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ISSN 2414-3146

Diethyl 2,2′-({[1,4-phenylenebis(azanediyl)]bis(methylene)}bis(1*H*-pyrrole-2,1-diyl))diacetate

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Received 6 January 2016
Accepted 8 January 2016

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

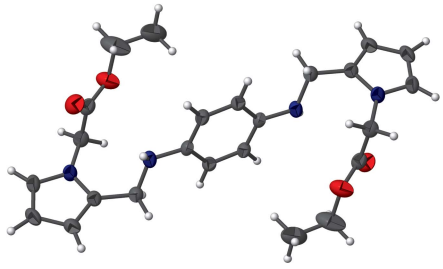
Keywords: crystal structure; bis(pyrrole ester); bis(secondary amine); C-H···O hydrogen bonding; C—H···π interactions..

CCDC reference: 1446459

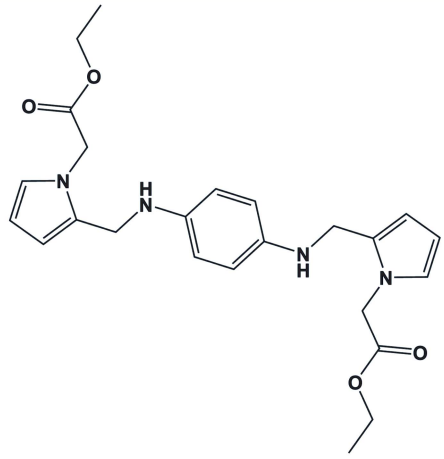
Structural data: full structural data are available from iucrdata.iucr.org

The complete molecule of the title compound, $C_{24}H_{30}N_4O_4$, is generated by crystallographic inversion symmetry. The molecule is S-shaped and the pyrrole groups have an *anti* or *trans* confirmation with respect to the central benzene ring, to which they are inclined by 76.38 (9)°. In the crystal, molecules are linked *via* C—H···O hydrogen bonds, forming layers parallel to the *ac* plane. Within the layers there are C—H···π interactions present. There are, however, no significant interactions between the layers.

3D view



Chemical scheme



Structure description

The preparation of the title secondary amine was based on three synthetic steps. The reaction of 1*H*-pyrrole-2-carbaldehyde with ethyl bromoproacetate resulted in the formation of ethyl(2-formyl-1*H*-pyrrole-1-yl)-acetate (Koriatopoulou *et al.*, 2008; Singh & Pal, 2010). The reaction of two moles of the above with *p*-phenylenediamine (Yang *et al.*, 2004; Ourari *et al.*, 2013) gave the Schiff base. The reduction of the Schiff base (Higuchi *et al.*, 2003; Nabipour *et al.*, 2010) gave the the title secondary amine.

The whole molecule of the title compound, Fig. 1, is generated by inversion symmetry. The pyrrole rings have an *anti* or *trans*-conformation with respect to the central benzene ring. They are inclined to the central benzene ring by 76.38 (9)°.

The infrared spectrum shows typical absorption bands of the functional N—H and carbonyl –C═O bonds at 3390 and 1630 cm^{-1}, respectively. The N7—C6 bond distance of 1.448 (2) Å is longer than the N7—C8 bond distance of 1.405 (2) Å, indicating single bond order. However, the N1—C5 bond distance of 1.371 (2) Å, confirms that a reso-

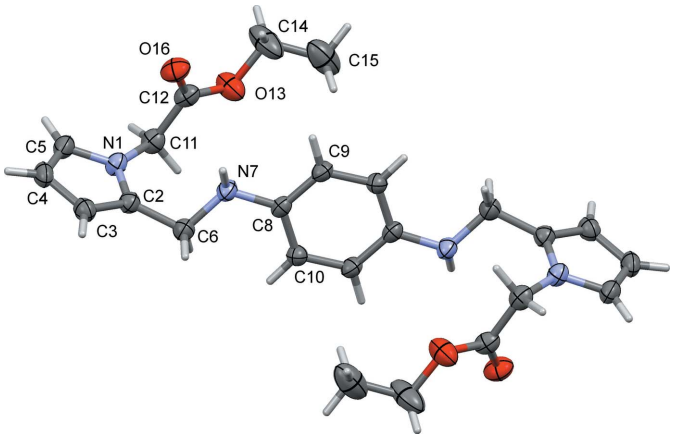


Figure 1
A view of the molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The unlabelled atoms are related to labelled atoms by the symmetry operation $-x+2, -y, -z+1$.

nance occurs in the pyrrole system between the lone-pair electron of the N atom and the pyrrole ring.

