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4-[3,4-Dimethyl-1-(4-methylphenyl)-5-oxo-4,5-dihydro-1*H*-pyrazol-4-yl]-3,4-dimethyl-1-(4-methylphenyl)-4,5-dihydro-1*H*-pyrazol-5-one

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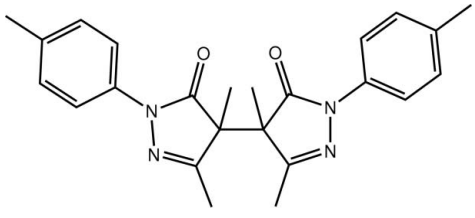
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.042; wR factor = 0.136; data-to-parameter ratio = 17.2.

In the title compound, $C_{24}H_{26}N_4O_2$, the complete molecule is generated by the application of twofold symmetry. The pyrazole ring is approximately planar [r.m.s. deviation = 0.026 Å] and the benzene ring is twisted out of this plane [dihedral angle = 21.94 (7)°]. A twist in the molecule about the central C—C bond [1.566 (3) Å] is also evident [C—C—C—C torsion angle = 44.30 (14)°]. Supramolecular layers in the *bc* plane are formed in the crystal packing *via* C—H···O and C—H···π interactions.

Related literature

For the therapeutic importance of pyrazole compounds, see: Sil *et al.* (2005); Haddad *et al.* (2004). For the diverse pharmacological activities of pyrazole compounds, see: Bekhit *et al.* (2010, 2012); Higashi *et al.* (2006). For synthetic background, see: Nef (1891): Veibel & Westöö (1953); Katritzky *et al.* (1997); Wardell *et al.* (2007); de Lima *et al.* (2010). For the synthesis of the title compound, see: Bernstein *et al.* (1947); Gryazeva & Golomolzin (2003).



Experimental

Crystal data

$C_{24}H_{26}N_4O_2$
M_r = 402.50
Monoclinic, $C2/c$
a = 23.0007 (8) Å
b = 6.6712 (2) Å
c = 13.5967 (5) Å
β = 92.566 (2)°
V = 2084.22 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 120 K
0.48 × 0.36 × 0.18 mm

Data collection

Rigaku Saturn724+ diffractometer
Absorption correction: multi-scan (*CrystalClear-SM Expert*; Rigaku, 2011)
T_{min} = 0.668, T_{max} = 0.746
11383 measured reflections
2384 independent reflections
1856 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.136
S = 0.83
2384 reflections
139 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

*Cg*1 is the centroid of the C6–C11 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4B···O1^{i}	0.98	2.60	3.5676 (16)	169
C4—H4A···Cg1^{ii}	0.98	2.82	3.6644 (15)	145

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

Data collection: *CrystalClear-SM Expert* (Rigaku, 2011); cell refinement: *CrystalClear-SM Expert*; data reduction: *CrystalClear-SM Expert*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5185).

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supporting information

Acta Cryst. (2012). E**68**, o992–o993 [https://doi.org/10.1107/S1600536812009208]

4-[3,4-Dimethyl-1-(4-methylphenyl)-5-oxo-4,5-dihydro-1*H*-pyrazol-4-yl]-3,4-dimethyl-1-(4-methylphenyl)-4,5-dihydro-1*H*-pyrazol-5-one

Solange M. S. V. Wardell, Alan H. Howie, Edward R. T. Tiekink and James L. Wardell

S1. Comment

Pyrazoles are key structures in numerous compounds of therapeutic importance (Sil *et al.*, 2005, Haddad *et al.*, 2004). Compounds containing this ring system are known to display diverse pharmacological activities, for example as anti-malarial agents (Bekhit *et al.*, 2012), anti-inflammatory agents (Bekhit *et al.*, 2010), and against cardiovascular disease (Higashi *et al.*, 2006). A general route to pyrazole derivatives involves reaction of an arylhydrazine, $ArNHNH_2$, with a *β*-dicarbonyl compound, $R'COCH_2COY$. This reaction provides initially a hydrazone derivative, $RNHN{=}CR'CH_2COY$, which can be isolated but which readily undergoes cyclization to a pyrazone derivative (Nef, 1891; Katritzky *et al.*, 1997; Wardell *et al.*, 2007; de Lima *et al.*, 2010). However, in some cases (Veibel & Westöö, 1953), a dimeric oxidation product is isolated, as found in the reaction between $4\text{-}MeC_6H_4NHNH_2$ and $MeCOCH_2CO_2Et$. The structure of this product, 4-[3,4-dimethyl-1-(4-methylphenyl)-5-oxopyrazol-4- yl]-4,5-dimethyl-2-(4-methylphenyl)pyrazol-3-one (I), is now reported.

