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4-(3-Methylphenyl)-3-[(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)methyl]-4,5-dihydro-1*H*-1,2,4-triazole-5-thione

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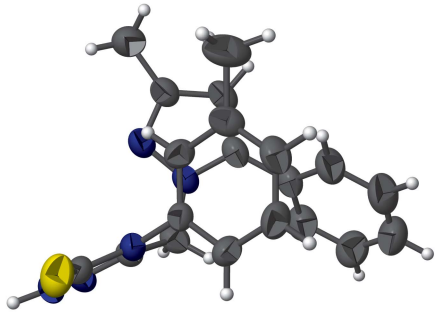
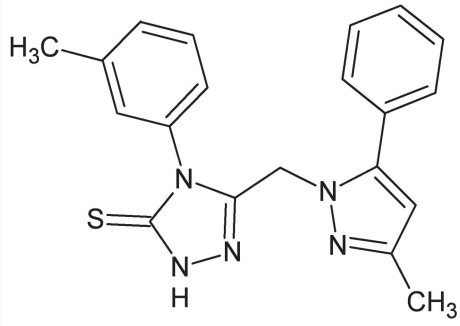
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{20}H_{19}N_5S$, adopts a 'contorted' conformation and the dihedral angle between the heterocyclic rings is 86.54 (6)°. In the crystal, complementary N—H···N hydrogen bonds form centrosymmetric dimers, which generate $R_2^2(14)$ loops. The dimers stack along the *a*-axis direction with adjacent stacks having their aromatic rings directed towards one another.

3D view



Chemical scheme



Structure description

As part of our ongoing studies of triazole derivatives (Mague *et al.*, 2015), we herein describe the synthesis and crystal structure of the title compound (Fig. 1). The dihedral angle between the planes of the C4–C8 and N1–N3/C1/C2 rings is 83.83 (5)° while that between the latter plane and that of the N4/N5/C11–C13 ring is 86.54 (6)°. The dihedral angle between the planes of the N4/N5/C11–C13 and C15–C20 rings is 52.92 (5)°. The molecule may be described as adopting a 'contorted' conformation.

In the crystal, complementary N3—H3···N5^{i} hydrogen bonds form centrosymmetric dimers, which generate $R_2^2(14)$ loops (Table 1 and Fig. 2). These dimers stack along the *a*-axis direction with the aromatic rings pointing towards those of adjacent stacks (Fig. 2).

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···N5^{i}	0.91	1.99	2.8765 (18)	164

Symmetry code: (i) $-x, -y+2, -z+1$.

Synthesis and crystallization

A solution of 2-(2-(5-phenyl-3-methyl-1*H*-pyrazol-1-yl)acetyl)-*N*-*p*-tolylhydrazinecarbothioamide (1.53 g; 4 mmol) in ethanol (50 ml) was added dropwise to 2 *N* sodium hydroxide solution (20 ml). The reaction mixture was then refluxed for 2 h, cooled, filtered and the filtrate was acidified with 2 *N* hydrochloric acid solution. The separated solid was collected, washed with water and recrystallized from pure EtOH.

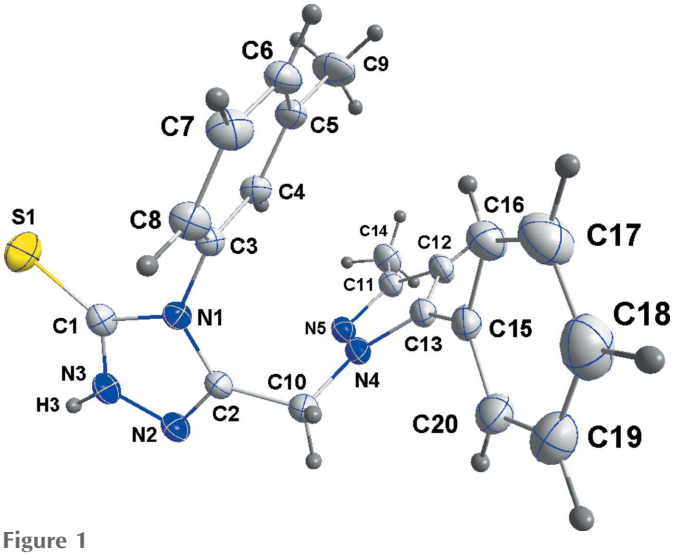


Figure 1
The title molecule with 25% probability ellipsoids.