In the crystal, molecules are linked *via* C—H···O hydrogen bonds, forming layers parallel to the *ac* plane (Table 1 and Fig. 2). Within the layers there are C—H···π interactions present. There are no significant interactions between the layers (Fig. 3).

Synthesis and crystallization

The title compound was synthesized in three steps.

1: ethyl (2-formyl-1*H*-pyrrole-1-yl)-acetate was prepared by reported procedures (Koriatopoulou *et al.*, 2008; Singh & Pal, 2010). To a mixture of 1*H*-pyrrole-2-carbaldehyde (1.00 g, 10.51 mmol), K_2CO_3 (2.90 g, 21.02 mmol) and (2.64 g, 10.51 mmol) of 18-crown-6 in dry 1,4-dioxane (20 ml) was added a solution of ethyl bromoacetate (2.00 g, 12 mmol) in dry 1,4-dioxane (20 ml) drop wise over a period of 30 min. The reaction mixture was allowed to reflux under nitrogen atmosphere for 6 h, and then the solvent was removed under reduced pressure. Water (50 ml) was added to the residue, and the mixture was extracted with ethyl acetate (3 × 15 ml). The combined organic layers were washed with brine (15 ml), and then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the oily residue was purified by flash chromatography with an eluent mixture (33% ethyl acetate/hexane), yielding the title compound as a yellow oil (yielded: 0.75 g, 75%). IR (ATR cm^{-1}): 1650 ν(C═O) aldehyde moiety. 1710 ν(C═O) ester group. ^{1}H (500 MHz, CDCl3, p.p.m.): 1.20 (3H, *t*, C1—H), 4.15 (2H, *q*, C2—H), 4.97 (2H, *s*, C4—H), 6.21 (1H, *t*, C6—H), 6.84 (1H, *d*, C7—H), 6.90 (1H, *d*, C5—H) and 9.45 (1H, *s*, C9—H). ^{13}C (125.75 MHz, CDCl3), 14.13 C1, 50.25 C4, 61.63 C2, 110.20 C6, 124.61 C7, 131.71 C8 and 132.10 C5. C═O to the carboxylate moiety 168.37 C9 and 179.74 C3, respectively. The positive ES mass spectrum at *m*/z = 182.4 $(M + H)^+$ (62%) for $C_9H_{11}NO_3$, requires = 181.1. The other peaks detected at *m*/*z* = 153.4 (100%), 109.3 (6%), 95 (9%) and 67 (4%) correspond to $[M - CH_2CH_3]^+$, $M - (CH_2CH_3 + CO_2)]^+$, $[M - (CH_2CH_3 + CO_2 + CH_2)]^+$ and $[M - (CH_2CH_3 + CO_2 + CH_2 + CO)]^+$, respectively.

2: Synthesis of the title Schiff base was achieved using standard procedures (Koriatopoulou *et al.*, 2008; Singh & Pal, 2010). To a mixture of ethyl (2-formyl-1*H*-pyrrole-1-yl)acetate (1.81 g, 10 mmol) in ethanol (20 ml) with 3 drops of glacial acetic acid, a solution of 1,4-phenylenediamine (0.5 g, 5 mmol) in ethanol (20 ml) was added drop wise over a period of 20 min. The reaction mixture was allowed to reflux for 3 h, and

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

*Cg*1 is the centroid of the C8–C10/C8′–C10′ ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7···O16^{i}	0.87 (2)	2.20 (2)	3.025 (2)	159.5 (18)
C5—H5···O16^{ii}	0.95	2.51	3.453 (2)	172
C11—H11*B*···O13^{iii}	0.99	2.47	3.435 (2)	164
C11—H11*A*···*Cg*1^{iv}	0.99	2.88	3.794 (2)	153
C11—H11*A*···*Cg*1^{iii}	0.99	2.88	3.794 (2)	153

