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Synthesis and crystal structure of 1,3-bis(acetoxymethyl)-5-{[(4,6-dimethylpyridin-2-yl)amino]methyl}-2,4,6-triethylbenzene

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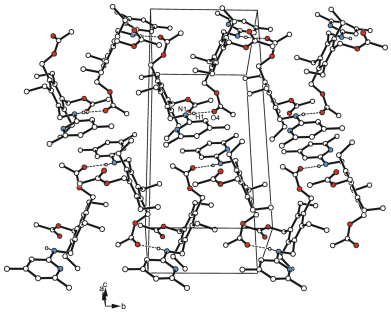
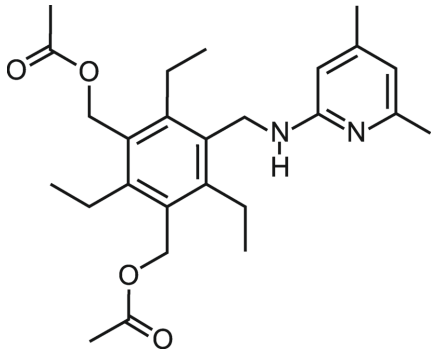
In the crystal structure of the title compound, $C_{26}H_{36}N_2O_4$, the tripodal molecule exists in a conformation in which the substituents attached to the central arene ring are arranged in an alternating order above and below the ring plane. The heterocyclic unit is inclined at an angle of 79.6 (1)° with respect to the plane of the benzene ring. In the crystal, the molecules are connected *via* N—H···O bonds, forming infinite supramolecular strands. Interstrand association involves weak C—H···O and C—H···π interactions, with the pyridine ring acting as an acceptor in the latter case.

1. Chemical context

Recognition units based on 2-aminopyridine have proved to be valuable building blocks for the construction of artificial carbohydrate receptors that act *via* non-covalent interactions (Mazik *et al.*, 2004, 2005; Mazik, 2009, 2012; Lippe & Mazik, 2015; Seidel *et al.*, 2023). Such units are able to participate in the formation of hydrogen-bonding motifs similar to those observed in natural complexes for the primary amide groups (side chains of asparagine and glutamine). The latter are used by carbohydrate-binding proteins in combination with other functional groups such as hydroxy, carboxy, imidazolyl and isopropyl groups (side chains of serine, aspartic acid, histidine and valine, respectively). The use of a combination of different functional groups enables not only the formation of neutral and charge-reinforced hydrogen bonds, but also of C—H···π interactions and numerous van der Waals contacts, and is responsible for the observed binding selectivities and efficiencies of the proteins (Quiocho, 1989; Sharon & Lis, 2007; Gabius, 2009; Gabius *et al.*, 2011). Our studies with various acyclic and macrocyclic artificial receptors have also shown that selective and effective binding is favourably influenced by the involvement of different functional groups in the binding process. Among the acyclic receptor molecules, 1,3,5-substituted 2,4,6-trialkylbenzene derivatives have been studied particularly intensively (Lippe *et al.*, 2015; Kaiser *et al.*, 2019; Stapf *et al.*, 2020*a*; Köhler *et al.*, 2020, 2021, 2024), and different binding properties have been observed depending on the nature of the receptor building blocks. In this article, we describe the crystal structure of 1,3-bis(acetoxymethyl)-5-{[(4,6-dimethylpyridin-2-yl)amino]methyl}-2,4,6-triethylbenzene, which is a precursor for the synthesis of a triethylbenzene derivative bearing a 2-aminopyridine-based recognition moiety and two hydroxymethyl groups.





2. Structural commentary

The crystal structure of the title compound, $C_{26}H_{36}N_2O_4$, was solved in the monoclinic space group $P2_1/n$ with the asymmetric unit containing one molecule. As shown in Fig. 1, the molecule adopts a conformation in which the pyridinylamino moiety and the two acetoxy groups are located on one side of the central benzene ring, whereas the ethyl substituents are directed to the opposite side of the ring plane (*ababab* arrangement; Das & Barbour, 2008*a*,*b*, 2009; Koch *et al.*, 2017; Schulze *et al.*, 2017). The molecule exists in a strongly distorted conformation with torsion angles of −166.6 (1) (*anti*) and −121.3 (1)° (eclipsed) along the C_{aryl}—C—O—C sequences and an interplanar angle of 79.6 (1)° between the aromatic rings. The conformation appears to be stabilized by an intramolecular C—H···N hydrogen bond [d(H···N) = 2.65 Å] and a C—H···O bond [d(H···O) = 2.52 Å] involving the ethyl hydrogen atoms H25*A*, H25*B* and the acceptor positions N1 and O3 (Table 1).

