IUCrData

ISSN 2414-3146

6,6′-Diheptyl-3,3′-bis[(pyridin-3-yl)ethynyl]-5*H*,5′*H*-dipyrrolo[1,2-*b*:1′,2′-*g*][2,6]naphthyridine-5,5′-dione

Juan Xiang, Huan Gao, Zhengyu Ma, Xiaohua Cai and Yu-Peng Zhang*

College of Chemical Engineering, Guizhou Minzu University, Guiyang,550025,Guizhou, People's Republic of China. *Correspondence e-mail: zhangyupeng2022@gzmu.edu.cn

Received 22 May 2023
Accepted 8 June 2023

Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

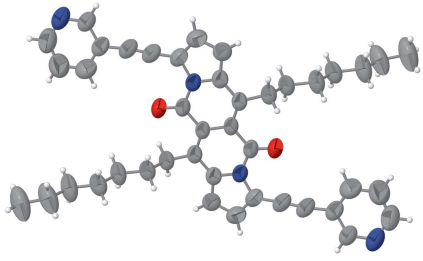
Keywords: crystal structure; cross-conjugated dye; dipyrrolo; photoluminescence spectroscopy.

CCDC reference: 2259343

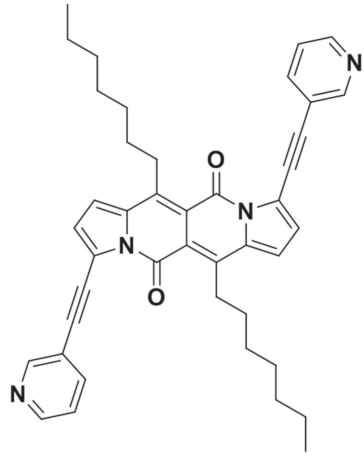
Structural data: full structural data are available from iucrdata.iucr.org

The complete molecule of the title compound, $C_{42}H_{42}N_4O_2$, is generated by a crystallographic centre of symmetry. The pendant heptyl chains adopt extended conformations and the dihedral angle between the pyrrole and pyridine rings is 8.18 (15)°. In the crystal, the molecules are arranged in columnar stacks propagating in the [010] direction *via* slipped aromatic π–π stacking interactions.

3D view



Chemical scheme



Structure description

5*H*,11*H*-dipyrrolo[1,2-*b*:1′,2′-*g*][2,6]naphthyridine-5,11-dione ($C_{18}H_{16}N_2O_2$; DPND) is a cross-conjugated dye that has attracted significant attention since it was first reported by Grzybowski *et al.* (2016). Such a skeleton is composed of electron-rich pyrrole rings and electron-poor carbonyl groups. Several studies have shown that it has interesting electrochemical and photophysical properties and it is widely used as a fluorescent dye (Sadowski *et al.*, 2017; Sadowski, Loebnitz, *et al.*, 2018; Sadowski, Rode, *et al.*, 2018). It also has become a potential candidate in singlet fission for enhancing the performance of photo-voltaic devices (Wang *et al.*, 2020), two-photon absorption materials (Sadowski *et al.*, 2017) and photodynamic therapy agents (Morgan, Yun, Jamhawi, *et al.*, 2023). In order to explore the luminescence properties of such molecules in the near infrared region, the strategy of expanding the DPND conjugated system by introducing a pendant pyridine unit was adapted and we synthesized the title compound $C_{42}H_{42}N_4O_2$, named DPND-3Py, and we now describe its structure and spectroscopic properties.

The complete molecule is generated by a crystallographic centre of symmetry (Fig. 1) and the central chromophore is almost planar (r.m.s. deviation for 16 atoms = 0.028 Å). The pyridine unit is connected to the pyrrole ring of the DPND core by an alkyne bond, which enhances the rigidity of the molecule: the dihedral angle between the N1/C1–C4

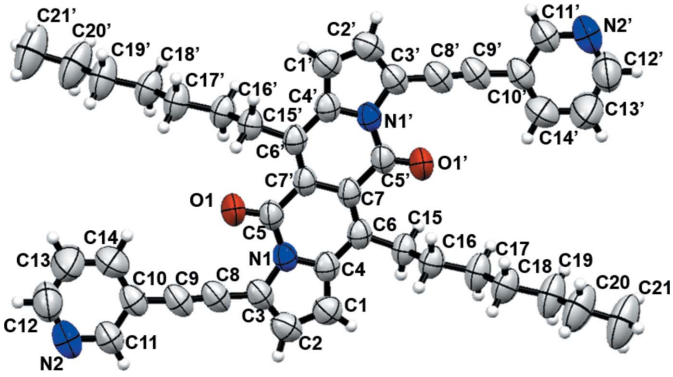


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Symmetry code for the primed atoms: $1-x, 2-y, 1-z$.

and N2/C10–C14 rings is 8.18 (15)°. The pendant heptyl chains adopt extended conformations.

