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Crystal structure of the 1,3,6,8-tetraazatricyclo-[4.3.1.1^{3,8}]undecane (TATU)–4-nitrophenol (1/2) adduct: the role of anomeric effect in the formation of a second hydrogen-bond interaction

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In the title ternary co-crystalline adduct, $C_7H_{14}N_4 \cdot 2C_6H_5NO_3$, molecules are linked by two intermolecular O—H···N hydrogen bonds, forming a tricomponent aggregates in the asymmetric unit. The hydrogen-bond formation to one of the N atoms is enough to induce structural stereoelectronic effects in the normal donor→acceptor direction. In the title adduct, the two independent nitrophenol molecules are essentially planar, with maximum deviations of 0.0157 (13) and 0.0039 (13) Å. The dihedral angles between the planes of the nitro group and the attached benzene rings are 4.04 (17) and 5.79 (17)°. In the crystal, aggregates are connected by C—H···O hydrogen bonds, forming a supramolecular dimer enclosing an $R_6^6(32)$ ring motif. Additional C—H···O intermolecular hydrogen-bonding interactions form a second supramolecular inversion dimer with an $R_2^2(10)$ motif. These units are linked via C—H···O and C—H···N hydrogen bonds, forming a three-dimensional network.

1. Chemical context

The chemistry of the aminoalkylation of aromatic substrates by the Mannich reaction is of great interest and chemical importance (Tramontini *et al.*, 1988). Some modern variants of Mannich reactions have been developed using preformed aminals or hemiaminals as Mannich electrophiles for amino-methylation reactions (Katritzky *et al.*, 2005). The use of these preformed aminomethylating reagents, particularly those derived from common amines, is becoming more frequent (Tramontini & Angiolini, 1990), a mechanism involving initial formation of a hydrogen-bonded complex between a Mannich preformed reagent and the phenolic substrate has been documented (Burckhalter & Leib, 1961). Electron density at the free *ortho* position of the phenol and the reactivity of the phenolic hydroxy group played a crucial role and the reaction does not occur in the absence of the hydroxy group (Deng *et al.* 2014). The phenol–N complex has also served as a good model for the investigation of proton and electron-transfer processes occurring in living matter, it being generally assumed that this interaction consists solely of the attraction between the lone pair of the amine N atom and the phenolic hydroxy proton (Lu *et al.* 2006). In addition to the typical features of intermolecular hydrogen bonding, these systems have an extra advantage over many other complexes because they play an important role in probing the anomeric effect in N—C—N (aminal) systems even though the anomeric effect is
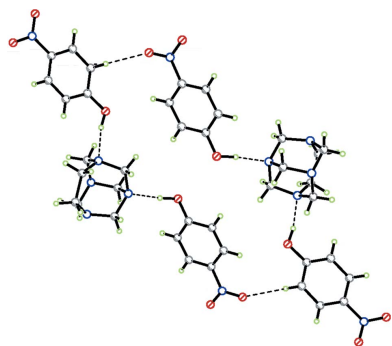
well recognized as an important factor in defining the predominant conformational state of many cyclic heteroatom-containing compounds (Dabbagh *et al.* 2002). There is little evidence in the literature for bond shortening and lengthening in cyclic aminals (Takahashi *et al.* 2007). We have undertaken a long-term project designed to systematically investigate the structures, chemical properties and reactivity of macrocyclic aminals as preformed electrophilic reagents for the synthesis of phenolic Mannich bases through simple and efficient methodologies. As part of this investigation we have recently reported the synthesis of 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]-undecane (TATU), (II) (Rivera *et al.