The molecule of (I), Fig. 1, has crystallographically imposed twofold symmetry. The pyrazole ring is planar with a r.m.s. deviation for the fitted atoms of 0.026 Å; the maximum deviations from this plane are 0.019 (1) Å (for the N1 and C2 atoms) and -0.023 (1) Å (C3). The benzene ring is inclined to this plane forming a dihedral angle of 21.94 (7)°. There is a twist in the molecule about the central C—C bond [1.566 (3) Å] with the C1—C2—$C2^i$—$C1^i$ torsion angle being 44.30 (14)°; symmetry operation *i*: -*x*, *y*, 3/2 - *z*. The dihedral angle between the pyrazole rings is 61.78 (4)°.

In the crystal packing, supramolecular layers in the *bc* plane are formed by C—H···O and C—H···*π* interactions, Fig. 2 and Table 1. These stack along the *a* axis with no specific intermolecular interactions between them, Fig. 3.

S2. Experimental

A solution of $4\text{-}MeC_6H_4NHNH_2.HCl$ (2 mmol) and $MeCOCH_2CO_2Et$ (2 mmol) in EtOH (2 0 ml) was refluxed for 2 h. The reaction was left to slowly evaporate in air. Crystals were collected after a week, *M*.pt: > 573 K; lit. *M*.pt: >573 K (Bernstein *et al.*, 1947; Gryazeva & Golomolzin, 2003). IR *ν*: 3391, 3084, 3041, 3012, 2974, 2920, 2858, 1706, 1663, 1614, 1511, 1441, 1390, 1363, 1288, 1140, 1083, 1004, 912, 816, 776, 654, 590, 507, 485 cm^{-1}.

S3. Refinement

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. Owing to poor agreement two reflections, *i.e.* ($\bar{5}$ 1 2) and ($\bar{2}$ 0 2), were omitted from the final cycles of refinement.

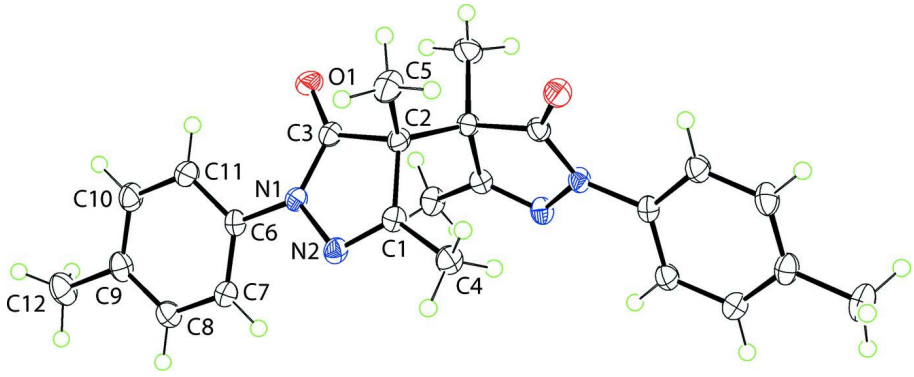

Figure 1

The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. Unlabelled atoms are related by the symmetry operation -*x*, *y*, 3/2 - *z*.

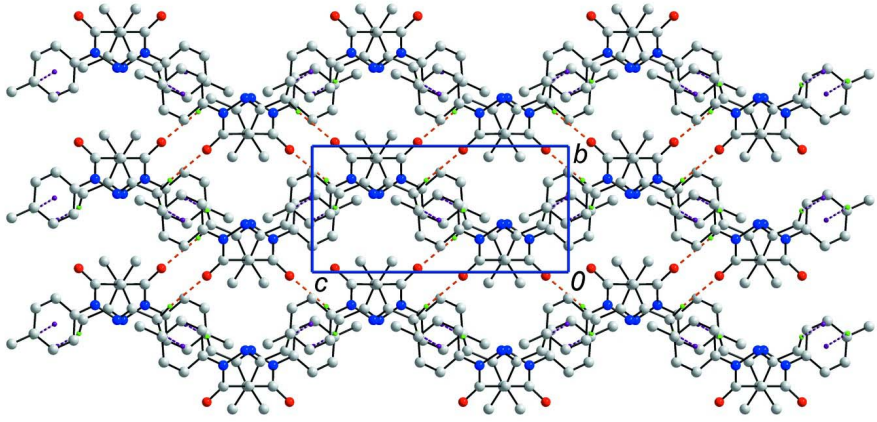

Figure 2

A view of the supramolecular layer in the *bc* plane of (I). The C—H···O and C—H···π interactions are shown as orange and purple dashed lines, respectively. Hydrogen atoms not involved in intermolecular interactions have been omitted for reasons of clarity.

