Crystal structure and Hirshfeld surface analysis of dibutyl 5,5′-(pentane-3,3-diyl)bis(1H-pyrrole-5-carboxylate)

Haijing Wang[a,b] and Zhenming Yin[a,b]*

[a]College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Tianjin Normal University, Tianjin 300387, People's Republic of China, and [b]Key Laboratory of Inorganic–Organic Hybrid Functional Materials Chemistry (Tianjin Normal University), Ministry of Education, Tianjin 300387, People's Republic of China. *Correspondence e-mail: tjyinzm@aliyun.com

The molecular structure of the title compound, $C_{23}H_{34}N_2O_4$, has $C2$ symmetry. In the crystal, interlocked dimers are formed through quadruple N—H···O hydrogen bonds between pyrrole N—H groups and carbonyl O atoms.

1. Chemical context

Hydrogen-bonding interactions play an important role in the design of functional assemblies that exhibit a variety of properties and functions (Prins *et al.*, 2001; Steiner, 2002). Pyrrole-2-carboxylate possesses one hydrogen-bond donor (N—H$_{pyrrole}$) and one acceptor (C=O), which favour the formation of centrosymmetric dimers with pairs of N—H···O hydrogen bonds (Figueira *et al.*, 2015). The dimer motif is structurally similar to classic Watson–Crick nucleotide base-pairs. Calculations have revealed the dimer motif to be a robust supramolecular synthon in crystal engineering (Dubis *et al.*, 2002). In previous work, we have shown a way to use the 2-carbonyl pyrrole dimer as a supramolecular connector to construct hexagonal and grid architectures (Yin *et al.*, 2006). Here, we report the self-assembly of the title compound, *via* quadruple N—H···N hydrogen bonds.
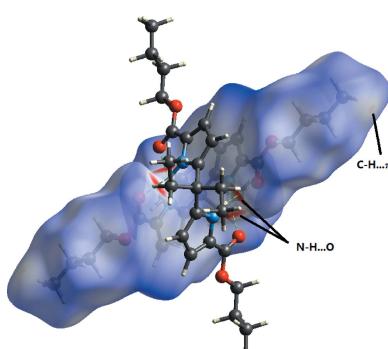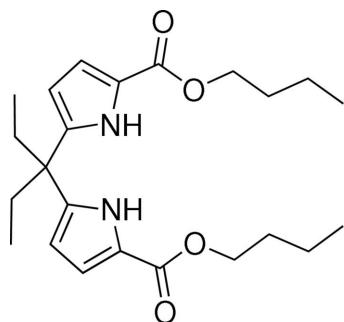
2. Structural commentary

The structure of the title compound is shown in Fig. 1. The asymmetric unit contains one half-molecule as it possesses $C2$ symmetry. In the molecule, the two pyrrole-2-carboxylate groups are both in a *syn* conformation, with the carbonyl group arranged *syn* to its adjacent pyrrole NH group. The O1—C8—C7—N1 torsion angle is −8.2 (5)°. The dihedral angle between the pyrrole rings is 72.8 (2)°.

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

$Cg1$ is the centroid of the N1/C4–C7 ring.

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N1—H1$\cdots$O1^{i}	0.86	2.12	2.962 (3)	165
C12—H12$C\cdots Cg1^{ii}$	0.96	3.21	3.944 (3)	135

Symmetry codes: (i) $-x + \frac{5}{4}, -y + \frac{1}{4}, z$; (ii) $x + \frac{1}{4}, y + \frac{1}{4}, -z$.

3. Supramolecular features

Pairs of molecules of the title compound form interlocked dimers through four N1—H1$\cdots$O1 hydrogen bonds between the pyrrole carbonyl oxygen atoms and pyrrole NH protons (Table 1, Fig. 2). This type of dimer has also been observed in our previous work (Yin *et al.*, 2007). The dimers are connected into a three-dimensional supramolecular structure through C—H$\cdots\pi$ contacts (Table 1).