* 2004). TATU which has two non-equivalent hydrogen-bond acceptor N-atom sites is a good model for the investigation of intermolecular hydrogen bonding with phenols and for studying the nature of the anomeric effect in the N—C—N molecular segment. One interesting feature of the structure of TATU is that two of the N atoms are similar to those in 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane [(III), also known as urotropine, and hexamethylenetetramine, HMTA] and the other two are similar to those in 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane [(IV), TATD]. We have previously studied the structure of the 1:1 complex produced by the reaction of TATU with hydroquinone (Rivera *et al.* 2007). In that work, we found that the preference for a particular hydrogen-bond interaction site depends strongly upon the lone-pair orbital hybridization of the N atom. We also demonstrated that a greater degree of sp^3 character favours the N···H—O interactions. Later (Rivera *et al.* 2011), we reported the preparation and structure of an acid–base adduct assembled from TATU and pentachlorophenol (PCP). X-ray diffraction analysis of this salt confirmed that the –OH group of the PCP transfers a proton to the N atoms of the aminal moiety. The main consequence of this protonation is the distortion of the cage structure which was attributed to the anomeric effect that governs the aminal group. Studies of phenol complexes with tertiary amines in the solid state show that the proton transfer depends not only on the ΔK_a (pK_a amine − pK_a acid) value, but also on steric and packing effects (Majerz & Sawka-Dobrowolska, 1996). Because of the acidity of the phenolic group, the proton potential of the hydrogen-bonded system can be fundamentally changed by substituents in the 4-position of the phenol ring (Xiong *et al.*, 2002). Because of this and as a logical extension of our previous efforts to understand the hydrogen-bonding interactions between TATU and phenols, we investigated the reaction of TATU with 4-nitrophenol. It is worth noting that, contrary to our initial expectation, the substitution
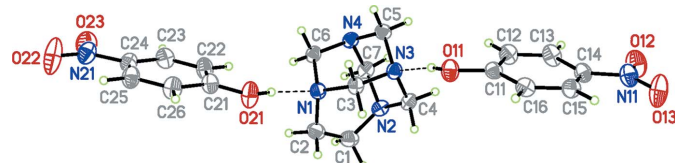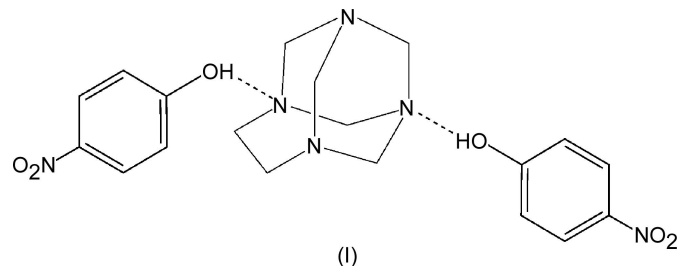
Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11···N3	0.98 (2)	1.69 (2)	2.6551 (13)	167.4 (19)
O21—H21···N1	0.93 (2)	1.82 (2)	2.7377 (14)	168.6 (19)
C26—H26···O13^{i}	0.95	2.39	3.3242 (17)	166
C5—H5A···O11^{ii}	0.99	2.56	3.4940 (15)	156
C5—H5B···O12^{iii}	0.99	2.53	3.4284 (16)	151
C6—H6A···O23^{iv}	0.99	2.47	3.4214 (16)	160
C25—H25···N2^{v}	0.95	2.60	3.5117 (16)	160

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

of hydroquinone by 4-nitrophenol afforded the title compound, (I). Its crystal structure shows a 1:2 stoichiometry. The aminal moiety is linked to two 4-nitrophenol molecules *via* O—H···N hydrogen bonds where one interaction is to a more basic site (N3) and the other one to an N atom adjacent to the ethylene bridge (N1).

(I)

2. Structural commentary

In the ternary cocrystal of TATU with two molecules of 4-nitrophenol, (I) (Fig. 1), the asymmetric unit was chosen such that the two nitrophenol molecules are linked by two intermolecular O—H···N hydrogen bonds (Table 1). This arrangement contrasts with related structures (Ng, 2008; Ng *et al.* 2001), where the urotropine (HMTA) moiety uses only one of its four N atoms to link to a 4-nitrophenol molecule *via* a hydrogen bond. It is possible, however, that the presence of a solvent water molecule may influence this observation.