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

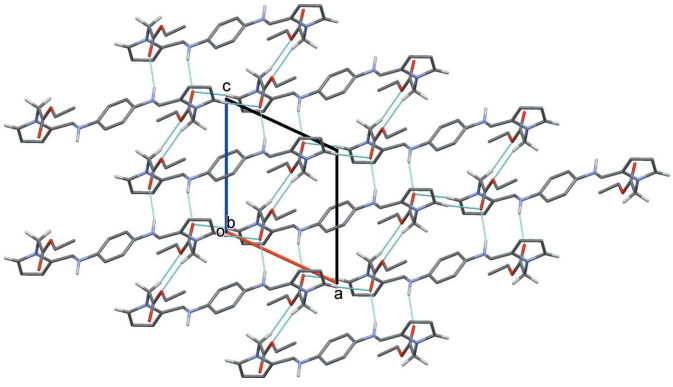


Figure 2
A view along the *b* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1). For clarity only the H atoms involved in the intermolecular contacts have been included.

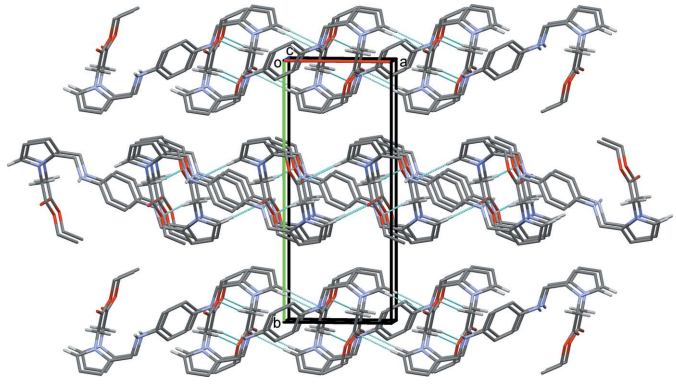


Figure 3
A view along the *c* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1). For clarity only the H atoms involved in the intermolecular contacts have been included.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{24}H_{30}N_4O_4$
M_r	438.52
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	8.1476 (2), 17.6289 (4), 8.8692 (3)
β (°)	114.835 (4)
V (Å^3)	1156.10 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.4 × 0.3 × 0.3
Data collection	
Diffractometer	Agilent SuperNova, Single source at offset, Atlas diffractometer
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min}, T_{max}	0.666, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19988, 2992, 1926
R_{int}	0.058
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.693
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.135, 1.03
No. of reflections	2992
No. of parameters	150
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.23

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *OLEX2* (Dolomanov *et al.*, 2009), *SHELXL2014* (Sheldrick, 2015).

then cooled to room temperature. A yellow precipitate was collected by filtration and recrystallized from ethanol, yield 1.18 g (65%). IR (cm^{-1}): 1600 ν(C═N), 1685 ν(C═O). NMR: ^{1}H (500 MHz, $CDCl_3$, p.p.m.): 1.17 (6H, *t*, C1, 1–H), 4.14 (4H, *Q*, C2, 2–H), 5.15 (4H, *s*, C4, 4–H), 6.20 (2H, *t*, C6, 6–H), 6.61 (2H, *d*, C7, 7–H), 6.74 (2H, *d*, C5, 5–H), 7.05 (4H, *s*, C11, 11-, C12, 12–H) and 8.26 (2H, *s*, C9, 9–H). ^{13}C (125.75 MHz, $CDCl_3$): 14.26 (C1, 1-), 51.36 (C4, 4-), 61.30 (C2, 2-.), 109.39 (C5, 5-), 119.54 (C7, 7-), 121.48 (C11, 11-, C12, 12-), 129.26 (C6, 6-), 130.31 (C8, 8-), 149.19 (C9, 9-) and 149.23 (C10, 10-). C=O of the carboxylate moiety 169.25 C3, 3-. The positive ES mass spectrum at m/z = 435.8 $(M + H)^+$ (100%) for $C_{24}H_{26}N4O_4$, requires = 434.5. The other peaks detected at m/z = 406 (100%), 377 (22%), 289 (3%) and 261.1 (10%) correspond to $[M - CH_2CH_3]^+$, $[M - (2CH_2CH_3)]^+$, $[M - (2CH_2CH_3 + 2CO_2)]^+$ and $[M\ (2CH_2CH_3 + 2CO_2 + 2CH_2)]^+$, respectively.