In the extended structure (Fig. 2), the molecules of the title compound are arranged in [010] columnar stacks *via* slipped aromatic π–π stacking interactions with the shortest atom–atom contacts being 3.544 (3) Å for N1···C5, 3.613 (3) Å for C4···C1 and 3.632 (3) Å for C2···C6.

UV–vis spectra were recorded on a TU-1810DPC spectrometer using dichloromethane (DCM) as solvent and a concentration of 2.5×10^{-6} mol l^{-1}. As shown in Fig. 3, the title compound has three distinct absorption peaks in the range 250 to 800 nm, with a maximum absorption peak of 582 nm. The spectrum features strong absorption in the 500–600 nm region ascribed to an optically allowed $S_0 \rightarrow S_1$ transition.

Photoluminescence spectra were recorded on a F-320 spectrometer or HORIB Fluorolog-3. Figs. 4 and 5 show the photoluminescence spectra both in solution (1.0×10^{-5} mol l^{-1} in dichloromethane) and the solid state. The solution spectrum displays two peaks (maximum emission wavelength 625 nm) in the range 550 nm to 800 nm. As shown in Fig. 5, the solid-state fluorescence spectrum exhibits a strong emission peak at 767 nm, a shift of over 100 nm compared with solution, indicating strong intermolecular interactions.

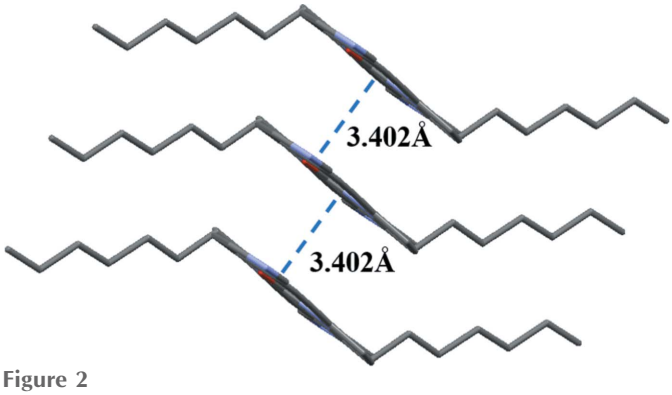


Figure 2
The packing arrangement of the title compound, which shows a slip-stack pattern with a π–π distance of 3.402 Å between the closest planes of these two molecules.

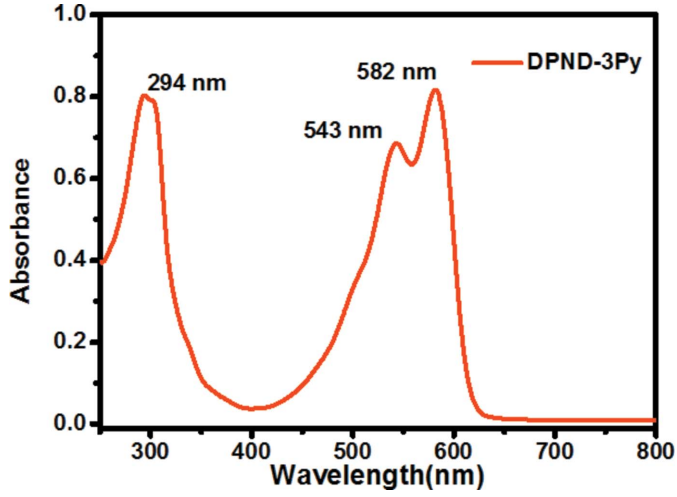


Figure 3
UV–vis absorption spectrum of the title compound.