4. Hirshfeld surface

A Hirshfeld surface analysis with *CrystalExplorer* (Turner *et al.*, 2017) was performed to give insights into the important intermolecular interactions. These are normalized by van der Waals radii through a red–white–blue color scheme, where the red spots denote close contacts of molecules. The three-dimensional d_{norm} surface of the title compound is shown in Fig. 3. The red points represent closer contacts and negative d_{norm} values on the surface corresponding to the N—H$\cdots$O and C—H$\cdots\pi$ interactions mentioned above. The two-dimensional fingerprint plots in Fig. 4 shown the inter-molecular contacts and their percentage distributions on the Hirshfeld surface. H$\cdots$H interactions (74.8%) are present as a major contributor while H$\cdots$O/O$\cdots$H (14.5%), H$\cdots$C/C$\cdots$H (5.4%), C$\cdots$C (2.7%) and H$\cdots$N/N$\cdots$H (0.9%) contacts also give significant contributions to the Hirshfeld surface.

5. Database survey

A search in the Cambridge Structural Database (Groom *et al.*, 2016) returned over 60 entries for dipyrromethane-1,9-

Figure 2
Part of the crystal packing showing molecules linked by N—H$\cdots$O hydrogen bonds (red dashed lines) and C—H$\cdots\pi$ contacts (green dashed lines). [Symmetry codes: (i) $-x + \frac{5}{4}, -y + \frac{1}{4}, z$; (ii) $x + \frac{1}{4}, y + \frac{1}{4} - z$.]

dicarbonyl derivatives, including seven entries whose supra-molecular structures feature interlocked dimers (ILITAY, Love *et al.*, 2003; ODUMOQ,Yin *et al.*, 2007; PIRJAB, Xie *et al.*, 1994; NIQBAR01, Mahanta *et al.*, 2012; VACRID, Delio-meroglu *et al.*, 2016; PUJMAJ, Kim, 2010 and SAVDUQ, Uppal *et al.*, 2012). In the crystal of PUJMAJ (Kim, 2010), only one of the carbonyl groups is involved in hydrogen bonds with two pyrrole N—H groups.

6. Synthesis and crystallization

n-Butyl alcohol (370 mg, 5 mmol), 2,2′-ditrichlordipyrrole-methane (980 mg, 2 mmol) and triethylamine (0.5 mL) were added to acetonitrile (20 mL), and then the mixture was refluxed for 2h. The solution was evaporated under reduced pressure and the residue was purified by column chromato-graphy on silica gel (ethyl acetate/petroleum ether = 1:2),
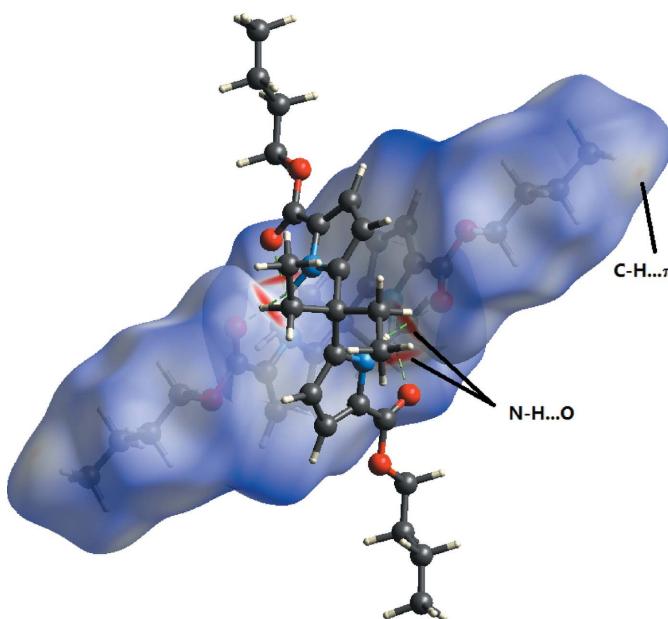
Figure 3
The Hirshfeld surface of the title compound mapped over d_{norm} in the range −0.486 to 1.895 a.u. The intermolecular contacts can be seen in the red regions.