3: The title compound was obtained by reduction of the Schiff base following reported procedures (Higuchi *et al.*, 2003; Nabipour *et al.*, 2010). A mixture of diethyl 2,2′-{2,2′-(1*Z*)-[1,4-phenylenebis(azan-1-yl-1-ylidene)]bis(methan-1-yl-1-ylidene)bis(1*H*-pyrrole-2,1-diyl)} diacetate (0.43 g, 1 mmol) and $SnCl_2$ (0.45 g, 2 mmol) in a (1:1) molar ratio mixture of dichloromethane/acetonitrile (100 ml), was added to a solution of sodium borohydrate in 1:1 dichloromethane/acetonitrile (0.38 g. 5 mmol) drop wise over a period of 10 min. The mixture was stirred under nitrogen for 1 h at room temperature, and then washed for four times with 1% triethylamine. The organic layer was dried over sodium sulfate and the solvent removed under reduced pressure. A colourless solid was collected by filtration (yield: 0.17 g, 40%). IR (KBr disc, cm^{-1}) 3390 (N—H), 1630 (C═O). NMR: ^{1}H (500 MHz, CDCl3, p.p.m.): 1.15 (6H, *t*,C1,1–H), 4.04 (4H, *s*, C9,9–H), 4.09 (4H, *q*, C2, 2–H), 4.60 (4H, *s*, C4, 4–H), 6.06 (2H, *d*, C6, 6-H, C7, 7–H), 6.49 (4H, *s*, C11, 11- and C12, 12–H), 6.56 (2H, *d*, C5, 5–H) and 3.29 to NH. ^{13}C (125.75 MHz, $CDCl_3$, p.p.m.): 14.31 (C1, 1-), 41.81 (C2, 2-), 51.38 (C4, 4-), 61.40 (C9, 9-), 107.63 (C7, 7-), 109.22 (C6, 6-), 116.71 (C11, 11), 116.78 (C12, 12-), 122.97 (C5, 5-), 130.65 (C8, 8-)and 140.90 (C10, 10-). C=O 159.45 (C3,3-). The positive ES mass spectrum at m/z = 439$(M + H)^+$ (78%) for $C_{24}H_{30}N_4O_4$, requires = 438.22. The other peaks detected at m/z = 410 (3%), 366 (2%), 337 (4%), 293 (12%) and 265(7%) correspond to $[M - (CH_2CH_3)]^+$, $[M - (CH_2CH_3 + CO_2)]^+$, $[M - (2CH_2CH_3 + CO_2)]^+$, $[M - (2CH_2CH_3 + 2CO_2]^+$ and $[M - (2CH_2CH_3 + 2CO_2 + 2CH_2)]^+$, respectively. Crystals for the X-ray diffraction study were obtained by recrystallization from a mixture of the title compound in dichlorometane/acetonitrile, in air at 291 K.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH H atom, attached to atom N7, was located in a difference Fourier map and freely refined.

Acknowledgements

The authors are grateful to the Iraqi Ministry for Higher Education for providing six months funding for JA's PhD scholarship. We also thank Dr Inigo Vitorica-yrezabal (School of Chemistry, University of Manchester) for his helpful advice.

References

Agilent (2013). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Higuchi, M., Tsuruta, M., Chiba, H., Shiki, S. & Yamamoto, K. (2003). *J. Am. Chem. Soc.* **125**, 9988–9997.