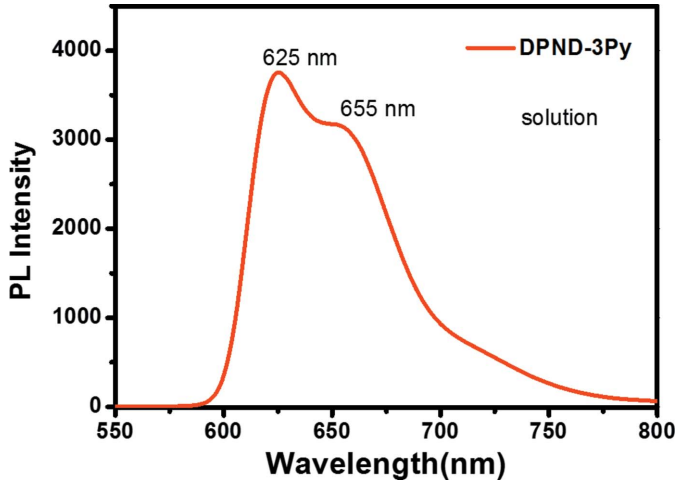


Figure 4
Fluorescence spectrum of the title compound dissolved in DCM.

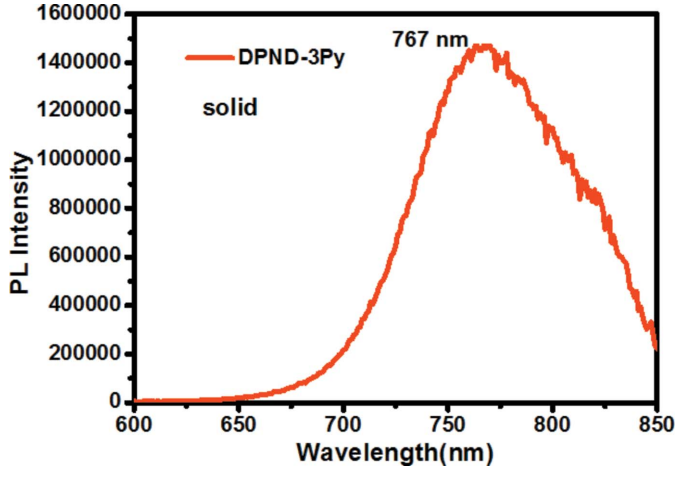


Figure 5
Solid-state emission spectrum of the title compound at an excitation wavelength of 470 nm.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{42}H_{42}N_4O_2$
M_r	634.79
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	300
a, b, c (Å)	12.3973 (4), 4.76620 (15), 31.5382 (10)
β (°)	99.318 (3)
V (Å^3)	1838.94 (10)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.56
Crystal size (mm)	0.24 × 0.06 × 0.04
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2022)
T_{min}, T_{max}	0.288, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10392, 3568, 2494
R_{int}	0.035
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.631
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.090, 0.255, 1.05
No. of reflections	3568
No. of parameters	218
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.34

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014/6* (Sheldrick, 2015*b*) and *Mercury* (Macrae *et al.*, 2020).

Synthesis and crystallization

In a reaction flask containing a magnetic stirring bar was placed: 3,3′-dibromo-6,6′-diheptyl-5*H*,5′*H*-dipyrrolo[1,2-*b*:1′,2′-*g*][2,6]naphthyridine-5,5′-dione (59.04 mg, 0.100 mmol), CuI (1.9 mg, 0.01 mmol), $Pd(PPh_3)_4$ (5.78 mg, 0.005 mmol) and 3-pyridine-acetylene (30.94 mg, 0.300 mmol). The vessel was evacuated and backfilled with argon (three times) and anhydrous, degassed tetrahydrofuran (THF) was added (3 ml) followed by dry triethylamine (56 µl, 0.40 mmol). The vessel was tightly closed and again carefully evacuated (until the mixture started to boil) and backfilled with argon (3 times). The content of the flask was stirred for 20 h at 70°C (above the boiling point), and it was cooled to room temperature. Dichloromethane (DCM) was added to dilute the reaction solution, which was washed three times with water and dried over sodium sulfate. The solvent was evaporated and the product was purified using column chromatography (silica, petroleum ether: ethyl acetate = 5:1), and recrystallized from mixed solvents of DCM and methanol to obtain a dark-purple solid (38.5 mg, yield of 35%) (Grzybowski *et al.*, 2016). Figure S1 in the supporting information shows the ^{1}H NMR spectrum of the title compound. The title compound dissolved in methylene chloride and methanol solution grew dark-red crystals suitable for crystallographic studies by slowly volatilizing the solvents.