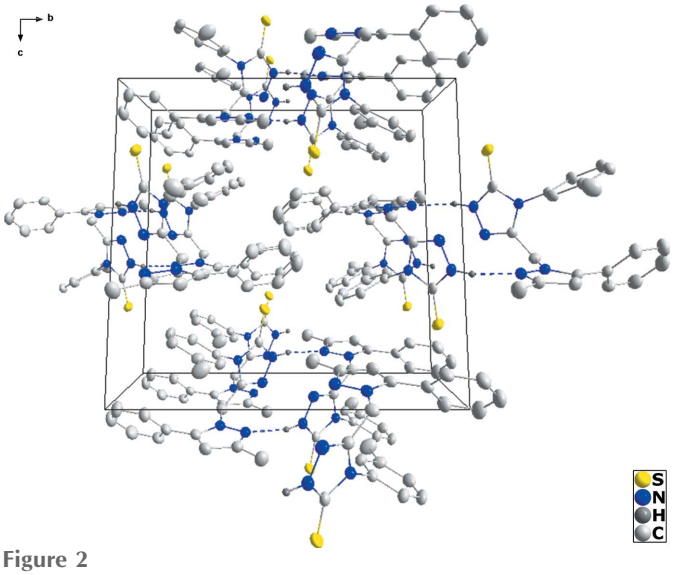


Figure 2
The packing, viewed along the *a* axis, with N—H···N hydrogen bonds shown as dotted lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{19}N_5S$
M_r	361.46
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	8.3386 (5), 15.5969 (9), 14.9334 (8)
β (°)	99.834 (1)
V (Å^3)	1913.65 (19)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.18
Crystal size (mm)	0.46 × 0.39 × 0.26
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.87, 0.95
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35813, 4940, 3778
R_{int}	0.030
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.676
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.146, 1.10
No. of reflections	4940
No. of parameters	236
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.26

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x170184 [https://doi.org/10.1107/S2414314617001845]

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4-(3-Methylphenyl)-3-[(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)methyl]-4,5-dihydro-1*H*-1,2,4-triazole-5-thione

Crystal data

$C_{20}H_{19}N_5S$
M_r = 361.46
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 8.3386 (5) Å
b = 15.5969 (9) Å
c = 14.9334 (8) Å
β = 99.834 (1)°
V = 1913.65 (19) Å^3
Z = 4
$F(000)$ = 760
D_x = 1.255 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9947 reflections
θ = 2.6–27.4°
μ = 0.18 mm^{-1}
T = 296 K
Block, colourless
0.46 × 0.39 × 0.26 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.87, T_{max} = 0.95
35813 measured reflections
4940 independent reflections
3778 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 28.7°, θ_{min} = 1.9°
h = −11→11
k = −21→20
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.146
S = 1.10
4940 reflections
236 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0824P)^2 + 0.1767P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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}
S1	0.08990 (6)	0.93018 (3)	0.76368 (3)	0.0686 (2)
N1	0.07577 (12)	0.84839 (7)	0.60041 (7)	0.0418 (3)
N2	−0.11285 (14)	0.92049 (8)	0.50918 (9)	0.0530 (4)
N3	−0.08851 (14)	0.95325 (8)	0.59569 (8)	0.0512 (4)
N4	0.15498 (13)	0.80095 (7)	0.40792 (7)	0.0472 (3)
N5	0.22539 (14)	0.87806 (8)	0.39760 (8)	0.0509 (4)
C1	0.02584 (16)	0.91209 (8)	0.65356 (10)	0.0466 (4)
C2	−0.01244 (15)	0.85699 (8)	0.51410 (9)	0.0441 (4)
C3	0.20542 (14)	0.78874 (8)	0.63013 (8)	0.0402 (3)
C4	0.36005 (15)	0.80791 (9)	0.61541 (9)	0.0472 (4)
C5	0.48769 (17)	0.75124 (11)	0.64334 (10)	0.0533 (4)
C6	0.45477 (19)	0.67623 (10)	0.68636 (10)	0.0575 (5)
C7	0.29975 (19)	0.65818 (9)	0.70153 (11)	0.0587 (5)
C8	0.17328 (17)	0.71456 (9)	0.67361 (10)	0.0509 (4)
C9	0.6570 (2)	0.77113 (16)	0.62645 (17)	0.0902 (8)
C10	−0.00265 (16)	0.79791 (10)	0.43684 (10)	0.0519 (4)
C11	0.37196 (18)	0.85957 (10)	0.37764 (10)	0.0536 (4)
C12	0.3940 (2)	0.77082 (11)	0.37496 (11)	0.0591 (5)
C13	0.25369 (18)	0.73447 (9)	0.39460 (9)	0.0508 (4)
C14	0.4856 (2)	0.93002 (13)	0.36231 (15)	0.0772 (7)
C15	0.20869 (18)	0.64418 (9)	0.40348 (10)	0.0536 (4)
C16	0.3127 (2)	0.59089 (11)	0.46143 (13)	0.0693 (6)
C17	0.2728 (3)	0.50589 (13)	0.47188 (16)	0.0860 (8)
C18	0.1284 (3)	0.47360 (13)	0.42448 (17)	0.0864 (8)
C19	0.0251 (2)	0.52531 (13)	0.36800 (14)	0.0785 (7)
C20	0.0639 (2)	0.61012 (12)	0.35723 (11)	0.0656 (5)
H3	−0.14120	1.00240	0.60600	0.0610*
H4	0.37920	0.85890	0.58670	0.0570*
H6	0.53840	0.63750	0.70530	0.0690*
H7	0.28010	0.60760	0.73080	0.0700*
H8	0.06870	0.70260	0.68400	0.0610*
H9A	0.71600	0.71860	0.62370	0.1350*
H9B	0.71230	0.80610	0.67500	0.1350*
H9C	0.65040	0.80130	0.56990	0.1350*
H10A	−0.02350	0.73980	0.45480	0.0620*
H10B	−0.08650	0.81310	0.38600	0.0620*
H12	0.48540	0.74210	0.36240	0.0710*
H14A	0.59530	0.91340	0.38630	0.1160*
H14B	0.45870	0.98110	0.39250	0.1160*