Figure 1
ORTEP diagram for the title compound, with displacement ellipsoids drawn at the 30% probability level. [Symmetry code: (A) $x, \frac{1}{4} - y, \frac{1}{4} - z$.]
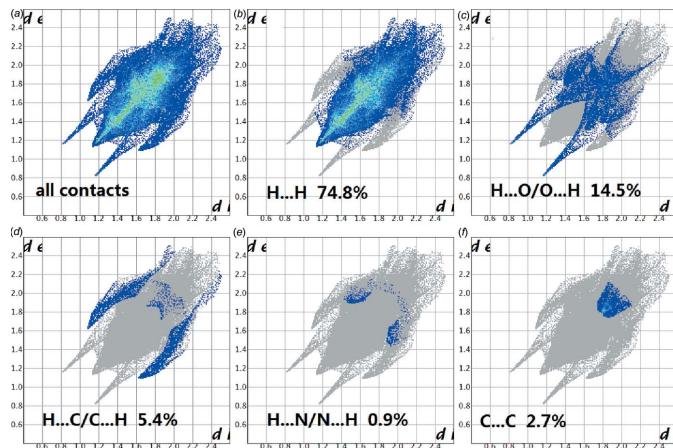
Figure 4
The two-dimensional fingerprint plots of title compound: (*a*) all contacts; (*b*) H$\cdots$H, (*c*) H$\cdots$O/O$\cdots$H, (*d*) H$\cdots$C/C$\cdots$H, (*e*) H$\cdots$N/N$\cdots$H and (*f*) C$\cdots$C.

affording the title compound (white powder, 672 mg, 71%), m.p. = 388 K. ^{1}H NMR (400 MHz, DMSO-d_6); δ 0.64 (*t*, 6H, *J* = 7.2 Hz, –CH$_3$), 0.90 (*t*, 6H, *J* = 7.2 Hz, –CH$_3$), 1.31–1.41 (*m*, 4H, –CH$_2$–), 1.58–1.65 (*m*, 4H, –CH$_2$–), 2.15 (*q*, 4H, *J* = 7.2 Hz, Å –CH$_2$–), 4.15 (q, 4H, *J* = 6.8 Hz, –CH$_2$–), 5.97 (*s*, 2H, PyCH), 6.66 (*s*, 2H, PyCH), 11.22 (*s*, 2H, NH); HRMS (ESI) *m/z* calculated for C$_{23}$H$_{34}$N$_2$O$_4$, (*M* + H)$^+$ 403.25186; found 403.25224. Crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation of a CH$_3$OH solution of the title compound.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. N—H hydrogen atoms were located from a difference-Fourier map and freely refined. Other H atoms were placed in difference calculated positions (C—H = 0.96 or 0.97 Å) and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2U_{eq}(C).

References

Bruker (2001). *SMART, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Deliomeroglu, M. K., Lynch, V. M. & Sessler, J. L. (2016). *Chem. Sci.* **7**, 3843–3850.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Table 2
Experimental details.

Crystal data	
Chemical formula	C$_{23}$H$_{34}$N$_2$O$_4$
M_r	402.52
Crystal system, space group	Orthorhombic, *Fddd*
Temperature (K)	296
a, b, c (Å)	14.358 (6), 17.333 (7), 38.902 (19)
V (Å^3)	9681 (7)
Z	16
Radiation type	Mo *K*α
μ (mm^{-1})	0.08
Crystal size (mm)	0.32 × 0.28 × 0.26
Data collection	
Diffractometer	Bruker SMART CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2001)
T_{min}, T_{max}	0.822, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11878, 2156, 1501
R_{int}	0.031
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.081, 0.278, 1.05
No. of reflections	2156
No. of parameters	134
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.34

Computer programs: *SMART* and *SAINT* (Bruker, 2001), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

