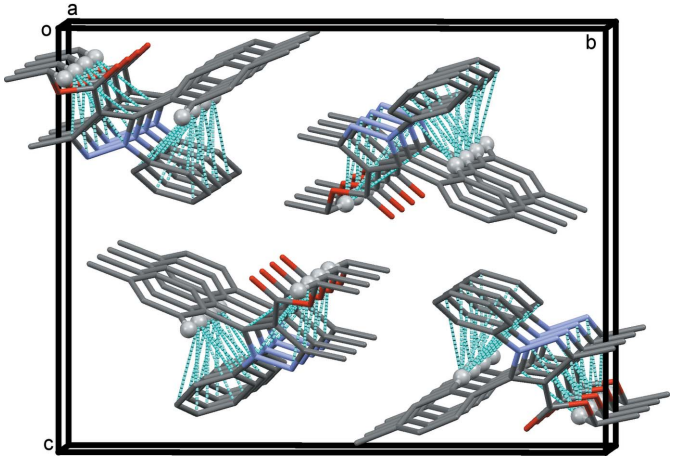


Figure 2
A view along the *a* axis of the crystal packing of the title compound. The C—H···π interactions are shown as dashed lines (see Table 1) and, for clarity, only H atoms H6*A* and H19 (grey balls) have been included.

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

*Cg*1 and *Cg*2 are the centroids of the N1/N2/C1–C3 and C8–C13 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6*A*···*Cg*1^{i}	0.97	2.93	3.794 (2)	149
C19—H19···*Cg*2^{i}	0.93	2.93	3.780 (2)	152

Symmetry code: (i) $x-1, y, z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{20}N_2O_2$
M_r	320.38
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, *b*, *c* (Å)	6.2796 (3), 18.9391 (9), 14.6430 (7)
β (°)	91.406 (2)
V (Å^3)	1740.97 (14)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.64
Crystal size (mm)	0.29 × 0.26 × 0.24
Data collection	
Diffractometer	Bruker X8 Proteum
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.837, 0.863
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13541, 2872, 2535
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.585
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.045, 0.143, 1.06
No. of reflections	2872
No. of parameters	221
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.13

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

Acknowledgements

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full crystallographic data

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Crystal data

$C_{20}H_{20}N_2O_2$
M_r = 320.38
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 6.2796 (3) Å
b = 18.9391 (9) Å
c = 14.6430 (7) Å
β = 91.406 (2)°
V = 1740.97 (14) Å^3
Z = 4
$F(000)$ = 680
D_x = 1.222 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 2535 reflections
θ = 4.7–64.5°
μ = 0.64 mm^{-1}
T = 296 K
Block, yellow
0.29 × 0.26 × 0.24 mm

Data collection

Bruker X8 Proteum diffractometer
Radiation source: Bruker MicroStar microfocus rotating anode
Helios multilayer optics monochromator
Detector resolution: 18.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.837, T_{max} = 0.863
13541 measured reflections
2872 independent reflections
2535 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 64.5°, θ_{min} = 4.7°
h = −6→7
k = −21→22
l = −16→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.143
S = 1.06
2872 reflections
221 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0929P)^2 + 0.1486P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 2008), $FC^*=KFC[1+0.001XFC^2\Lambda^3/SIN(2\Theta)]^{-1/4}$
Extinction coefficient: 0.0058 (12)