H14C	0.47560	0.94090	0.29830	0.1160*
H16	0.40980	0.61260	0.49330	0.0830*
H17	0.34280	0.47050	0.51060	0.1030*
H18	0.10170	0.41630	0.43120	0.1040*
H19	−0.07210	0.50330	0.33660	0.0940*
H20	−0.00750	0.64490	0.31860	0.0790*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0942 (3)	0.0526 (3)	0.0590 (3)	−0.0063 (2)	0.0135 (2)	−0.0143 (2)
N1	0.0412 (5)	0.0361 (5)	0.0482 (6)	0.0022 (4)	0.0082 (4)	0.0000 (4)
N2	0.0463 (6)	0.0538 (7)	0.0604 (7)	0.0110 (5)	0.0133 (5)	0.0060 (5)
N3	0.0516 (6)	0.0418 (6)	0.0639 (7)	0.0090 (5)	0.0201 (5)	0.0011 (5)
N4	0.0472 (6)	0.0481 (6)	0.0462 (6)	0.0087 (5)	0.0078 (4)	−0.0016 (4)
N5	0.0524 (6)	0.0498 (7)	0.0513 (6)	0.0098 (5)	0.0114 (5)	0.0030 (5)
C1	0.0487 (7)	0.0339 (6)	0.0601 (8)	−0.0036 (5)	0.0179 (6)	−0.0014 (5)
C2	0.0378 (6)	0.0455 (7)	0.0495 (7)	0.0043 (5)	0.0089 (5)	0.0028 (5)
C3	0.0423 (6)	0.0348 (6)	0.0425 (6)	0.0004 (5)	0.0046 (5)	−0.0011 (4)
C4	0.0456 (7)	0.0466 (7)	0.0486 (7)	−0.0031 (5)	0.0062 (5)	0.0065 (5)
C5	0.0430 (7)	0.0669 (9)	0.0490 (7)	0.0044 (6)	0.0052 (5)	0.0031 (6)
C6	0.0579 (8)	0.0548 (8)	0.0562 (8)	0.0165 (7)	−0.0002 (6)	0.0037 (6)
C7	0.0686 (9)	0.0406 (7)	0.0651 (9)	0.0015 (7)	0.0061 (7)	0.0111 (6)
C8	0.0492 (7)	0.0417 (7)	0.0618 (8)	−0.0047 (6)	0.0097 (6)	0.0056 (6)
C9	0.0484 (9)	0.1214 (18)	0.1018 (15)	0.0083 (10)	0.0156 (9)	0.0256 (13)
C10	0.0438 (7)	0.0600 (8)	0.0504 (7)	0.0060 (6)	0.0035 (5)	−0.0050 (6)
C11	0.0536 (8)	0.0561 (8)	0.0528 (7)	0.0089 (6)	0.0136 (6)	0.0021 (6)
C12	0.0555 (8)	0.0613 (9)	0.0630 (9)	0.0152 (7)	0.0171 (7)	−0.0034 (7)
C13	0.0547 (8)	0.0513 (8)	0.0457 (7)	0.0122 (6)	0.0069 (6)	−0.0048 (5)
C14	0.0703 (11)	0.0725 (12)	0.0953 (14)	0.0010 (9)	0.0328 (10)	0.0082 (10)
C15	0.0619 (8)	0.0487 (8)	0.0504 (7)	0.0101 (6)	0.0099 (6)	−0.0078 (6)
C16	0.0652 (10)	0.0574 (9)	0.0821 (12)	0.0139 (8)	0.0035 (8)	−0.0019 (8)
C17	0.0882 (14)	0.0589 (11)	0.1089 (16)	0.0201 (10)	0.0110 (11)	0.0110 (10)
C18	0.0987 (15)	0.0530 (10)	0.1094 (16)	−0.0030 (10)	0.0233 (12)	−0.0076 (10)
C19	0.0836 (12)	0.0680 (11)	0.0808 (12)	−0.0094 (10)	0.0056 (9)	−0.0170 (9)
C20	0.0743 (10)	0.0635 (10)	0.0548 (8)	0.0051 (8)	−0.0011 (7)	−0.0083 (7)