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 1.

Funding information

We gratefully acknowledge support by the Guizhou Provincial Science and Technology Projects (grant No. ZK[2021]1Y 048).

References

Grzybowski, M., Deperasińska, I., Chotkowski, M., Banasiewicz, M., Makarewicz, A., Kozankiewicz, B. & Gryko, D. T. (2016). *Chem. Commun.* **52**, 5108–5111.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Morgan, J., Yun, Y. J., Jamhawi, A. M., Islam, S. M. & Ayitou, A. J. (2023). *Photochem. & Photobiol.* **99**, 761–768.
Rigaku OD (2022). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
Sadowski, B., Kita, H., Grzybowski, M., Kamada, K. & Gryko, D. T. (2017). *J. Org. Chem.* **82**, 7254–7264.
Sadowski, B., Loebnitz, M., Dombrowski, D. R., Friese, D. H. & Gryko, D. T. (2018). *J. Org. Chem.* **83**, 11645–11653.
Sadowski, B., Rode, M. F. & Gryko, D. T. (2018). *Chem. Eur. J.* **24**, 855–864.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Wang, L. L. L., Lin, L., Yang, J., Wu, Y., Wang, H., Zhu, J., Yao, J. & Fu, H. (2020). *J. Am. Chem. Soc.* **142**, 10235–10239.

full crystallographic data

IUCrData (2023). **8**, x230513 [https://doi.org/10.1107/S2414314623005138]

6,6′-Diheptyl-3,3′-bis[(pyridin-3-yl)ethynyl]-5*H*,5′*H*-dipyrrolo[1,2-*b*:1′,2′-*g*][2,6]naphthyridine-5,5′-dione

Juan Xiang, Huan Gao, Zhengyu Ma, Xiaohua Cai and Yu-Peng Zhang

6,6′-Diheptyl-3,3′-bis[(pyridin-3-yl)ethynyl]-5*H*,5′*H*-dipyrrolo[1,2-*b*:1′,2′-*g*][2,6]naphthyridine-5,5′-dione

Crystal data

$C_{42}H_{42}N_4O_2$
M_r = 634.79
Monoclinic, $P2_1/c$
a = 12.3973 (4) Å
b = 4.76620 (15) Å
c = 31.5382 (10) Å
β = 99.318 (3)°
V = 1838.94 (10) Å^3
Z = 2
$F(000)$ = 676
D_x = 1.146 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 4194 reflections
θ = 3.6–76.0°
μ = 0.56 mm^{-1}
T = 300 K
Needle, clear light black
0.24 × 0.06 × 0.04 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: Rotating-anodeX-raytube
Detector resolution: 10.0000 pixels mm^{-1}
fαndωscans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2022)
T_{min} = 0.288, T_{max} = 1.000
10392 measured reflections
3568 independent reflections
2494 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 76.5°, θ_{min} = 2.8°
h = −15→15
k = −5→4
l = −36→39