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating -R-factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.0474 (2)	0.37329 (6)	0.57248 (10)	0.0816 (5)
O2	−0.06959 (18)	0.48057 (6)	0.63324 (9)	0.0694 (4)
N1	0.48074 (19)	0.36844 (6)	0.76439 (8)	0.0500 (4)
N2	0.4568 (2)	0.43678 (6)	0.79382 (9)	0.0585 (4)
C1	0.3333 (2)	0.35112 (7)	0.69887 (9)	0.0457 (4)
C2	0.2068 (2)	0.41063 (7)	0.68588 (10)	0.0497 (5)
C3	0.2920 (2)	0.46213 (8)	0.74707 (11)	0.0558 (5)
C4	0.2198 (3)	0.53571 (9)	0.76614 (16)	0.0826 (7)
C5	0.0209 (2)	0.41723 (8)	0.62416 (11)	0.0537 (5)
C6	−0.2603 (3)	0.49523 (10)	0.57961 (14)	0.0736 (6)
C7	−0.3193 (4)	0.56968 (13)	0.5990 (2)	0.1036 (10)
C8	0.6407 (2)	0.32691 (7)	0.81037 (9)	0.0486 (4)
C9	0.8308 (2)	0.35962 (8)	0.83481 (10)	0.0551 (5)
C10	0.9844 (3)	0.32222 (9)	0.88330 (11)	0.0623 (5)
C11	0.9497 (3)	0.25341 (9)	0.90858 (11)	0.0660 (6)
C12	0.7601 (3)	0.22121 (9)	0.88390 (12)	0.0673 (6)
C13	0.6040 (3)	0.25754 (8)	0.83511 (11)	0.0600 (5)
C14	0.3253 (2)	0.28043 (7)	0.65589 (9)	0.0459 (4)
C15	0.4968 (2)	0.25452 (8)	0.60870 (10)	0.0559 (5)
C16	0.4894 (3)	0.18672 (9)	0.57228 (11)	0.0627 (6)
C17	0.3139 (3)	0.14384 (8)	0.58204 (10)	0.0586 (5)
C18	0.1417 (3)	0.17121 (8)	0.62768 (11)	0.0600 (5)
C19	0.1455 (2)	0.23851 (8)	0.66403 (10)	0.0523 (5)
C20	0.3068 (4)	0.06983 (9)	0.54428 (14)	0.0861 (8)
H4A	0.07700	0.53470	0.78810	0.1240*
H4B	0.22330	0.56310	0.71100	0.1240*
H4C	0.31270	0.55670	0.81160	0.1240*
H6A	−0.37410	0.46360	0.59660	0.0880*
H6B	−0.23410	0.48910	0.51510	0.0880*
H7A	−0.34320	0.57510	0.66310	0.1550*
H7B	−0.44700	0.58160	0.56500	0.1550*
H7C	−0.20590	0.60040	0.58130	0.1550*
H9	0.85470	0.40640	0.81870	0.0660*
H10	1.11310	0.34390	0.89910	0.0750*
H11	1.05320	0.22880	0.94210	0.0790*
H12	0.73690	0.17440	0.90030	0.0810*
H13	0.47590	0.23560	0.81910	0.0720*
H15	0.61700	0.28240	0.60130	0.0670*
H16	0.60540	0.16990	0.54060	0.0750*

H18	0.02060	0.14360	0.63400	0.0720*
H19	0.02750	0.25580	0.69400	0.0630*
H20A	0.35410	0.03720	0.59070	0.1290*
H20B	0.39830	0.06660	0.49290	0.1290*
H20C	0.16350	0.05850	0.52520	0.1290*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0878 (9)	0.0628 (8)	0.0926 (9)	0.0055 (6)	−0.0325 (7)	−0.0182 (6)
O2	0.0634 (7)	0.0566 (7)	0.0874 (8)	0.0107 (5)	−0.0141 (6)	−0.0085 (6)
N1	0.0539 (7)	0.0411 (6)	0.0547 (7)	−0.0030 (5)	−0.0019 (5)	−0.0072 (5)
N2	0.0651 (8)	0.0435 (7)	0.0665 (8)	−0.0021 (6)	−0.0072 (6)	−0.0127 (6)
C1	0.0480 (7)	0.0416 (7)	0.0476 (7)	−0.0049 (6)	0.0024 (6)	−0.0036 (6)
C2	0.0514 (8)	0.0425 (8)	0.0554 (8)	−0.0028 (6)	0.0036 (6)	−0.0040 (6)
C3	0.0599 (9)	0.0429 (8)	0.0646 (9)	−0.0014 (6)	0.0004 (7)	−0.0075 (7)
C4	0.0880 (13)	0.0513 (10)	0.1075 (15)	0.0084 (9)	−0.0172 (11)	−0.0246 (10)
C5	0.0553 (8)	0.0458 (8)	0.0602 (9)	−0.0034 (6)	0.0028 (7)	−0.0008 (7)
C6	0.0557 (9)	0.0732 (11)	0.0914 (13)	0.0050 (8)	−0.0087 (8)	0.0075 (9)
C7	0.0825 (14)	0.0865 (15)	0.141 (2)	0.0298 (12)	−0.0146 (14)	0.0011 (14)
C8	0.0544 (8)	0.0471 (8)	0.0443 (7)	−0.0018 (6)	0.0004 (6)	−0.0050 (6)
C9	0.0596 (9)	0.0526 (8)	0.0529 (8)	−0.0065 (7)	−0.0002 (7)	−0.0024 (6)
C10	0.0606 (9)	0.0696 (10)	0.0562 (9)	−0.0026 (7)	−0.0073 (7)	−0.0046 (7)
C11	0.0734 (11)	0.0681 (11)	0.0561 (9)	0.0117 (8)	−0.0079 (8)	−0.0008 (7)
C12	0.0848 (12)	0.0527 (9)	0.0642 (10)	0.0019 (8)	−0.0040 (8)	0.0054 (7)
C13	0.0653 (9)	0.0509 (9)	0.0635 (9)	−0.0079 (7)	−0.0024 (7)	−0.0001 (7)
C14	0.0527 (8)	0.0401 (7)	0.0447 (7)	−0.0015 (6)	−0.0015 (6)	−0.0028 (5)
C15	0.0555 (9)	0.0538 (9)	0.0586 (9)	−0.0014 (7)	0.0039 (7)	−0.0049 (7)
C16	0.0736 (10)	0.0595 (10)	0.0551 (9)	0.0184 (8)	0.0023 (7)	−0.0074 (7)
C17	0.0862 (11)	0.0392 (8)	0.0497 (8)	0.0059 (7)	−0.0135 (8)	−0.0011 (6)
C18	0.0748 (10)	0.0437 (8)	0.0610 (9)	−0.0127 (7)	−0.0065 (8)	0.0006 (7)
C19	0.0557 (8)	0.0460 (8)	0.0554 (8)	−0.0045 (6)	0.0028 (6)	−0.0041 (6)
C20	0.1353 (18)	0.0453 (9)	0.0765 (12)	0.0147 (10)	−0.0200 (12)	−0.0094 (8)