In the three-component aggregates observed here, the O1···N3 distance [2.6551 (13) Å], is similar to those observed previously in hydrogen-bond adducts between HMTA and 4-nitrophenol (Ng, 2008; Ng *et al.* 2001). However, this is shorter than the O21···N1 distance in the second contact [2.7377 (14) Å]. This is a consequence of the relative proton affinities of the N atoms in TATU (Rivera *et al.*, 2007). Though this polyamine has four potential protonation sites it is evident that atoms N1 and N3 are not equivalent to one another. In particular, they differ in terms of their pyramidal character which can be estimated from the sum of the bond angles around each N atom, $\Sigma\alpha$(CNC) (339.5° for N1 and 328.3° for N3). The greater sp^3 character of the N atom contributes to the increase in proton affinity for N3. The main questions concerning the structure of this ternary cocrystal concerns the site of the formation of the second hydrogen bond. If all N atoms were equivalent, as in HMTA, the second hydrogen-
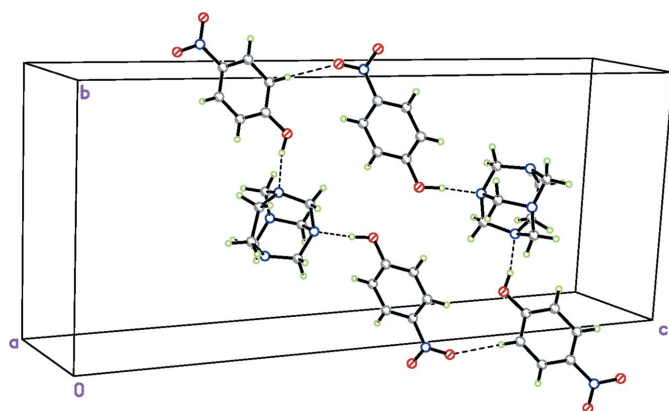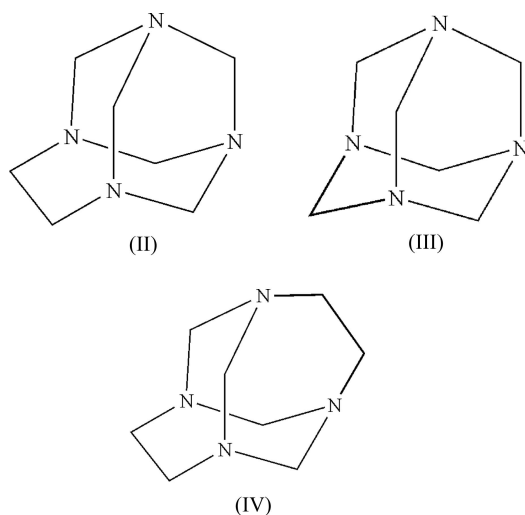

Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Hydrogen bonds are drawn as dashed lines.

Figure 2
The hydrogen-bonded inversion dimer displaying an $R_4^4(32)$ motif in the crystal of the title compound, with hydrogen bonds drawn as dashed lines. [Symmetry code: (i) $-x, -y + 1, -z + 1$.]
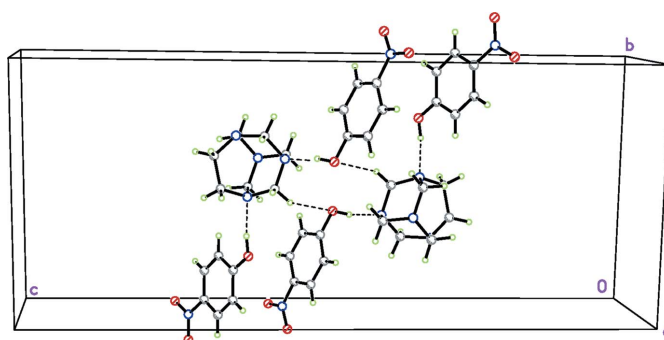

Figure 3
The hydrogen-bonded inversion dimer displaying an $R_2^2(10)$ motif in the crystal of the title compound, with hydrogen bonds drawn as dashed lines. [Symmetry code: (ii) $-x + 1, -y + 1, -z + 1$.]

bond interaction would be possible with any of the amino groups. However, in TATU, as expected, the first hydrogen bond involves more basic site (N3) rather than forming at a site than to adjacent to the ethylene bridge (N1 or N2). For the second hydrogen-bond contact, there are three potential alternative sites. First, a symmetric structure using the more basic N4 site. Alternatively, one of the less basic N1 or N2 atoms linked by the ethylene bridge could be used, resulting in a less symmetric cocrystal.