Koriatopoulou, K., Karousis, N. & Varvounis, G. (2008). *Tetrahedron*, **64**, 10009–10013.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Nabipour, H., Ghammamy, S., Ashuri, S. & Aghbolagh, Z. S. (2010). *Org. Chem. J.* **2**, 75–80.

Ourari, A., Aggoun, D. & Ouahab, L. (2013). *Inorg. Chem. Commun.* **33**, 118–124.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Singh, K. & Pal, D. (2010). *J. Serb. Chem. Soc.* **75**, 917–927.

Yang, C.-T., Vetrichelvan, M., Yang, X., Moubaraki, B., Murray, K. S. & Vittal, J. J. (2004). *Dalton Trans.* pp. 113–121.

full crystallographic data

IUCrData (2016). **1**, x160046 [doi:10.1107/S2414314616000468]

Diethyl 2,2′-({[1,4-phenylenebis(azanediyl)]bis(methylene)}bis(1*H*-pyrrole-2,1-diyl))diacetate

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Diethyl 2,2′-({[1,4-phenylenebis(azanediyl)]bis(methylene)}bis(1*H*-pyrrole-2,1-diyl))diacetate

Crystal data

$C_{24}H_{30}N_4O_4$
M_r = 438.52
Monoclinic, $P2_1/n$
a = 8.1476 (2) Å
b = 17.6289 (4) Å
c = 8.8692 (3) Å
β = 114.835 (4)°
V = 1156.10 (6) Å^3
Z = 2
$F(000)$ = 468
D_x = 1.260 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5079 reflections
θ = 3.4–24.1°
μ = 0.09 mm^{-1}
T = 150 K
Block, colourless
0.4 × 0.3 × 0.3 mm

Data collection

Agilent SuperNova, Single source at offset, Atlas diffractometer
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.3705 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min} = 0.666, T_{max} = 1.000
19988 measured reflections
2992 independent reflections
1926 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 29.5°, θ_{min} = 2.9°
h = −11→10
k = −24→23
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.135
S = 1.03
2992 reflections
150 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.3701P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O13	0.4133 (2)	−0.08680 (7)	0.32272 (16)	0.0505 (4)
O16	0.30365 (17)	−0.04392 (8)	0.06056 (15)	0.0453 (4)
N1	0.27770 (17)	0.10235 (8)	0.17147 (17)	0.0329 (3)
N7	0.66678 (18)	0.05720 (8)	0.26714 (19)	0.0324 (3)
H7	0.651 (3)	0.0463 (11)	0.166 (3)	0.045 (6)*
C2	0.4147 (2)	0.14531 (9)	0.1631 (2)	0.0309 (4)
C3	0.3366 (2)	0.19677 (10)	0.0379 (2)	0.0359 (4)
H3	0.3986	0.2340	0.0042	0.043*
C4	0.1478 (2)	0.18484 (10)	−0.0325 (2)	0.0403 (4)
H4	0.0597	0.2125	−0.1217	0.048*
C5	0.1156 (2)	0.12641 (10)	0.0511 (2)	0.0387 (4)
H5	0.0003	0.1057	0.0299	0.046*
C6	0.6077 (2)	0.13331 (9)	0.2811 (2)	0.0337 (4)
H6A	0.6848	0.1705	0.2572	0.040*
H6B	0.6217	0.1420	0.3961	0.040*
C8	0.83593 (19)	0.03144 (9)	0.38338 (19)	0.0273 (4)
C9	0.9039 (2)	−0.03605 (9)	0.3509 (2)	0.0302 (4)
H9	0.8393	−0.0611	0.2479	0.036*
C10	0.9362 (2)	0.06744 (9)	0.53483 (19)	0.0300 (4)
H10	0.8944	0.1140	0.5597	0.036*
C11	0.3011 (2)	0.03733 (10)	0.2779 (2)	0.0356 (4)
H11A	0.1900	0.0300	0.2956	0.043*
H11B	0.4023	0.0472	0.3873	0.043*
C12	0.3398 (2)	−0.03424 (10)	0.2052 (2)	0.0352 (4)
C14	0.4517 (4)	−0.16067 (13)	0.2705 (3)	0.0762 (8)
H14A	0.4647	−0.1555	0.1650	0.091*
H14B	0.3505	−0.1960	0.2520	0.091*
C15	0.6209 (4)	−0.19104 (13)	0.4013 (4)	0.0742 (8)
H15A	0.6428	−0.2422	0.3705	0.111*
H15B	0.6099	−0.1931	0.5071	0.111*
H15C	0.7222	−0.1579	0.4129	0.111*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O13	0.0797 (10)	0.0383 (7)	0.0357 (7)	0.0102 (7)	0.0263 (7)	0.0031 (6)
O16	0.0497 (8)	0.0538 (8)	0.0283 (7)	−0.0077 (6)	0.0123 (6)	−0.0049 (6)
N1	0.0286 (7)	0.0376 (8)	0.0291 (8)	0.0010 (6)	0.0087 (6)	0.0030 (6)
N7	0.0271 (7)	0.0374 (8)	0.0270 (8)	0.0027 (6)	0.0058 (6)	−0.0035 (6)