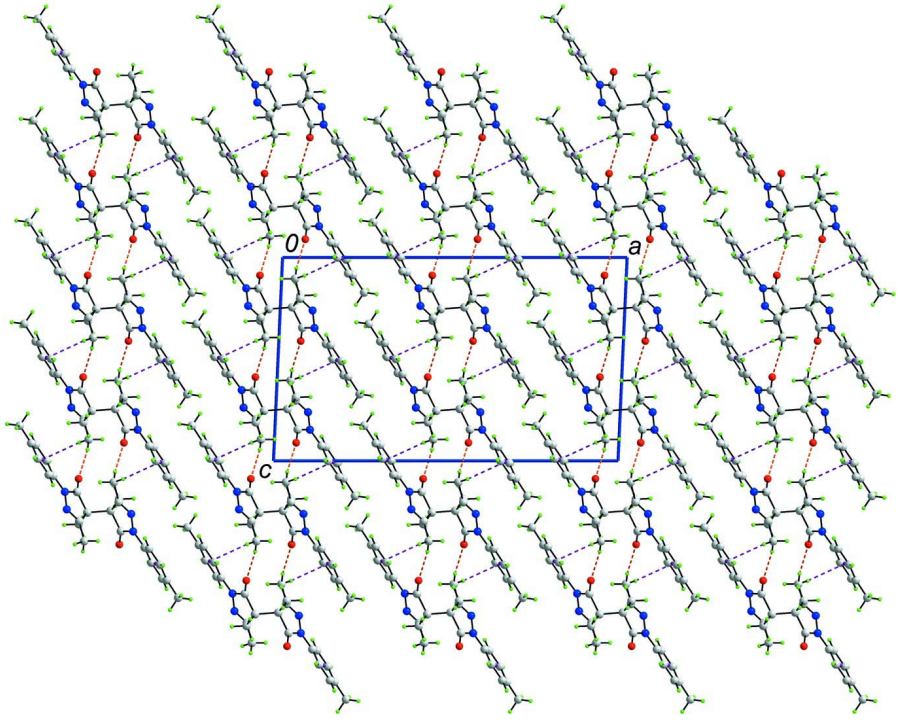

Figure 3

A view in projection down the *b* axis of the stacking of supramolecular layers along the *a* direction in (I). The C—H···O and C—H···π interactions are shown as orange and purple dashed lines, respectively.

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Crystal data

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M_r = 402.50
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 23.0007 (8) Å
b = 6.6712 (2) Å
c = 13.5967 (5) Å
β = 92.566 (2)°
V = 2084.22 (12) Å^3
Z = 4
F(000) = 856
D_x = 1.283 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 6506 reflections
θ = 2.9–27.5°
μ = 0.08 mm^{-1}
T = 120 K
Block, light-yellow
0.48 × 0.36 × 0.18 mm