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.090
$wR(F^2)$ = 0.255
S = 1.05
3568 reflections
218 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1846P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −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	0.36140 (17)	0.5877 (4)	0.44237 (5)	0.1191 (7)
N1	0.32675 (13)	0.7409 (3)	0.50605 (5)	0.0727 (5)
N2	−0.0384 (2)	−0.2956 (5)	0.38938 (10)	0.1224 (8)
C7	0.51047 (16)	1.0897 (3)	0.51924 (6)	0.0707 (5)
C4	0.34537 (16)	0.9202 (4)	0.54140 (6)	0.0744 (5)
C3	0.23135 (17)	0.5896 (4)	0.50748 (7)	0.0832 (6)
C5	0.39073 (17)	0.7351 (4)	0.47350 (6)	0.0788 (6)
C6	0.43898 (16)	1.0958 (4)	0.54828 (6)	0.0715 (5)
C15	0.45368 (17)	1.2647 (4)	0.58936 (6)	0.0786 (6)
H15A	0.3828	1.3005	0.5975	0.094*
H15B	0.4867	1.4440	0.5846	0.094*
C10	0.09962 (17)	0.0370 (4)	0.41748 (8)	0.0877 (6)
C1	0.26186 (19)	0.8770 (4)	0.56470 (8)	0.0874 (6)
H1	0.2532	0.9685	0.5900	0.105*
C11	0.0089 (2)	−0.1250 (5)	0.41994 (9)	0.0959 (7)
H11	−0.0215	−0.1137	0.4450	0.115*
C8	0.18723 (18)	0.3892 (4)	0.47647 (8)	0.0891 (7)
C2	0.1927 (2)	0.6726 (5)	0.54376 (9)	0.0948 (7)
H2	0.1303	0.6034	0.5530	0.114*
C16	0.5257 (2)	1.1103 (4)	0.62572 (6)	0.0847 (6)
H16A	0.4877	0.9427	0.6327	0.102*
H16B	0.5922	1.0512	0.6158	0.102*
C12	0.0069 (3)	−0.3101 (8)	0.35413 (13)	0.1385 (12)
H12	−0.0252	−0.4274	0.3321	0.166*
C9	0.14449 (18)	0.2220 (4)	0.45104 (8)	0.0920 (7)
C17	0.5558 (2)	1.2804 (5)	0.66556 (7)	0.1010 (8)
H17A	0.4892	1.3449	0.6749	0.121*
H17B	0.5956	1.4450	0.6587	0.121*
C18	0.6239 (2)	1.1297 (6)	0.70235 (7)	0.1040 (8)
H18A	0.5835	0.9655	0.7090	0.125*
H18B	0.6898	1.0636	0.6927	0.125*
C19	0.6565 (3)	1.2890 (7)	0.74240 (9)	0.1299 (12)
H19A	0.5905	1.3511	0.7524	0.156*
H19B	0.6952	1.4556	0.7356	0.156*
C14	0.1440 (3)	0.0156 (9)	0.38057 (11)	0.1317 (11)
H14	0.2051	0.1210	0.3771	0.158*
C13	0.0965 (3)	−0.1660 (10)	0.34829 (13)	0.1589 (15)
H13	0.1261	−0.1870	0.3232	0.191*
C20	0.7258 (4)	1.1427 (10)	0.77840 (10)	0.1596 (17)
H20A	0.6901	0.9677	0.7835	0.192*
H20B	0.7945	1.0954	0.7692	0.192*
C21	0.7502 (5)	1.2915 (11)	0.81890 (12)	0.188 (2)
H21A	0.7859	1.4656	0.8146	0.282*
H21B	0.7974	1.1788	0.8393	0.282*
H21C	0.6835	1.3287	0.8297	0.282*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1286 (15)	0.1399 (14)	0.0870 (10)	−0.0598 (12)	0.0124 (10)	−0.0351 (10)
N1	0.0735 (9)	0.0680 (8)	0.0707 (9)	−0.0054 (6)	−0.0064 (7)	0.0048 (6)
N2	0.1047 (16)	0.1198 (16)	0.134 (2)	−0.0282 (13)	−0.0080 (15)	−0.0193 (14)
C7	0.0774 (11)	0.0665 (9)	0.0618 (9)	−0.0030 (8)	−0.0083 (8)	0.0020 (7)
C4	0.0786 (11)	0.0704 (9)	0.0691 (10)	0.0029 (8)	−0.0034 (9)	0.0059 (7)
C3	0.0769 (12)	0.0730 (10)	0.0930 (14)	−0.0106 (9)	−0.0064 (10)	0.0129 (9)
C5	0.0828 (12)	0.0779 (11)	0.0694 (11)	−0.0107 (9)	−0.0067 (9)	−0.0006 (8)
C6	0.0772 (11)	0.0672 (9)	0.0639 (9)	0.0028 (8)	−0.0071 (8)	0.0044 (7)
C15	0.0868 (13)	0.0763 (10)	0.0676 (11)	0.0057 (9)	−0.0032 (9)	−0.0035 (8)
C10	0.0705 (11)	0.0816 (11)	0.1037 (15)	−0.0044 (9)	−0.0073 (11)	0.0043 (11)
C1	0.0882 (14)	0.0868 (12)	0.0859 (12)	0.0009 (10)	0.0100 (11)	0.0094 (10)
C11	0.0850 (14)	0.0896 (13)	0.1082 (16)	−0.0149 (11)	0.0008 (12)	−0.0049 (12)
C8	0.0763 (12)	0.0753 (11)	0.1081 (16)	−0.0108 (9)	−0.0082 (11)	0.0152 (10)
C2	0.0845 (14)	0.0918 (13)	0.1073 (17)	−0.0084 (11)	0.0131 (12)	0.0155 (12)
C16	0.0983 (14)	0.0830 (12)	0.0673 (11)	0.0077 (10)	−0.0031 (10)	0.0001 (8)
C12	0.126 (3)	0.152 (3)	0.129 (3)	−0.018 (2)	−0.004 (2)	−0.036 (2)
C9	0.0744 (12)	0.0784 (11)	0.1149 (17)	−0.0124 (9)	−0.0097 (12)	0.0100 (11)
C17	0.1199 (19)	0.1020 (15)	0.0712 (13)	0.0131 (13)	−0.0143 (12)	−0.0085 (10)
C18	0.1181 (19)	0.1188 (17)	0.0680 (12)	0.0100 (14)	−0.0066 (12)	0.0023 (11)
C19	0.151 (3)	0.141 (2)	0.0823 (16)	0.0299 (19)	−0.0262 (17)	−0.0199 (14)
C14	0.0939 (18)	0.171 (3)	0.132 (2)	−0.0288 (19)	0.0242 (17)	−0.007 (2)
C13	0.135 (3)	0.218 (4)	0.127 (3)	−0.023 (3)	0.032 (2)	−0.048 (3)
C20	0.186 (4)	0.195 (4)	0.0822 (17)	0.057 (3)	−0.023 (2)	−0.0110 (19)
C21	0.225 (5)	0.216 (4)	0.101 (2)	0.065 (4)	−0.044 (3)	−0.030 (2)