Geometric parameters (Å, º)

S1—C1	1.6641 (15)	C15—C20	1.390 (2)
N1—C1	1.3796 (17)	C15—C16	1.391 (2)
N1—C2	1.3771 (17)	C16—C17	1.382 (3)
N1—C3	1.4379 (16)	C17—C18	1.383 (3)
N2—N3	1.3717 (18)	C18—C19	1.362 (3)
N2—C2	1.2909 (18)	C19—C20	1.378 (3)
N3—C1	1.3367 (18)	C4—H4	0.9300
N4—N5	1.3586 (17)	C6—H6	0.9300
N4—C10	1.4527 (18)	C7—H7	0.9300

N4—C13	1.3595 (18)	C8—H8	0.9300
N5—C11	1.3380 (19)	C9—H9A	0.9600
C2—C10	1.490 (2)	C9—H9B	0.9600
C3—C4	1.3774 (17)	C9—H9C	0.9600
C3—C8	1.3753 (19)	C10—H10A	0.9700
N3—H3	0.9100	C10—H10B	0.9700
C4—C5	1.392 (2)	C12—H12	0.9300
C5—C9	1.508 (2)	C14—H14A	0.9600
C5—C6	1.385 (2)	C14—H14B	0.9600
C6—C7	1.379 (2)	C14—H14C	0.9600
C7—C8	1.382 (2)	C16—H16	0.9300
C11—C14	1.494 (2)	C17—H17	0.9300
C11—C12	1.398 (2)	C18—H18	0.9300
C12—C13	1.376 (2)	C19—H19	0.9300
C13—C15	1.469 (2)	C20—H20	0.9300

C1—N1—C2	107.63 (11)	C17—C18—C19	120.29 (19)
C1—N1—C3	124.98 (11)	C18—C19—C20	120.30 (18)
C2—N1—C3	127.24 (10)	C15—C20—C19	120.69 (16)
N3—N2—C2	104.00 (12)	C3—C4—H4	120.00
N2—N3—C1	113.86 (12)	C5—C4—H4	120.00
N5—N4—C10	119.55 (11)	C5—C6—H6	120.00
N5—N4—C13	111.99 (11)	C7—C6—H6	120.00
C10—N4—C13	128.30 (12)	C6—C7—H7	120.00
N4—N5—C11	105.27 (12)	C8—C7—H7	120.00
S1—C1—N1	127.82 (10)	C3—C8—H8	121.00
S1—C1—N3	129.10 (11)	C7—C8—H8	121.00
N1—C1—N3	103.06 (12)	C5—C9—H9A	109.00
N1—C2—N2	111.44 (12)	C5—C9—H9B	109.00
N1—C2—C10	124.99 (11)	C5—C9—H9C	109.00
N2—C2—C10	123.46 (13)	H9A—C9—H9B	109.00
N1—C3—C4	119.03 (11)	H9A—C9—H9C	109.00
N1—C3—C8	119.55 (11)	H9B—C9—H9C	110.00
C4—C3—C8	121.41 (12)	N4—C10—H10A	109.00
N2—N3—H3	118.00	N4—C10—H10B	109.00
C1—N3—H3	127.00	C2—C10—H10A	109.00
C3—C4—C5	120.21 (13)	C2—C10—H10B	109.00
C6—C5—C9	121.12 (16)	H10A—C10—H10B	108.00
C4—C5—C6	118.27 (13)	C11—C12—H12	127.00
C4—C5—C9	120.61 (16)	C13—C12—H12	127.00
C5—C6—C7	120.96 (14)	C11—C14—H14A	109.00
C6—C7—C8	120.60 (14)	C11—C14—H14B	109.00
C3—C8—C7	118.53 (13)	C11—C14—H14C	109.00
N4—C10—C2	112.47 (11)	H14A—C14—H14B	109.00
C12—C11—C14	129.35 (15)	H14A—C14—H14C	110.00
N5—C11—C14	120.20 (14)	H14B—C14—H14C	109.00
N5—C11—C12	110.45 (14)	C15—C16—H16	120.00
C11—C12—C13	106.33 (14)	C17—C16—H16	120.00