Data collection

Rigaku Saturn724+ diffractometer
Radiation source: Rotating Anode
Confocal monochromator
Detector resolution: 28.5714 pixels mm^{-1}
profile data from ω–scans
Absorption correction: multi-scan (*CrystalClear-SM Expert*; Rigaku, 2011)
T_{min} = 0.668, T_{max} = 0.746
11383 measured reflections
2384 independent reflections
1856 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −29→29
k = −8→8
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.136$
$S = 0.83$
2384 reflections
139 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
$w = 1/[\sigma^2(F_o^2) + (0.104P)^2 + 1.4411P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness 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 threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *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	0.06343 (4)	0.52970 (14)	0.91141 (7)	0.0292 (3)
N1	0.10162 (5)	0.23866 (16)	0.84739 (8)	0.0202 (3)
N2	0.09381 (5)	0.12079 (17)	0.76120 (8)	0.0217 (3)
C1	0.05610 (5)	0.2093 (2)	0.70361 (9)	0.0194 (3)
C2	0.03383 (5)	0.40353 (18)	0.74559 (9)	0.0197 (3)
C3	0.06614 (6)	0.40447 (19)	0.84662 (9)	0.0205 (3)
C4	0.03921 (6)	0.1236 (2)	0.60511 (9)	0.0253 (3)
H4A	0.0658	0.0144	0.5900	0.038*
H4B	0.0413	0.2284	0.5549	0.038*
H4C	−0.0006	0.0718	0.6057	0.038*
C5	0.05690 (7)	0.5851 (2)	0.68862 (11)	0.0310 (3)
H5A	0.0993	0.5753	0.6856	0.046*
H5B	0.0468	0.7092	0.7224	0.046*
H5C	0.0392	0.5861	0.6217	0.046*
C6	0.13732 (5)	0.1626 (2)	0.92676 (9)	0.0198 (3)
C7	0.15049 (6)	−0.0403 (2)	0.93131 (10)	0.0245 (3)
H7	0.1366	−0.1285	0.8807	0.029*
C8	0.18434 (6)	−0.1132 (2)	1.01097 (10)	0.0271 (3)
H8	0.1931	−0.2523	1.0140	0.033*
C9	0.20565 (6)	0.0114 (2)	1.08617 (9)	0.0258 (3)
C10	0.19226 (6)	0.2144 (2)	1.07910 (10)	0.0282 (3)
H10	0.2065	0.3028	1.1294	0.034*
C11	0.15862 (6)	0.2913 (2)	1.00071 (10)	0.0253 (3)
H11	0.1502	0.4306	0.9974	0.030*
C12	0.24118 (7)	−0.0698 (3)	1.17294 (10)	0.0350 (4)

H12A	0.2499	−0.2116	1.1618	0.052*
H12B	0.2191	−0.0564	1.2326	0.052*
H12C	0.2776	0.0057	1.1809	0.052*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0374 (6)	0.0238 (5)	0.0256 (5)	0.0034 (4)	−0.0081 (4)	−0.0085 (4)
N1	0.0224 (6)	0.0217 (5)	0.0161 (5)	0.0010 (4)	−0.0031 (4)	−0.0038 (4)
N2	0.0221 (6)	0.0267 (6)	0.0163 (5)	0.0006 (4)	−0.0001 (4)	−0.0047 (4)
C1	0.0198 (6)	0.0233 (6)	0.0153 (6)	−0.0011 (5)	0.0025 (5)	−0.0007 (5)
C2	0.0227 (7)	0.0197 (6)	0.0163 (6)	−0.0015 (5)	−0.0021 (5)	0.0008 (5)
C3	0.0217 (6)	0.0210 (6)	0.0184 (6)	−0.0028 (5)	−0.0010 (5)	−0.0002 (5)
C4	0.0276 (7)	0.0312 (7)	0.0170 (6)	0.0030 (6)	0.0002 (5)	−0.0037 (5)
C5	0.0361 (8)	0.0295 (8)	0.0269 (7)	−0.0107 (6)	−0.0036 (6)	0.0081 (6)
C6	0.0166 (6)	0.0260 (7)	0.0167 (6)	−0.0003 (5)	0.0004 (5)	0.0003 (5)
C7	0.0237 (7)	0.0250 (7)	0.0242 (7)	−0.0012 (5)	−0.0036 (5)	−0.0025 (5)
C8	0.0257 (7)	0.0262 (7)	0.0290 (7)	0.0027 (6)	−0.0025 (6)	0.0026 (5)
C9	0.0220 (7)	0.0363 (8)	0.0191 (6)	0.0025 (6)	0.0005 (5)	0.0023 (5)
C10	0.0266 (7)	0.0350 (8)	0.0224 (7)	0.0018 (6)	−0.0051 (6)	−0.0068 (6)
C11	0.0270 (7)	0.0254 (7)	0.0232 (7)	0.0002 (6)	−0.0037 (5)	−0.0033 (5)
C12	0.0338 (8)	0.0464 (9)	0.0242 (7)	0.0091 (7)	−0.0054 (6)	0.0028 (6)

Geometric parameters (Å, º)