3. Supramolecular features

The crystal structure is composed of zigzag-like strands of N-H···O=C bonded molecules [N1—H1···O4, 2.10 (1) Å, 173 (1)°], that extend parallel to the crystallographic *b* axis (Fig. 2). Interstrand association is confined to only one C—H···π contact (Nishio *et al.*, 2009, 2012) per molecule with the pyridine ring acting as an acceptor [C14—H14*B*···*Cg*, 2.73 Å, 147°] as well as a weak C—H···O bond (Desiraju & Steiner, 1999) involving the oxygen atom O2 [C19—H19*C*···O2, 2.61 Å, 117°].

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

Cg represents the centroid of the C8–C12/N2 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.88 (1)	2.10 (1)	2.9776 (16)	173 (1)
C19—H19*C*···O2^{ii}	0.98	2.61	3.1785 (18)	117
C14—H14*B*···*Cg*^{iii}	0.98	2.73	3.5955 (17)	147
C25—H25*A*···N1	0.99	2.65	3.3598 (17)	128
C25—H25*B*···O3	0.99	2.52	3.2250 (15)	128

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x, -y+1, -z+1$.

4. Database survey

Our previous studies have shown that representatives of 1,3,5-substituted 2,4,6-trialkylbenzenes with side arms bearing different functional groups have a better ability to discriminate between various carbohydrate substrates than compounds possessing identical functionalized side arms. In this context, the combination of 2-aminopyridine-based building blocks with other functional groups was shown to provide compounds capable of acting as effective and selective carbohydrate receptors. The search in the Cambridge Structural Database (CSD, Version 5.45, update June 2024; Groom *et al.*, 2016) for such molecules with one or two pyridin-2-ylaminomethyl unit(s) yielded thirteen hits. All crystal structures of the triethylbenzene derivatives listed below have in common that the tripodal molecules adopt a conformation with an alternating arrangement of the substituents above and below the plane of the central benzene ring. The crystal

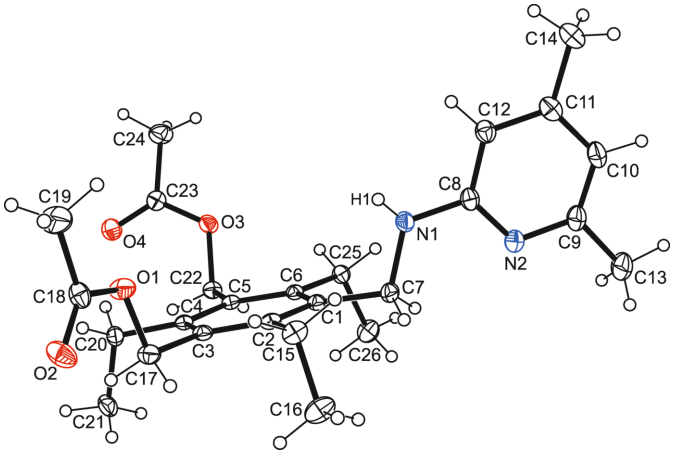


Figure 1
Perspective view of the title molecule including atom labelling. Anisotropic displacement ellipsoids are drawn at the 50% probability level.

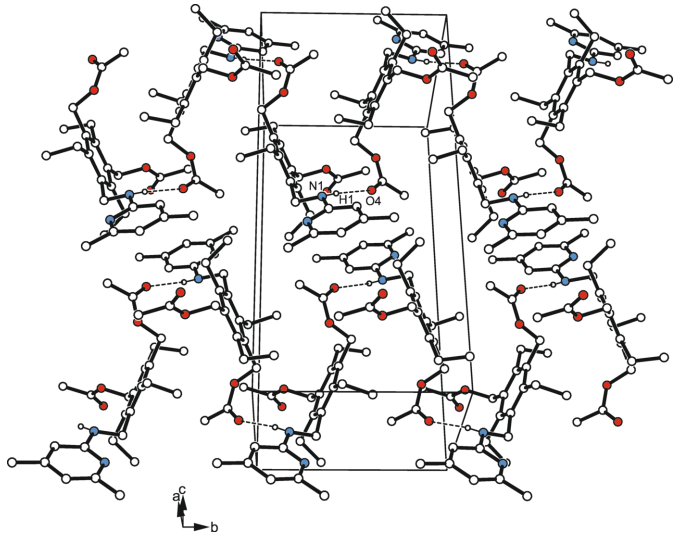


Figure 2
Packing diagram of the title compound. The N—H···O hydrogen bonds are shown as dashed lines.