Dubis, A. T. & Grabowski, S. J. (2002). *New J. Chem.* **26**, 165–169.
Figueira, C. A., Lopes, P. S., Gomes, C. S. B., Veiros, L. F. & Gomes, P. T. (2015). *CrystEngComm*, **17**, 6406–6419.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Kim, H.-J. (2010). *Acta Cryst.* E**66**, o566.
Love, J. B., Blake, A. J., Wilson, C., Reid, S. D., Novak, A. & Hitchcock, P. B. (2003). *Chem. Commun.* pp. 1682–1683.
Mahanta, S. P., Kumar, B. S., Baskaran, S., Sivasankar, C. & Panda, P. K. (2012). *Org. Lett.* **14**, 548–551.
Prins, L. J., Reinhoudt, D. N. & Timmerman, P. (2001). *Angew. Chem. Int. Ed.* **40**, 2382–2426.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.
Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia.
Uppal, T., Hu, X., Fronczek, F. R., Maschek, S., Bobadova-Parvanova, P. & Vicente, M. G. H. (2012). *Chem. Eur. J.* **18**, 3893–3905.
Xie, H., Lee, D. A., Senge, M. O. & Smith, K. M. (1994). *J. Chem. Soc. Chem. Commun.* pp. 791–792.
Yin, Z. & Li, Z. (2006). *Tetrahedron Lett.* **47**, 7875–7879.
Yin, Z., Zhang, Y., He, J. & Cheng, J.-P. (2007). *Chem. Commun.* pp. 2599–2601.

Crystal structure and Hirshfeld surface analysis of dibutyl 5,5′-(pentane-3,3-diyl)bis(1*H*-pyrrole-5-carboxylate)

Haijing Wang and Zhenming Yin

Computing details

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART* (Bruker, 2001); data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Dibutyl 5,5′-(pentane-3,3-diyl)bis(1*H*-pyrrole-5-carboxylate)

Crystal data

$C_{23}H_{34}N_2O_4$	$D_x = 1.105$ Mg m^{-3}
$M_r = 402.52$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Fddd*	Cell parameters from 3608 reflections
$a = 14.358$ (6) Å	$\theta = 2.4–23.4°$
$b = 17.333$ (7) Å	$\mu = 0.08$ mm^{-1}
$c = 38.902$ (19) Å	$T = 296$ K
$V = 9681$ (7) Å^3	Block, colourless
$Z = 16$	$0.32 \times 0.28 \times 0.26$ mm
$F(000) = 3488$	

Data collection

Bruker SMART CCD area detector diffractometer	2156 independent reflections
Graphite monochromator	1501 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{int} = 0.031$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$\theta_{max} = 25.0°$, $\theta_{min} = 1.9°$
$T_{min} = 0.822$, $T_{max} = 1.000$	$h = -17\rightarrow16$
11878 measured reflections	$k = -20\rightarrow18$
	$l = -46\rightarrow44$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.081$	H-atom parameters constrained
$wR(F^2) = 0.278$	$w = 1/[\sigma^2(F_o^2) + (0.1517P)^2 + 16.1858P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	
2156 reflections	$(\Delta/\sigma)_{max} = 0.002$
134 parameters	$\Delta\rho_{max} = 0.38$ e Å^{-3}
2 restraints	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.68341 (16)	0.20703 (14)	0.05576 (7)	0.0943 (8)
O2	0.65735 (17)	0.33467 (14)	0.05760 (8)	0.1078 (10)
N1	0.51592 (15)	0.18458 (13)	0.09406 (6)	0.0673 (7)
H1	0.5364	0.1412	0.0865	0.081*
C1	0.2522 (3)	0.1657 (3)	0.08110 (13)	0.1320 (17)
H1A	0.2131	0.1822	0.0997	0.198*
H1B	0.2142	0.1459	0.0628	0.198*
H1C	0.2880	0.2087	0.0729	0.198*
C2	0.3186 (2)	0.1018 (2)	0.09382 (9)	0.0941 (11)
H2A	0.3591	0.0869	0.0750	0.113*
H2B	0.2819	0.0570	0.1001	0.113*
C3	0.3798 (3)	0.1250	0.1250	0.0756 (11)
C4	0.44025 (19)	0.19324 (17)	0.11502 (7)	0.0704 (8)
C5	0.4317 (2)	0.27091 (19)	0.12144 (10)	0.0906 (10)
H5	0.3864	0.2937	0.1352	0.109*
C6	0.5026 (3)	0.31011 (19)	0.10378 (10)	0.0919 (10)
H6	0.5126	0.3631	0.1036	0.110*
C7	0.5546 (2)	0.25550 (17)	0.08689 (8)	0.0749 (8)
C8	0.6375 (2)	0.26101 (19)	0.06550 (9)	0.0810 (9)
C9	0.7383 (3)	0.3480 (3)	0.03496 (16)	0.141 (2)
H9A	0.7953	0.3356	0.0471	0.169*
H9B	0.7342	0.3149	0.0149	0.169*
C10	0.7401 (4)	0.4274 (4)	0.02437 (19)	0.164 (2)
H10A	0.7967	0.4359	0.0113	0.197*
H10B	0.7440	0.4592	0.0448	0.197*
C11	0.6604 (5)	0.4549 (4)	0.0035 (2)	0.193 (3)
H11A	0.6551	0.4210	−0.0162	0.232*
H11B	0.6045	0.4478	0.0172	0.232*
C12	0.6597 (7)	0.5314 (4)	−0.0088 (2)	0.211 (4)
H12A	0.6611	0.5666	0.0102	0.316*
H12B	0.6042	0.5399	−0.0221	0.316*
H12C	0.7133	0.5398	−0.0231	0.316*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0756 (14)	0.0847 (16)	0.1227 (19)	0.0097 (12)	0.0142 (12)	0.0162 (13)
O2	0.0842 (17)	0.0826 (16)	0.157 (2)	0.0004 (12)	0.0174 (15)	0.0302 (14)
N1	0.0571 (13)	0.0653 (13)	0.0796 (15)	0.0047 (10)	−0.0016 (10)	0.0003 (11)