Geometric parameters (Å, º)

O1—C5	1.197 (2)	C17—C18	1.386 (2)
O2—C5	1.3354 (19)	C17—C20	1.507 (2)
O2—C6	1.443 (2)	C18—C19	1.381 (2)
N1—N2	1.3736 (16)	C4—H4A	0.9600
N1—C1	1.3571 (17)	C4—H4B	0.9600
N1—C8	1.4310 (17)	C4—H4C	0.9600
N2—C3	1.3173 (19)	C6—H6A	0.9700
C1—C2	1.3893 (18)	C6—H6B	0.9700
C1—C14	1.4797 (19)	C7—H7A	0.9600
C2—C3	1.420 (2)	C7—H7B	0.9600
C2—C5	1.4640 (19)	C7—H7C	0.9600
C3—C4	1.494 (2)	C9—H9	0.9300

C6—C7	1.487 (3)	C10—H10	0.9300
C8—C9	1.3842 (18)	C11—H11	0.9300
C8—C13	1.384 (2)	C12—H12	0.9300
C9—C10	1.379 (2)	C13—H13	0.9300
C10—C11	1.374 (2)	C15—H15	0.9300
C11—C12	1.378 (3)	C16—H16	0.9300
C12—C13	1.382 (3)	C18—H18	0.9300
C14—C15	1.3837 (19)	C19—H19	0.9300
C14—C19	1.3878 (19)	C20—H20A	0.9600
C15—C16	1.391 (2)	C20—H20B	0.9600
C16—C17	1.379 (3)	C20—H20C	0.9600