Geometric parameters (Å, º)

O1—C5	1.214 (2)	C2—H2	0.9300
N1—C3	1.392 (3)	C16—C17	1.491 (3)
N1—C4	1.394 (2)	C16—H16A	0.9700
N1—C5	1.396 (3)	C16—H16B	0.9700
N2—C11	1.323 (3)	C12—C13	1.343 (6)
N2—C12	1.327 (5)	C12—H12	0.9300
C7—C6	1.374 (3)	C17—C18	1.502 (3)
C7—C5^{i}	1.470 (3)	C17—H17A	0.9700
C7—C7^{i}	1.473 (3)	C17—H17B	0.9700
C4—C1	1.378 (3)	C18—C19	1.473 (3)
C4—C6	1.419 (3)	C18—H18A	0.9700
C3—C2	1.368 (4)	C18—H18B	0.9700
C3—C8	1.413 (3)	C19—C20	1.483 (4)
C5—C7^{i}	1.470 (3)	C19—H19A	0.9700
C6—C15	1.511 (3)	C19—H19B	0.9700
C15—C16	1.524 (3)	C14—C13	1.392 (5)
C15—H15A	0.9700	C14—H14	0.9300
C15—H15B	0.9700	C13—H13	0.9300

C10—C14	1.370 (4)	C20—C21	1.450 (5)
C10—C11	1.377 (3)	C20—H20A	0.9700
C10—C9	1.420 (3)	C20—H20B	0.9700
C1—C2	1.392 (3)	C21—H21A	0.9600
C1—H1	0.9300	C21—H21B	0.9600
C11—H11	0.9300	C21—H21C	0.9600
C8—C9	1.192 (3)		