C1	0.089 (3)	0.169 (4)	0.138 (4)	−0.001 (3)	−0.041 (3)	0.027 (3)
C2	0.072 (2)	0.116 (3)	0.095 (2)	−0.0173 (18)	−0.0137 (16)	0.0109 (19)
C3	0.053 (2)	0.090 (3)	0.083 (2)	0.000	0.000	0.006 (2)
C4	0.0570 (15)	0.0767 (18)	0.0775 (17)	0.0077 (13)	−0.0020 (12)	0.0027 (14)
C5	0.084 (2)	0.083 (2)	0.104 (2)	0.0180 (17)	0.0106 (18)	−0.0065 (18)
C6	0.088 (2)	0.0640 (18)	0.124 (3)	0.0049 (15)	0.005 (2)	0.0003 (18)
C7	0.0648 (17)	0.0672 (17)	0.093 (2)	0.0018 (13)	−0.0053 (15)	0.0099 (14)
C8	0.0659 (18)	0.0748 (19)	0.102 (2)	0.0011 (15)	−0.0014 (16)	0.0153 (16)
C9	0.075 (2)	0.129 (3)	0.219 (6)	−0.003 (2)	0.039 (3)	0.043 (4)
C10	0.136 (4)	0.149 (4)	0.206 (6)	−0.016 (4)	0.033 (4)	0.071 (4)
C11	0.156 (6)	0.205 (6)	0.219 (7)	0.028 (5)	0.033 (5)	0.085 (6)
C12	0.276 (11)	0.175 (5)	0.182 (6)	0.040 (7)	0.051 (6)	0.036 (5)

Geometric parameters (Å, º)

O1—C8	1.205 (4)	C5—H5	0.9300
O2—C8	1.344 (4)	C5—C6	1.404 (5)
O2—C9	1.477 (5)	C6—H6	0.9300
N1—H1	0.8600	C6—C7	1.372 (5)
N1—C4	1.367 (4)	C7—C8	1.456 (5)
N1—C7	1.377 (4)	C9—H9A	0.9700
C1—H1A	0.9600	C9—H9B	0.9700
C1—H1B	0.9600	C9—C10	1.436 (7)
C1—H1C	0.9600	C10—H10A	0.9700
C1—C2	1.542 (6)	C10—H10B	0.9700
C2—H2A	0.9700	C10—C11	1.481 (9)
C2—H2B	0.9700	C11—H11A	0.9700
C2—C3	1.551 (4)	C11—H11B	0.9700
C3—C2^i	1.551 (4)	C11—C12	1.412 (8)
C3—C4	1.518 (4)	C12—H12A	0.9600
C3—C4^i	1.518 (4)	C12—H12B	0.9600
C4—C5	1.375 (4)	C12—H12C	0.9600
C8—O2—C9	116.9 (3)	N1—C7—C8	120.3 (3)
C4—N1—H1	125.0	C6—C7—N1	107.4 (3)
C4—N1—C7	110.1 (2)	C6—C7—C8	132.3 (3)
C7—N1—H1	125.0	O1—C8—O2	123.4 (3)
H1A—C1—H1B	109.5	O1—C8—C7	125.1 (3)
H1A—C1—H1C	109.5	O2—C8—C7	111.5 (3)
H1B—C1—H1C	109.5	O2—C9—H9A	109.8
C2—C1—H1A	109.5	O2—C9—H9B	109.8
C2—C1—H1B	109.5	H9A—C9—H9B	108.2
C2—C1—H1C	109.5	C10—C9—O2	109.6 (4)
C1—C2—H2A	108.6	C10—C9—H9A	109.8
C1—C2—H2B	108.6	C10—C9—H9B	109.8
C1—C2—C3	114.5 (3)	C9—C10—H10A	108.1
H2A—C2—H2B	107.6	C9—C10—H10B	108.1
C3—C2—H2A	108.6	C9—C10—C11	116.8 (6)