structures of the monohydrate and the methanol solvate of {1-[(3,5-bis{[(4,6-dimethylpyridin-2-yl)amino]methyl}-2,4,6-triethylbenzyl)amino]cyclopentyl}methanol (CADTAG, CADTEK; Stapf *et al.*, 2020*b*) as well as that of the methanol solvate of 1-{[*N*,*N*′-bis(*tert*-butoxycarbonyl)guanidino]methyl}-3,5-bis{[(6-methylpyridin-2-yl)amino]methyl}-2,4,6-triethylbenzene (HEXVAI; Mazik & Cavga, 2007) are composed of inversion-symmetric molecular dimers in which the water or methanol molecules are enclosed. Thus, the dimers are held together by solvent-mediated hydrogen bonds. In a similar way, the solvent-free crystal structures of 1,3-bis{[*N*,*N*-bis(2-hydroxyethyl)amino]methyl}-5-{[(4,6-dimethylpyridin-2-yl)-amino]methyl}-2,4,6-triethylbenzene (BEFGAY; Stapf *et al.*, 2022) and 1-{[*N*,*N*-bis(ethoxycarbonylmethyl)amino]methyl}-3,5-bis{[(6-methylpyridin-2-yl)amino]methyl}-2,4,6-trimethylbenzene (KEGWID; Mazik & Cavga, 2006) also consist of centrosymmetric dimers as the smallest supramolecular entity. In the crystal structure of 1,3-bis{[*N*-(1,10-phenanthrolin-2-ylcarbonyl)amino]methyl-5-{[(4,6-dimethylpyridin-2-yl)-amino]methyl}-2,4,6-triethylbenzene (TUGVEX; Mazik *et al.*, 2009), two water molecules and one ethanol molecule are accommodated in the binding pocket created by the heterocyclic units (one pyridinyl and two phenanthrolinyl groups) of the host molecule. The related compound 1-{[*N*-(1,10-phenanthrolin-2-ylcarbonyl)amino]methyl}-3,5-bis{[(4,6-dimethylpyridin-2-yl)amino]methyl}-2,4,6-triethylbenzene (ROKJEH, ROKJEH01; Mazik & Hartmann, 2008; Mazik *et al.*, 2009), possessing one phenanthrolinyl and two pyridinyl groups, encloses three water molecules in the binding pocket. Both host–water/ethanol aggregates are stabilized by O—H···O, N—H···O and O—H···N hydrogen bonds. In the crystal structures of the formamide monosolvate and the *n*-propanol/H_2O solvate of 1-{[2,6-bis(hydroxymethyl)-4-methylphenoxy]-methyl}-3,5-bis{[(4,6-dimethylpyridin-2-yl)amino]methyl}-2,4,6-triethylbenzene (FIZDOL, FIZDUR; Stapf *et al.*, 2023), the tripodal host molecules adopt similar conformations despite the different solvent molecules. 1-(Bromomethyl)-3,5-bis{[(4,6-dimethylpyridin-2-yl)amino]methyl}-2,4,6-triethylbenzene was found to crystallize as a diethyl ether solvate (BIYTOT; Mazik & Kuschel, 2008), with the ether oxygen bound to one of the amino groups by hydrogen bonding. Finally, the crystal structures of triethylbenzene derivatives bearing one or two cationic moieties, namely 3-methylpyridinium group(s), in combination with 4,6-dimethylpyridin-2-yl unit(s) (hexafluorophosphate salts; ZITRAZ and ZITRON, respectively; Weisse *et al.*, 2023) should be mentioned.

5. Synthesis and crystallization

A suspension of 1,3-bis(bromomethyl)-5-{[(4,6-dimethylpyridin-2-yl)amino]methyl}-2,4,6-triethylbenzene (0.30 g, 0.62 mmol) and anhydrous sodium acetate (0.42 g, 5.12 mmol) in acetic acid (3 mL) was stirred at 373 K for 12 h. The solvent was evaporated under reduced pressure. To the obtained white solid, water (3 mL) and CH_2Cl_2 (3 mL) were added. The aqueous phase was extracted twice with CH_2Cl_2 (5 mL). The combined organic extracts were treated with a saturated $NaHCO_3$ solution (3 mL), washed with water (5 mL), dried (Na_2SO_4) and then concentrated. The pale yellow resin was recrystallized from methanol to give the title compound (0.17 g, 62%) as colourless crystals. Single crystals suitable for X-ray diffraction were obtained by slow evaporation from a solution of the title compound in *N*,*N*-dimethylacetamide.