C3—N1—C4	108.86 (18)	C15—C16—H16B	108.7
C3—N1—C5	126.90 (16)	H16A—C16—H16B	107.6
C4—N1—C5	124.08 (16)	N2—C12—C13	124.1 (3)
C11—N2—C12	116.4 (3)	N2—C12—H12	118.0
C6—C7—C5^{i}	119.69 (17)	C13—C12—H12	118.0
C6—C7—C7^{i}	121.0 (2)	C8—C9—C10	173.9 (3)
C5^{i}—C7—C7^{i}	119.3 (2)	C16—C17—C18	115.0 (2)
C1—C4—N1	107.06 (17)	C16—C17—H17A	108.5
C1—C4—C6	132.29 (19)	C18—C17—H17A	108.5
N1—C4—C6	120.62 (19)	C16—C17—H17B	108.5
C2—C3—N1	106.95 (18)	C18—C17—H17B	108.5
C2—C3—C8	128.7 (2)	H17A—C17—H17B	107.5
N1—C3—C8	124.3 (2)	C19—C18—C17	117.2 (2)
O1—C5—N1	118.36 (19)	C19—C18—H18A	108.0
O1—C5—C7^{i}	126.0 (2)	C17—C18—H18A	108.0
N1—C5—C7^{i}	115.64 (16)	C19—C18—H18B	108.0
C7—C6—C4	119.04 (17)	C17—C18—H18B	108.0
C7—C6—C15	125.57 (18)	H18A—C18—H18B	107.2
C4—C6—C15	115.30 (19)	C18—C19—C20	117.3 (3)
C6—C15—C16	111.27 (15)	C18—C19—H19A	108.0
C6—C15—H15A	109.4	C20—C19—H19A	108.0
C16—C15—H15A	109.4	C18—C19—H19B	108.0
C6—C15—H15B	109.4	C20—C19—H19B	108.0
C16—C15—H15B	109.4	H19A—C19—H19B	107.2
H15A—C15—H15B	108.0	C10—C14—C13	119.1 (3)
C14—C10—C11	116.8 (2)	C10—C14—H14	120.4
C14—C10—C9	121.1 (2)	C13—C14—H14	120.4
C11—C10—C9	122.1 (3)	C12—C13—C14	118.6 (4)
C4—C1—C2	108.0 (2)	C12—C13—H13	120.7
C4—C1—H1	126.0	C14—C13—H13	120.7
C2—C1—H1	126.0	C21—C20—C19	117.2 (3)
N2—C11—C10	125.0 (3)	C21—C20—H20A	108.0
N2—C11—H11	117.5	C19—C20—H20A	108.0
C10—C11—H11	117.5	C21—C20—H20B	108.0
C9—C8—C3	176.3 (3)	C19—C20—H20B	108.0
C3—C2—C1	109.1 (2)	H20A—C20—H20B	107.2
C3—C2—H2	125.5	C20—C21—H21A	109.5
C1—C2—H2	125.5	C20—C21—H21B	109.5
C17—C16—C15	114.06 (17)	H21A—C21—H21B	109.5
C17—C16—H16A	108.7	C20—C21—H21C	109.5

C15—C16—H16A	108.7	H21A—C21—H21C	109.5
C17—C16—H16B	108.7	H21B—C21—H21C	109.5
C3—N1—C4—C1	0.5 (2)	C7—C6—C15—C16	−83.8 (2)
C5—N1—C4—C1	176.21 (16)	C4—C6—C15—C16	92.7 (2)
C3—N1—C4—C6	178.77 (15)	N1—C4—C1—C2	0.1 (2)
C5—N1—C4—C6	−5.5 (3)	C6—C4—C1—C2	−177.94 (19)
C4—N1—C3—C2	−0.9 (2)	C12—N2—C11—C10	0.6 (4)
C5—N1—C3—C2	−176.42 (18)	C14—C10—C11—N2	−0.7 (4)
C4—N1—C3—C8	179.55 (17)	C9—C10—C11—N2	178.1 (2)
C5—N1—C3—C8	4.0 (3)	N1—C3—C2—C1	0.9 (2)
C3—N1—C5—O1	1.3 (3)	C8—C3—C2—C1	−179.55 (19)
C4—N1—C5—O1	−173.68 (18)	C4—C1—C2—C3	−0.6 (3)
C3—N1—C5—C7^{i}	−178.28 (15)	C6—C15—C16—C17	172.3 (2)
C4—N1—C5—C7^{i}	6.8 (3)	C11—N2—C12—C13	0.5 (6)
C5^{i}—C7—C6—C4	−178.44 (15)	C15—C16—C17—C18	178.2 (2)
C7^{i}—C7—C6—C4	1.8 (3)	C16—C17—C18—C19	179.6 (3)
C5^{i}—C7—C6—C15	−2.1 (3)	C17—C18—C19—C20	−178.6 (3)
C7^{i}—C7—C6—C15	178.13 (18)	C11—C10—C14—C13	−0.3 (5)
C1—C4—C6—C7	178.65 (19)	C9—C10—C14—C13	−179.2 (3)
N1—C4—C6—C7	0.9 (2)	N2—C12—C13—C14	−1.5 (7)
C1—C4—C6—C15	1.9 (3)	C10—C14—C13—C12	1.4 (6)
N1—C4—C6—C15	−175.86 (14)	C18—C19—C20—C21	−175.0 (4)

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