O1—C3	1.2177 (15)	C5—H5C	0.9800
N1—C3	1.3743 (17)	C6—C7	1.3882 (19)
N1—N2	1.4160 (14)	C6—C11	1.3943 (18)
N1—C6	1.4202 (16)	C7—C8	1.3928 (18)
N2—C1	1.2859 (17)	C7—H7	0.9500
C1—C4	1.4917 (17)	C8—C9	1.390 (2)
C1—C2	1.5142 (17)	C8—H8	0.9500
C2—C3	1.5323 (17)	C9—C10	1.391 (2)
C2—C5	1.5446 (18)	C9—C12	1.5057 (19)
C2—C2^{i}	1.566 (3)	C10—C11	1.3873 (19)
C4—H4A	0.9800	C10—H10	0.9500
C4—H4B	0.9800	C11—H11	0.9500
C4—H4C	0.9800	C12—H12A	0.9800
C5—H5A	0.9800	C12—H12B	0.9800
C5—H5B	0.9800	C12—H12C	0.9800
C3—N1—N2	112.79 (10)	H5A—C5—H5C	109.5
C3—N1—C6	128.04 (11)	H5B—C5—H5C	109.5
N2—N1—C6	118.56 (10)	C7—C6—C11	119.98 (12)
C1—N2—N1	107.82 (10)	C7—C6—N1	119.99 (12)
N2—C1—C4	120.81 (12)	C11—C6—N1	120.03 (12)
N2—C1—C2	113.19 (11)	C6—C7—C8	119.23 (13)
C4—C1—C2	125.98 (11)	C6—C7—H7	120.4

C1—C2—C3	100.53 (10)	C8—C7—H7	120.4
C1—C2—C5	110.64 (10)	C9—C8—C7	121.98 (13)
C3—C2—C5	106.41 (10)	C9—C8—H8	119.0
C1—C2—C2^{i}	112.51 (8)	C7—C8—H8	119.0
C3—C2—C2^{i}	112.02 (12)	C8—C9—C10	117.50 (13)
C5—C2—C2^{i}	113.78 (9)	C8—C9—C12	121.48 (14)
O1—C3—N1	126.61 (12)	C10—C9—C12	121.02 (13)
O1—C3—C2	127.80 (12)	C11—C10—C9	121.84 (13)
N1—C3—C2	105.52 (10)	C11—C10—H10	119.1
C1—C4—H4A	109.5	C9—C10—H10	119.1
C1—C4—H4B	109.5	C10—C11—C6	119.47 (13)
H4A—C4—H4B	109.5	C10—C11—H11	120.3
C1—C4—H4C	109.5	C6—C11—H11	120.3
H4A—C4—H4C	109.5	C9—C12—H12A	109.5
H4B—C4—H4C	109.5	C9—C12—H12B	109.5
C2—C5—H5A	109.5	H12A—C12—H12B	109.5
C2—C5—H5B	109.5	C9—C12—H12C	109.5
H5A—C5—H5B	109.5	H12A—C12—H12C	109.5
C2—C5—H5C	109.5	H12B—C12—H12C	109.5

C3—N1—N2—C1	2.35 (15)	C1—C2—C3—N1	3.64 (12)
C6—N1—N2—C1	174.14 (10)	C5—C2—C3—N1	−111.74 (12)
N1—N2—C1—C4	178.79 (11)	C2^{i}—C2—C3—N1	123.33 (8)
N1—N2—C1—C2	0.36 (14)	C3—N1—C6—C7	152.61 (13)
N2—C1—C2—C3	−2.51 (13)	N2—N1—C6—C7	−17.78 (17)
C4—C1—C2—C3	179.15 (12)	C3—N1—C6—C11	−26.66 (19)
N2—C1—C2—C5	109.65 (13)	N2—N1—C6—C11	162.95 (11)
C4—C1—C2—C5	−68.69 (16)	C11—C6—C7—C8	0.90 (19)
N2—C1—C2—C2^{i}	−121.85 (13)	N1—C6—C7—C8	−178.37 (11)
C4—C1—C2—C2^{i}	59.82 (17)	C6—C7—C8—C9	−0.3 (2)
N2—N1—C3—O1	179.21 (12)	C7—C8—C9—C10	−0.4 (2)
C6—N1—C3—O1	8.4 (2)	C7—C8—C9—C12	178.74 (12)
N2—N1—C3—C2	−3.87 (13)	C8—C9—C10—C11	0.4 (2)
C6—N1—C3—C2	−174.71 (11)	C12—C9—C10—C11	−178.70 (13)
C1—C2—C3—O1	−179.48 (13)	C9—C10—C11—C6	0.2 (2)
C5—C2—C3—O1	65.14 (17)	C7—C6—C11—C10	−0.9 (2)
C2^{i}—C2—C3—O1	−59.80 (14)	N1—C6—C11—C10	178.41 (11)

Symmetry code: (i) $-x, y, -z+3/2$.

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C6–C11 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···O1^{ii}	0.98	2.60	3.5676 (16)	169
C4—H4*A*···*Cg*1^{iii}	0.98	2.82	3.6644 (15)	145

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