Analytical data: m.p. 429–431 K; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.18–1.22 (*m*, 9H, CH_3), 2.09 (*s*, 6H, CH_3), 2.24 (*s*, 3H, CH_3), 2.36 (*s*, 3H, CH_3), 2.76 (*q*, 6H, *J* = 7.6 Hz, CH_2), 4.15 (*br s*, 1H, NH), 4.39 (*d*, 2H, *J* = 4.2 Hz, CH_2), 5.21 (*s*, 4H, OCH_2), 6.08 (*s*, 1H, aryl), 6.36 (*s*, 1H, aryl); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 16.3, 16.5 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 22.8, 23.0 (CH_2), 24.1 (CH_3), 40.4 ($NHCH_2$), 60.9 (OCH_2), 103.5, 114.0, 130.0, 133.2, 145.4, 145.8, 148.9, 156.7, 158.1 (all aryl), 171.1 (C═O); MS (APCI): *m*/*z* calculated for $C_{26}H_{37}N_2O_4$: 441.3 $[M + H]^+$, found 441.2. Elemental analysis for $C_{26}H_{36}N_2O_4$ (%): calculated C 70.88, H 8.24, N 6.36; found C 70.68, H 8.20, N 6.40. TLC: R_f = 0.41 [SiO_2, toluene/ethyl acetate 3:1 (*v*/*v*)].

The educt, 1,3-bis(bromomethyl)-5-{[(4,6-dimethylpyridin-2-yl)amino]methyl}-2,4,6-triethylbenzene, was synthesized according to the reported procedure (Weisse *et al.*, 2023).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{26}H_{36}N_2O_4$
M_r	440.57
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, *b*, *c* (Å)	12.5184 (4), 9.1855 (2), 22.1339 (6)
β (°)	105.1331 (15)
V (Å^3)	2456.87 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.42 × 0.11 × 0.06
Data collection	
Diffractometer	Bruker Kappa APEXII CCD area detector
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23620, 5984, 4634
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.663
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.042, 0.120, 1.03
No. of reflections	5984
No. of parameters	300
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.24

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *SHELXTL* (Sheldrick, 2008).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned

geometrically and refined isotropically using a riding model with C—H = 0.98–0.99 Å (alkyl), 0.95 Å (aryl); U_{iso}(H) = 1.2–1.5U_{eq}(C).

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Synthesis and crystal structure of 1,3-bis(acetoxymethyl)-5-{[(4,6-dimethylpyridin-2-yl)amino]methyl}-2,4,6-triethylbenzene

Manuel Stapf, Venugopal Rao Miyyapuram, Wilhelm Seichter and Monika Mazik

Computing details

{3-[(Acetyloxy)methyl]-5-{[(4,6-dimethylpyridin-2-yl)amino]methyl}-2,4,6-triethylphenyl}methyl acetate

Crystal data

$C_{26}H_{36}N_2O_4$
$M_r = 440.57$
Monoclinic, $P2_1/n$
$a = 12.5184$ (4) Å
$b = 9.1855$ (2) Å
$c = 22.1339$ (6) Å
$\beta = 105.1331$ (15)°
$V = 2456.87$ (12) Å^3
$Z = 4$
$F(000) = 952$
$D_x = 1.191$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6078 reflections
$\theta = 2.4$–$28.3°$
$\mu = 0.08$ mm^{-1}
$T = 100$ K
Needle, colourless
0.42 × 0.11 × 0.06 mm