C3—C2—H2B	108.6	H10A—C10—H10B	107.3
C2—C3—C2ⁱ	111.0 (4)	C11—C10—H10A	108.1
C4ⁱ—C3—C2ⁱ	109.02 (17)	C11—C10—H10B	108.1
C4ⁱ—C3—C2	108.81 (18)	C10—C11—H11A	107.4
C4—C3—C2ⁱ	108.81 (18)	C10—C11—H11B	107.4
C4—C3—C2	109.02 (17)	H11A—C11—H11B	106.9
C4ⁱ—C3—C4	110.2 (3)	C12—C11—C10	119.7 (8)
N1—C4—C3	121.5 (2)	C12—C11—H11A	107.4
N1—C4—C5	106.7 (3)	C12—C11—H11B	107.4
C5—C4—C3	131.7 (3)	C11—C12—H12A	109.5
C4—C5—H5	125.7	C11—C12—H12B	109.5
C4—C5—C6	108.7 (3)	C11—C12—H12C	109.5
C6—C5—H5	125.7	H12A—C12—H12B	109.5
C5—C6—H6	126.4	H12A—C12—H12C	109.5
C7—C6—C5	107.1 (3)	H12B—C12—H12C	109.5
C7—C6—H6	126.4		
O2—C9—C10—C11	−62.9 (8)	C4ⁱ—C3—C4—N1	44.80 (19)
N1—C4—C5—C6	0.7 (4)	C4ⁱ—C3—C4—C5	−140.2 (4)
N1—C7—C8—O1	−8.2 (5)	C4—C5—C6—C7	−0.5 (4)
N1—C7—C8—O2	171.6 (3)	C5—C6—C7—N1	0.1 (4)
C1—C2—C3—C2ⁱ	59.3 (3)	C5—C6—C7—C8	−178.0 (3)
C1—C2—C3—C4	−60.5 (4)	C6—C7—C8—O1	169.8 (4)
C1—C2—C3—C4ⁱ	179.2 (3)	C6—C7—C8—O2	−10.4 (5)
C2—C3—C4—N1	−74.5 (3)	C7—N1—C4—C3	175.5 (2)
C2ⁱ—C3—C4—N1	164.3 (3)	C7—N1—C4—C5	−0.6 (3)
C2—C3—C4—C5	100.5 (4)	C8—O2—C9—C10	170.1 (5)
C2ⁱ—C3—C4—C5	−20.7 (4)	C9—O2—C8—O1	1.8 (6)
C3—C4—C5—C6	−174.9 (3)	C9—O2—C8—C7	−178.0 (4)
C4—N1—C7—C6	0.3 (3)	C9—C10—C11—C12	−177.5 (6)
C4—N1—C7—C8	178.7 (3)		

Symmetry code: (i) x, $-y+1/4$, $-z+1/4$.

Hydrogen-bond geometry (Å, °)

$Cg1$ is the centroid of the N1/C4–C7 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1ⁱⁱ	0.86	2.12	2.962 (3)	165
C12—H12C···Cg1ⁱⁱⁱ	0.96	3.21	3.944 (3)	135

Symmetry codes: (ii) $-x+5/4$, $-y+1/4$, z; (iii) $x+1/4$, $y+1/4$, $-z$.