C2	0.0295 (8)	0.0325 (9)	0.0290 (9)	0.0015 (7)	0.0105 (7)	−0.0008 (7)
C3	0.0404 (10)	0.0312 (9)	0.0340 (10)	0.0048 (7)	0.0135 (8)	0.0032 (7)
C4	0.0390 (10)	0.0375 (10)	0.0333 (10)	0.0129 (8)	0.0045 (8)	0.0019 (8)
C5	0.0274 (8)	0.0432 (10)	0.0373 (10)	0.0034 (8)	0.0055 (7)	−0.0038 (8)
C6	0.0298 (8)	0.0339 (9)	0.0347 (10)	0.0000 (7)	0.0108 (7)	0.0011 (7)
C8	0.0228 (8)	0.0328 (8)	0.0253 (8)	−0.0029 (6)	0.0091 (6)	0.0004 (7)
C9	0.0264 (8)	0.0346 (9)	0.0261 (8)	−0.0028 (7)	0.0076 (7)	−0.0037 (7)
C10	0.0284 (8)	0.0293 (8)	0.0312 (9)	−0.0005 (7)	0.0115 (7)	−0.0034 (7)
C11	0.0356 (9)	0.0409 (10)	0.0306 (9)	−0.0019 (8)	0.0142 (7)	0.0034 (8)
C12	0.0336 (9)	0.0411 (10)	0.0296 (9)	−0.0068 (7)	0.0121 (7)	0.0004 (8)
C14	0.131 (2)	0.0439 (13)	0.0537 (15)	0.0229 (15)	0.0394 (15)	−0.0021 (11)
C15	0.0881 (18)	0.0460 (13)	0.118 (2)	0.0066 (12)	0.0718 (18)	0.0090 (14)

Geometric parameters (Å, º)

O13—C12	1.334 (2)	C6—H6B	0.9900
O13—C14	1.459 (2)	C8—C9	1.393 (2)
O16—C12	1.202 (2)	C8—C10	1.397 (2)
N1—C5	1.371 (2)	C9—C10^{i}	1.386 (2)
N1—C2	1.376 (2)	C9—H9	0.9500
N1—C11	1.445 (2)	C10—C9^{i}	1.386 (2)
N7—C8	1.405 (2)	C10—H10	0.9500
N7—C6	1.448 (2)	C11—C12	1.509 (2)
N7—H7	0.87 (2)	C11—H11A	0.9900
C2—C3	1.366 (2)	C11—H11B	0.9900
C2—C6	1.494 (2)	C14—C15	1.480 (4)
C3—C4	1.412 (2)	C14—H14A	0.9900
C3—H3	0.9500	C14—H14B	0.9900
C4—C5	1.358 (3)	C15—H15A	0.9800
C4—H4	0.9500	C15—H15B	0.9800
C5—H5	0.9500	C15—H15C	0.9800
C6—H6A	0.9900		