Data collection

Bruker Kappa APEXII CCD area detector diffractometer
phi and ω scans
23620 measured reflections
5984 independent reflections
4634 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 28.1°$, $\theta_{min} = 2.8°$
$h = -15\rightarrow16$
$k = -12\rightarrow11$
$l = -29\rightarrow29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.120$
$S = 1.02$
5984 reflections
300 parameters
1 restraint
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.589P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ 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	0.57195 (8)	0.63700 (10)	0.27696 (5)	0.0206 (2)
O2	0.75502 (8)	0.62688 (10)	0.28844 (5)	0.0251 (2)
O3	0.11605 (8)	0.87452 (10)	0.19905 (4)	0.0185 (2)
O4	0.13164 (10)	0.90318 (11)	0.10076 (4)	0.0284 (2)
N1	0.27865 (10)	0.66995 (12)	0.44466 (5)	0.0184 (2)
N2	0.22044 (10)	0.74686 (12)	0.53067 (5)	0.0187 (2)
C1	0.35590 (11)	0.83570 (12)	0.38032 (5)	0.0133 (2)
C2	0.45669 (10)	0.79830 (12)	0.36834 (6)	0.0136 (2)
C3	0.47462 (10)	0.83050 (12)	0.30955 (6)	0.0135 (2)
C4	0.39092 (11)	0.89452 (12)	0.26199 (6)	0.0129 (2)
C5	0.28887 (10)	0.92766 (12)	0.27416 (5)	0.0122 (2)
C6	0.27068 (10)	0.89825 (12)	0.33303 (5)	0.0125 (2)
C7	0.33606 (11)	0.80813 (13)	0.44406 (6)	0.0166 (3)
H7A	0.4078	0.8061	0.4762	0.020*
H7B	0.2911	0.8883	0.4545	0.020*
C8	0.23040 (11)	0.63821 (14)	0.49228 (6)	0.0166 (3)
C9	0.16947 (12)	0.71630 (15)	0.57598 (6)	0.0216 (3)
C10	0.12987 (12)	0.58025 (16)	0.58463 (6)	0.0234 (3)
H10	0.0956	0.5637	0.6176	0.028*
C11	0.14056 (11)	0.46587 (15)	0.54437 (6)	0.0205 (3)
C12	0.19076 (11)	0.49616 (14)	0.49736 (6)	0.0186 (3)
H12	0.1986	0.4224	0.4687	0.022*
C13	0.15911 (15)	0.84358 (17)	0.61719 (7)	0.0320 (4)
H13A	0.2330	0.8761	0.6403	0.048*
H13B	0.1172	0.8137	0.6468	0.048*
H13C	0.1204	0.9236	0.5912	0.048*
C14	0.09729 (13)	0.31615 (16)	0.55260 (7)	0.0262 (3)
H14A	0.1176	0.2486	0.5232	0.039*
H14B	0.0165	0.3197	0.5445	0.039*
H14C	0.1296	0.2827	0.5955	0.039*
C15	0.54724 (11)	0.72755 (14)	0.41921 (6)	0.0186 (3)
H15A	0.5922	0.6634	0.3996	0.022*
H15B	0.5130	0.6664	0.4459	0.022*
C16	0.62274 (12)	0.84108 (16)	0.46005 (7)	0.0260 (3)
H16A	0.6584	0.9000	0.4340	0.039*
H16B	0.6795	0.7916	0.4925	0.039*
H16C	0.5786	0.9043	0.4798	0.039*
C17	0.58334 (11)	0.78884 (13)	0.29743 (6)	0.0176 (3)
H17A	0.5994	0.8517	0.2645	0.021*
H17B	0.6442	0.7992	0.3360	0.021*
C18	0.66651 (11)	0.56814 (14)	0.27606 (6)	0.0182 (3)
C19	0.64560 (13)	0.41217 (15)	0.25739 (8)	0.0301 (3)
H19A	0.6259	0.4045	0.2116	0.045*
H19B	0.5847	0.3748	0.2732	0.045*
H19C	0.7125	0.3550	0.2751	0.045*

C20	0.41205 (11)	0.93293 (13)	0.19939 (6)	0.0161 (3)
H20A	0.3421	0.9246	0.1661	0.019*
H20B	0.4656	0.8629	0.1899	0.019*
C21	0.45783 (12)	1.08797 (14)	0.19947 (7)	0.0217 (3)
H21A	0.4083	1.1567	0.2125	0.033*
H21B	0.4629	1.1129	0.1573	0.033*
H21C	0.5315	1.0932	0.2287	0.033*
C22	0.19501 (11)	0.99175 (13)	0.22362 (6)	0.0154 (3)
H22A	0.1582	1.0705	0.2412	0.018*
H22B	0.2238	1.0332	0.1897	0.018*
C23	0.09262 (11)	0.84169 (14)	0.13812 (6)	0.0171 (3)
C24	0.01268 (13)	0.71748 (16)	0.12222 (6)	0.0248 (3)
H24A	−0.0613	0.7550	0.1019	0.037*
H24B	0.0107	0.6656	0.1606	0.037*
H24C	0.0363	0.6506	0.0937	0.037*
C25	0.16236 (11)	0.93941 (13)	0.34683 (6)	0.0155 (2)
H25A	0.1467	0.8708	0.3780	0.019*
H25B	0.1016	0.9312	0.3080	0.019*
C26	0.16604 (12)	1.09505 (14)	0.37219 (7)	0.0229 (3)
H26A	0.2244	1.1025	0.4114	0.034*
H26B	0.0945	1.1191	0.3800	0.034*
H26C	0.1815	1.1631	0.3415	0.034*
H1	0.3047 (13)	0.5952 (13)	0.4283 (7)	0.022 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0143 (5)	0.0159 (5)	0.0321 (5)	0.0015 (3)	0.0069 (4)	−0.0065 (4)
O2	0.0159 (5)	0.0221 (5)	0.0394 (6)	0.0014 (4)	0.0107 (4)	0.0042 (4)
O3	0.0164 (5)	0.0236 (5)	0.0143 (4)	−0.0058 (4)	0.0019 (3)	0.0013 (3)
O4	0.0416 (7)	0.0271 (5)	0.0184 (5)	−0.0097 (5)	0.0111 (4)	0.0003 (4)
N1	0.0270 (7)	0.0129 (5)	0.0186 (5)	−0.0006 (4)	0.0117 (5)	−0.0002 (4)
N2	0.0195 (6)	0.0203 (5)	0.0172 (5)	0.0008 (4)	0.0065 (4)	−0.0007 (4)
C1	0.0170 (6)	0.0103 (5)	0.0127 (5)	−0.0019 (4)	0.0038 (4)	−0.0007 (4)
C2	0.0149 (6)	0.0094 (5)	0.0152 (6)	−0.0004 (4)	0.0014 (5)	−0.0012 (4)
C3	0.0131 (6)	0.0096 (5)	0.0181 (6)	−0.0014 (4)	0.0046 (5)	−0.0025 (4)
C4	0.0159 (6)	0.0087 (5)	0.0150 (6)	−0.0016 (4)	0.0052 (5)	−0.0013 (4)
C5	0.0129 (6)	0.0093 (5)	0.0138 (5)	−0.0008 (4)	0.0024 (4)	−0.0013 (4)
C6	0.0138 (6)	0.0093 (5)	0.0149 (6)	−0.0009 (4)	0.0047 (4)	−0.0016 (4)
C7	0.0219 (7)	0.0151 (6)	0.0130 (6)	−0.0013 (5)	0.0046 (5)	0.0006 (4)
C8	0.0163 (7)	0.0191 (6)	0.0141 (6)	0.0024 (5)	0.0037 (5)	0.0032 (5)
C9	0.0211 (7)	0.0271 (7)	0.0184 (6)	0.0025 (5)	0.0085 (5)	−0.0010 (5)
C10	0.0239 (8)	0.0300 (7)	0.0193 (6)	−0.0005 (6)	0.0110 (5)	0.0028 (5)
C11	0.0168 (7)	0.0226 (7)	0.0218 (6)	0.0015 (5)	0.0046 (5)	0.0057 (5)
C12	0.0202 (7)	0.0181 (6)	0.0183 (6)	0.0024 (5)	0.0065 (5)	0.0022 (5)
C13	0.0421 (10)	0.0322 (8)	0.0286 (8)	−0.0012 (7)	0.0214 (7)	−0.0069 (6)
C14	0.0265 (8)	0.0247 (7)	0.0291 (7)	−0.0021 (6)	0.0107 (6)	0.0070 (6)
C15	0.0179 (7)	0.0164 (6)	0.0188 (6)	0.0042 (5)	−0.0002 (5)	0.0010 (5)