N4—C13—C12	105.96 (13)	C16—C17—H17	120.00
N4—C13—C15	123.20 (13)	C18—C17—H17	120.00
C12—C13—C15	130.82 (14)	C17—C18—H18	120.00
C13—C15—C16	119.15 (14)	C19—C18—H18	120.00
C16—C15—C20	118.49 (14)	C18—C19—H19	120.00
C13—C15—C20	122.35 (14)	C20—C19—H19	120.00
C15—C16—C17	120.45 (17)	C15—C20—H20	120.00
C16—C17—C18	119.8 (2)	C19—C20—H20	120.00

C2—N1—C1—S1	178.75 (11)	N2—C2—C10—N4	117.70 (14)
C2—N1—C1—N3	0.48 (14)	N1—C3—C4—C5	−179.89 (12)
C3—N1—C1—S1	−5.43 (19)	C8—C3—C4—C5	1.0 (2)
C3—N1—C1—N3	176.31 (11)	N1—C3—C8—C7	179.98 (13)
C1—N1—C2—N2	−0.05 (16)	C4—C3—C8—C7	−0.9 (2)
C1—N1—C2—C10	−176.41 (12)	C3—C4—C5—C6	−0.4 (2)
C3—N1—C2—N2	−175.76 (12)	C3—C4—C5—C9	179.21 (16)
C3—N1—C2—C10	7.9 (2)	C4—C5—C6—C7	−0.3 (2)
C1—N1—C3—C4	−93.20 (15)	C9—C5—C6—C7	−179.87 (17)
C1—N1—C3—C8	85.91 (16)	C5—C6—C7—C8	0.3 (2)
C2—N1—C3—C4	81.80 (16)	C6—C7—C8—C3	0.3 (2)
C2—N1—C3—C8	−99.09 (15)	N5—C11—C12—C13	−0.20 (18)
C2—N2—N3—C1	0.74 (15)	C14—C11—C12—C13	179.49 (17)
N3—N2—C2—N1	−0.39 (15)	C11—C12—C13—N4	0.06 (16)
N3—N2—C2—C10	176.03 (12)	C11—C12—C13—C15	−178.41 (14)
N2—N3—C1—S1	−179.00 (11)	N4—C13—C15—C16	−125.72 (16)
N2—N3—C1—N1	−0.76 (15)	N4—C13—C15—C20	53.1 (2)
C10—N4—N5—C11	175.47 (12)	C12—C13—C15—C16	52.5 (2)
C13—N4—N5—C11	−0.21 (15)	C12—C13—C15—C20	−128.71 (18)
N5—N4—C10—C2	−45.23 (16)	C13—C15—C16—C17	179.33 (17)
C13—N4—C10—C2	129.67 (14)	C20—C15—C16—C17	0.5 (3)
N5—N4—C13—C12	0.09 (15)	C13—C15—C20—C19	−179.33 (15)
N5—N4—C13—C15	178.71 (12)	C16—C15—C20—C19	−0.6 (2)
C10—N4—C13—C12	−175.12 (13)	C15—C16—C17—C18	−0.1 (3)
C10—N4—C13—C15	3.5 (2)	C16—C17—C18—C19	−0.4 (4)
N4—N5—C11—C12	0.25 (16)	C17—C18—C19—C20	0.3 (3)
N4—N5—C11—C14	−179.47 (14)	C18—C19—C20—C15	0.1 (3)
N1—C2—C10—N4	−66.37 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···N5^{i}	0.91	1.99	2.8765 (18)	164

Symmetry code: (i) −*x*, −*y*+2, −*z*+1.