C5—O2—C6	117.92 (13)	H4A—C4—H4B	109.00
N2—N1—C1	111.81 (11)	H4A—C4—H4C	109.00
N2—N1—C8	116.83 (11)	H4B—C4—H4C	109.00
C1—N1—C8	131.19 (11)	O2—C6—H6A	110.00
N1—N2—C3	105.73 (12)	O2—C6—H6B	110.00
N1—C1—C2	106.18 (12)	C7—C6—H6A	110.00
N1—C1—C14	122.33 (12)	C7—C6—H6B	110.00
C2—C1—C14	131.49 (12)	H6A—C6—H6B	109.00
C1—C2—C3	105.40 (12)	C6—C7—H7A	110.00
C1—C2—C5	126.75 (13)	C6—C7—H7B	109.00
C3—C2—C5	127.82 (12)	C6—C7—H7C	109.00
N2—C3—C2	110.89 (13)	H7A—C7—H7B	109.00
N2—C3—C4	118.75 (14)	H7A—C7—H7C	110.00
C2—C3—C4	130.33 (14)	H7B—C7—H7C	109.00
O1—C5—O2	122.73 (14)	C8—C9—H9	120.00
O1—C5—C2	126.78 (14)	C10—C9—H9	120.00
O2—C5—C2	110.49 (13)	C9—C10—H10	120.00
O2—C6—C7	106.61 (17)	C11—C10—H10	120.00
N1—C8—C9	117.82 (12)	C10—C11—H11	120.00
N1—C8—C13	121.71 (13)	C12—C11—H11	120.00
C9—C8—C13	120.36 (13)	C11—C12—H12	120.00
C8—C9—C10	119.41 (14)	C13—C12—H12	120.00
C9—C10—C11	120.82 (16)	C8—C13—H13	120.00
C10—C11—C12	119.40 (16)	C12—C13—H13	120.00
C11—C12—C13	120.83 (16)	C14—C15—H15	120.00
C8—C13—C12	119.17 (16)	C16—C15—H15	120.00
C1—C14—C15	120.97 (12)	C15—C16—H16	119.00
C1—C14—C19	120.02 (12)	C17—C16—H16	119.00
C15—C14—C19	119.00 (13)	C17—C18—H18	119.00
C14—C15—C16	119.99 (13)	C19—C18—H18	119.00
C15—C16—C17	121.55 (16)	C14—C19—H19	120.00
C16—C17—C18	117.69 (15)	C18—C19—H19	120.00
C16—C17—C20	121.75 (17)	C17—C20—H20A	109.00
C18—C17—C20	120.56 (17)	C17—C20—H20B	110.00
C17—C18—C19	121.65 (15)	C17—C20—H20C	109.00
C14—C19—C18	120.08 (13)	H20A—C20—H20B	109.00

C3—C4—H4A	110.00	H20A—C20—H20C	109.00
C3—C4—H4B	109.00	H20B—C20—H20C	109.00
C3—C4—H4C	109.00		

C6—O2—C5—O1	1.5 (2)	C5—C2—C3—N2	178.10 (14)
C6—O2—C5—C2	−177.83 (13)	C5—C2—C3—C4	0.1 (3)
C5—O2—C6—C7	−176.98 (16)	C1—C2—C5—O1	−3.0 (3)
C1—N1—N2—C3	0.62 (16)	C1—C2—C5—O2	176.28 (13)
C8—N1—N2—C3	−175.18 (12)	C3—C2—C5—O1	179.34 (16)
N2—N1—C1—C2	−0.61 (15)	C3—C2—C5—O2	−1.4 (2)
N2—N1—C1—C14	179.93 (12)	N1—C8—C9—C10	176.73 (13)
C8—N1—C1—C2	174.41 (13)	C13—C8—C9—C10	0.7 (2)
C8—N1—C1—C14	−5.1 (2)	N1—C8—C13—C12	−176.41 (14)
N2—N1—C8—C9	−39.04 (17)	C9—C8—C13—C12	−0.5 (2)
N2—N1—C8—C13	136.99 (14)	C8—C9—C10—C11	−0.9 (2)
C1—N1—C8—C9	146.15 (14)	C9—C10—C11—C12	1.0 (3)
C1—N1—C8—C13	−37.8 (2)	C10—C11—C12—C13	−0.8 (3)
N1—N2—C3—C2	−0.38 (16)	C11—C12—C13—C8	0.6 (3)
N1—N2—C3—C4	177.88 (14)	C1—C14—C15—C16	177.18 (13)
N1—C1—C2—C3	0.35 (15)	C19—C14—C15—C16	−1.6 (2)
N1—C1—C2—C5	−177.75 (13)	C1—C14—C19—C18	−176.92 (13)
C14—C1—C2—C3	179.74 (14)	C15—C14—C19—C18	1.9 (2)
C14—C1—C2—C5	1.6 (2)	C14—C15—C16—C17	−0.1 (2)
N1—C1—C14—C15	−60.00 (19)	C15—C16—C17—C18	1.6 (2)
N1—C1—C14—C19	118.79 (15)	C15—C16—C17—C20	−178.80 (16)
C2—C1—C14—C15	120.70 (17)	C16—C17—C18—C19	−1.3 (2)
C2—C1—C14—C19	−60.5 (2)	C20—C17—C18—C19	179.07 (16)
C1—C2—C3—N2	0.03 (16)	C17—C18—C19—C14	−0.4 (2)
C1—C2—C3—C4	−177.97 (16)		

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the centroids of the N1/N2/C1–C3 and C8–C13 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6*A*···*Cg*1^{i}	0.97	2.93	3.794 (2)	149
C19—H19···*Cg*2^{i}	0.93	2.93	3.780 (2)	152

Symmetry code: (i) *x*−1, *y*, *z*.