C16	0.0218 (8)	0.0269 (7)	0.0234 (7)	0.0033 (6)	−0.0046 (5)	−0.0039 (6)
C17	0.0145 (6)	0.0149 (6)	0.0241 (6)	−0.0002 (5)	0.0061 (5)	−0.0034 (5)
C18	0.0164 (7)	0.0194 (6)	0.0207 (6)	0.0044 (5)	0.0079 (5)	0.0036 (5)
C19	0.0254 (8)	0.0191 (7)	0.0486 (9)	0.0040 (6)	0.0144 (7)	−0.0057 (6)
C20	0.0188 (7)	0.0154 (6)	0.0162 (6)	0.0001 (5)	0.0081 (5)	−0.0001 (5)
C21	0.0279 (8)	0.0163 (6)	0.0257 (7)	−0.0013 (5)	0.0157 (6)	0.0026 (5)
C22	0.0155 (6)	0.0141 (6)	0.0157 (6)	0.0001 (5)	0.0024 (5)	0.0011 (4)
C23	0.0168 (7)	0.0174 (6)	0.0156 (6)	0.0028 (5)	0.0018 (5)	0.0027 (5)
C24	0.0233 (8)	0.0270 (7)	0.0201 (6)	−0.0070 (6)	−0.0015 (5)	0.0009 (5)
C25	0.0127 (6)	0.0173 (6)	0.0173 (6)	0.0004 (5)	0.0053 (5)	−0.0015 (5)
C26	0.0248 (8)	0.0190 (6)	0.0260 (7)	0.0052 (5)	0.0085 (6)	−0.0033 (5)

Geometric parameters (Å, º)