C12—O13—C14	117.26 (15)	C10^{i}—C9—C8	121.52 (15)
C5—N1—C2	108.99 (14)	C10^{i}—C9—H9	119.2
C5—N1—C11	124.99 (14)	C8—C9—H9	119.2
C2—N1—C11	125.74 (13)	C9^{i}—C10—C8	120.82 (15)
C8—N7—C6	119.71 (14)	C9^{i}—C10—H10	119.6
C8—N7—H7	111.2 (13)	C8—C10—H10	119.6
C6—N7—H7	112.4 (13)	N1—C11—C12	112.22 (14)
C3—C2—N1	107.35 (14)	N1—C11—H11A	109.2
C3—C2—C6	131.07 (16)	C12—C11—H11A	109.2
N1—C2—C6	121.55 (14)	N1—C11—H11B	109.2
C2—C3—C4	108.01 (16)	C12—C11—H11B	109.2
C2—C3—H3	126.0	H11A—C11—H11B	107.9
C4—C3—H3	126.0	O16—C12—O13	124.30 (17)
C5—C4—C3	107.20 (15)	O16—C12—C11	124.97 (16)
C5—C4—H4	126.4	O13—C12—C11	110.68 (14)

C3—C4—H4	126.4	O13—C14—C15	109.1 (2)
C4—C5—N1	108.44 (15)	O13—C14—H14A	109.9
C4—C5—H5	125.8	C15—C14—H14A	109.9
N1—C5—H5	125.8	O13—C14—H14B	109.9
N7—C6—C2	111.19 (13)	C15—C14—H14B	109.9
N7—C6—H6A	109.4	H14A—C14—H14B	108.3
C2—C6—H6A	109.4	C14—C15—H15A	109.5
N7—C6—H6B	109.4	C14—C15—H15B	109.5
C2—C6—H6B	109.4	H15A—C15—H15B	109.5
H6A—C6—H6B	108.0	C14—C15—H15C	109.5
C9—C8—C10	117.65 (14)	H15A—C15—H15C	109.5
C9—C8—N7	118.49 (14)	H15B—C15—H15C	109.5
C10—C8—N7	123.76 (15)		

C5—N1—C2—C3	0.62 (19)	C6—N7—C8—C9	−168.51 (14)
C11—N1—C2—C3	174.76 (15)	C6—N7—C8—C10	15.1 (2)
C5—N1—C2—C6	178.91 (15)	C10—C8—C9—C10^{i}	1.1 (3)
C11—N1—C2—C6	−6.9 (2)	N7—C8—C9—C10^{i}	−175.50 (15)
N1—C2—C3—C4	−0.29 (19)	C9—C8—C10—C9^{i}	−1.1 (3)
C6—C2—C3—C4	−178.36 (17)	N7—C8—C10—C9^{i}	175.31 (15)
C2—C3—C4—C5	−0.1 (2)	C5—N1—C11—C12	91.1 (2)
C3—C4—C5—N1	0.5 (2)	C2—N1—C11—C12	−82.1 (2)
C2—N1—C5—C4	−0.7 (2)	C14—O13—C12—O16	0.0 (3)
C11—N1—C5—C4	−174.91 (15)	C14—O13—C12—C11	177.48 (19)
C8—N7—C6—C2	−171.17 (14)	N1—C11—C12—O16	−21.2 (2)
C3—C2—C6—N7	−121.41 (19)	N1—C11—C12—O13	161.25 (14)
N1—C2—C6—N7	60.8 (2)	C12—O13—C14—C15	143.89 (19)

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

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C8–C10/C8′–C10′ ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7···O16^{ii}	0.87 (2)	2.20 (2)	3.025 (2)	159.5 (18)
C5—H5···O16^{iii}	0.95	2.51	3.453 (2)	172
C11—H11*B*···O13^{iv}	0.99	2.47	3.435 (2)	164
C11—H11*A*···*Cg*1^{v}	0.99	2.88	3.794 (2)	153
C11—H11*A*···*Cg*1^{iv}	0.99	2.88	3.794 (2)	153

Symmetry codes: (ii) −*x*+1, −*y*, −*z*; (iii) −*x*, −*y*, −*z*; (iv) −*x*+1, −*y*, −*z*+1; (v) *x*−1, *y*, *z*.