O1—C18	1.3469 (16)	C13—H13C	0.9800
O1—C17	1.4619 (15)	C14—H14A	0.9800
O2—C18	1.1980 (17)	C14—H14B	0.9800
O3—C23	1.3377 (15)	C14—H14C	0.9800
O3—C22	1.4669 (15)	C15—C16	1.5336 (19)
O4—C23	1.2051 (16)	C15—H15A	0.9900
N1—C8	1.3761 (16)	C15—H15B	0.9900
N1—C7	1.4603 (16)	C16—H16A	0.9800
N1—H1	0.878 (9)	C16—H16B	0.9800
N2—C8	1.3375 (17)	C16—H16C	0.9800
N2—C9	1.3511 (17)	C17—H17A	0.9900
C1—C2	1.3982 (18)	C17—H17B	0.9900
C1—C6	1.4073 (17)	C18—C19	1.4952 (19)
C1—C7	1.5164 (16)	C19—H19A	0.9800
C2—C3	1.4083 (17)	C19—H19B	0.9800
C2—C15	1.5194 (17)	C19—H19C	0.9800
C3—C4	1.4057 (17)	C20—C21	1.5349 (17)
C3—C17	1.5038 (18)	C20—H20A	0.9900
C4—C5	1.4060 (17)	C20—H20B	0.9900
C4—C20	1.5185 (16)	C21—H21A	0.9800
C5—C6	1.4063 (16)	C21—H21B	0.9800
C5—C22	1.5140 (16)	C21—H21C	0.9800
C6—C25	1.5137 (17)	C22—H22A	0.9900
C7—H7A	0.9900	C22—H22B	0.9900
C7—H7B	0.9900	C23—C24	1.4977 (19)
C8—C12	1.4108 (18)	C24—H24A	0.9800
C9—C10	1.376 (2)	C24—H24B	0.9800
C9—C13	1.5092 (19)	C24—H24C	0.9800
C10—C11	1.406 (2)	C25—C26	1.5322 (17)
C10—H10	0.9500	C25—H25A	0.9900
C11—C12	1.3770 (18)	C25—H25B	0.9900
C11—C14	1.5064 (19)	C26—H26A	0.9800
C12—H12	0.9500	C26—H26B	0.9800
C13—H13A	0.9800	C26—H26C	0.9800

C13—H13B	0.9800

C18—O1—C17	115.95 (10)	H15A—C15—H15B	107.9
C23—O3—C22	119.24 (10)	C15—C16—H16A	109.5
C8—N1—C7	120.44 (10)	C15—C16—H16B	109.5
C8—N1—H1	115.8 (11)	H16A—C16—H16B	109.5
C7—N1—H1	116.1 (11)	C15—C16—H16C	109.5
C8—N2—C9	117.18 (12)	H16A—C16—H16C	109.5
C2—C1—C6	120.38 (11)	H16B—C16—H16C	109.5
C2—C1—C7	120.69 (11)	O1—C17—C3	106.17 (10)
C6—C1—C7	118.92 (11)	O1—C17—H17A	110.5
C1—C2—C3	119.53 (11)	C3—C17—H17A	110.5
C1—C2—C15	120.01 (11)	O1—C17—H17B	110.5
C3—C2—C15	120.43 (11)	C3—C17—H17B	110.5
C4—C3—C2	120.82 (11)	H17A—C17—H17B	108.7
C4—C3—C17	120.35 (11)	O2—C18—O1	123.31 (12)
C2—C3—C17	118.78 (11)	O2—C18—C19	125.41 (13)
C3—C4—C5	118.95 (11)	O1—C18—C19	111.28 (12)
C3—C4—C20	120.47 (11)	C18—C19—H19A	109.5
C5—C4—C20	120.53 (11)	C18—C19—H19B	109.5
C4—C5—C6	120.72 (11)	H19A—C19—H19B	109.5
C4—C5—C22	120.75 (10)	C18—C19—H19C	109.5
C6—C5—C22	118.50 (11)	H19A—C19—H19C	109.5
C5—C6—C1	119.53 (11)	H19B—C19—H19C	109.5
C5—C6—C25	120.62 (11)	C4—C20—C21	111.62 (10)
C1—C6—C25	119.80 (11)	C4—C20—H20A	109.3
N1—C7—C1	110.74 (10)	C21—C20—H20A	109.3
N1—C7—H7A	109.5	C4—C20—H20B	109.3
C1—C7—H7A	109.5	C21—C20—H20B	109.3
N1—C7—H7B	109.5	H20A—C20—H20B	108.0
C1—C7—H7B	109.5	C20—C21—H21A	109.5
H7A—C7—H7B	108.1	C20—C21—H21B	109.5
N2—C8—N1	117.44 (11)	H21A—C21—H21B	109.5
N2—C8—C12	123.12 (12)	C20—C21—H21C	109.5
N1—C8—C12	119.40 (11)	H21A—C21—H21C	109.5
N2—C9—C10	123.30 (12)	H21B—C21—H21C	109.5
N2—C9—C13	114.79 (12)	O3—C22—C5	107.84 (9)
C10—C9—C13	121.90 (13)	O3—C22—H22A	110.1
C9—C10—C11	119.53 (12)	C5—C22—H22A	110.1
C9—C10—H10	120.2	O3—C22—H22B	110.1
C11—C10—H10	120.2	C5—C22—H22B	110.1
C12—C11—C10	117.74 (13)	H22A—C22—H22B	108.5
C12—C11—C14	121.68 (13)	O4—C23—O3	124.38 (12)
C10—C11—C14	120.58 (12)	O4—C23—C24	124.16 (12)
C11—C12—C8	119.11 (12)	O3—C23—C24	111.45 (11)
C11—C12—H12	120.4	C23—C24—H24A	109.5
C8—C12—H12	120.4	C23—C24—H24B	109.5
C9—C13—H13A	109.5	H24A—C24—H24B	109.5

C9—C13—H13B	109.5	C23—C24—H24C	109.5
H13A—C13—H13B	109.5	H24A—C24—H24C	109.5
C9—C13—H13C	109.5	H24B—C24—H24C	109.5
H13A—C13—H13C	109.5	C6—C25—C26	111.35 (11)
H13B—C13—H13C	109.5	C6—C25—H25A	109.4
C11—C14—H14A	109.5	C26—C25—H25A	109.4
C11—C14—H14B	109.5	C6—C25—H25B	109.4
H14A—C14—H14B	109.5	C26—C25—H25B	109.4
C11—C14—H14C	109.5	H25A—C25—H25B	108.0
H14A—C14—H14C	109.5	C25—C26—H26A	109.5
H14B—C14—H14C	109.5	C25—C26—H26B	109.5
C2—C15—C16	111.82 (10)	H26A—C26—H26B	109.5
C2—C15—H15A	109.3	C25—C26—H26C	109.5
C16—C15—H15A	109.3	H26A—C26—H26C	109.5
C2—C15—H15B	109.3	H26B—C26—H26C	109.5
C16—C15—H15B	109.3		

C6—C1—C2—C3	3.27 (17)	C7—N1—C8—N2	11.94 (18)
C7—C1—C2—C3	−177.42 (11)	C7—N1—C8—C12	−170.12 (12)
C6—C1—C2—C15	−178.56 (11)	C8—N2—C9—C10	1.1 (2)
C7—C1—C2—C15	0.75 (17)	C8—N2—C9—C13	−179.11 (13)
C1—C2—C3—C4	−2.52 (17)	N2—C9—C10—C11	−0.9 (2)
C15—C2—C3—C4	179.31 (11)	C13—C9—C10—C11	179.24 (14)
C1—C2—C3—C17	−179.72 (11)	C9—C10—C11—C12	−0.1 (2)
C15—C2—C3—C17	2.11 (17)	C9—C10—C11—C14	−179.63 (13)
C2—C3—C4—C5	0.69 (17)	C10—C11—C12—C8	1.0 (2)
C17—C3—C4—C5	177.86 (10)	C14—C11—C12—C8	−179.52 (12)
C2—C3—C4—C20	178.20 (10)	N2—C8—C12—C11	−0.9 (2)
C17—C3—C4—C20	−4.63 (17)	N1—C8—C12—C11	−178.70 (12)
C3—C4—C5—C6	0.39 (17)	C1—C2—C15—C16	−88.79 (15)
C20—C4—C5—C6	−177.12 (10)	C3—C2—C15—C16	89.37 (14)
C3—C4—C5—C22	−177.83 (10)	C18—O1—C17—C3	−166.61 (11)
C20—C4—C5—C22	4.67 (17)	C4—C3—C17—O1	−92.28 (13)
C4—C5—C6—C1	0.36 (17)	C2—C3—C17—O1	84.94 (13)
C22—C5—C6—C1	178.61 (10)	C17—O1—C18—O2	−3.15 (18)
C4—C5—C6—C25	177.60 (11)	C17—O1—C18—C19	177.29 (11)
C22—C5—C6—C25	−4.15 (16)	C3—C4—C20—C21	−89.67 (14)
C2—C1—C6—C5	−2.21 (17)	C5—C4—C20—C21	87.81 (14)
C7—C1—C6—C5	178.47 (10)	C23—O3—C22—C5	−121.28 (12)
C2—C1—C6—C25	−179.47 (11)	C4—C5—C22—O3	102.10 (12)
C7—C1—C6—C25	1.21 (16)	C6—C5—C22—O3	−76.15 (13)
C8—N1—C7—C1	−165.33 (11)	C22—O3—C23—O4	−0.62 (19)
C2—C1—C7—N1	−95.56 (14)	C22—O3—C23—C24	178.70 (11)
C6—C1—C7—N1	83.76 (14)	C5—C6—C25—C26	−88.44 (13)
C9—N2—C8—N1	177.71 (12)	C1—C6—C25—C26	88.80 (14)
C9—N2—C8—C12	−0.15 (19)		

Hydrogen-bond geometry (Å, º)

Cg represents the centroid of the C8–C12/N2 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.88 (1)	2.10 (1)	2.9776 (16)	173 (1)
C19—H19*C*···O2^{ii}	0.98	2.61	3.1785 (18)	117
C14—H14*B*···*Cg*^{iii}	0.98	2.73	3.5955 (17)	147
C25—H25*A*···N1	0.99	2.65	3.3598 (17)	128
C25—H25*B*···O3	0.99	2.52	3.2250 (15)	128

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+1/2; (ii) −*x*+3/2, *y*−1/2, −*z*+1/2; (iii) −*x*, −*y*+1, −*z*+1.