(II)

(III)

(IV)

In principle, it might be expected that the supramolecular structure of the title compound could be considered to be similar to that of the cocrystal formed between hydroquinone and TATU (Rivera *et al.*, 2007). In that case, however, the asymmetric unit contains only one half of hydroquinone molecule and the aminal cage structure, and self-assembly into a symmetric supramolecular structure via hydrogen bonds join them into a zigzag chain extending along the crystal *b* axis (Rivera *et al.*, 2007). Certainly each aminal unit links to two hydroquinone molecules *via* O—H···N hydrogen bonds once the symmetry operation is applied, but, in the present case, the asymmetric unit comprises a pair of 4-nitrophenol molecules

and one complete molecule of the aminal cage not related by symmetry elements. Account should also be taken of the effect that the phenol pK_a and the extent of polarization of the N—CH$_2$—N bonds upon hydrogen-bond formation. In fact, although the values of the bond lengths and angles in the aminal cage of the title compound are within expected values, there are notable differences when compared to the related TUTU/hydroquinone system (Rivera *et al.*, 2007).

Comparison of the C—N bond lengths in the title compound with respect to the mean value of 1.469 Å (Allen *et al.*, 1987) points out that the presence of strong hydrogen bonds in the title compound affect the length of the CH$_2$—N single bonds in the heterocyclic cage system. While in the related structure, the formation of a hydrogen bond with hydroquinone does not effect the CH$_2$—N single-bond lengths significantly [mean values 1.469 (2) Å] (Rivera *et al.*, 2007), for the title compound, the C5—N3 bond is lengthened [1.4815 (14) Å], while C5—N4 is shortened to 1.4639 (15) Å. In addition, the C4—N3 bond in the title compound is longer than in the related structure by 0.016 Å. The shortest C—N bond within the aminal cage ring in the title compound is the N2—C4 bond at 1.4517 (15) Å. These results are probably
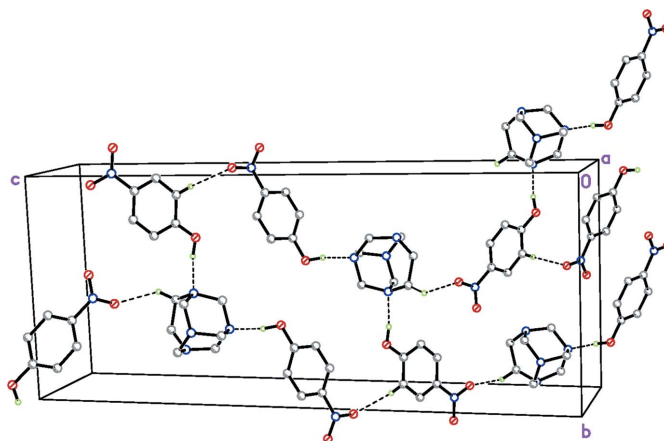

Figure 4
The overall packing of (I). H atoms not involved in hydrogen bonds have been omitted.

connected to presence of the very strong O—H···N hydrogen bonds, between the N atoms of the aminal cage structure and the 4-nitrophenol molecules. Thus, in the title compound, the aminal cage structure acquires a more pronounced anomeric effect due to these hydrogen-bond interactions (Alder *et al.*, 1999). It noteworthy that in the title compound the lengthening of C5—N3 facilitates the interaction of the nonbonding molecular orbitals of N4 and N2 with the σ*C5—N3 antibonding orbital and thus these N atoms are less likely to form the second hydrogen bond and results in the observed second hydrogen-bond interaction between the N1 atom from the aminal cage and the O21—H21 group of the second 4-nitrophenol molecule.

The two independent nitrophenol molecules are essentially planar, with maximum deviations of 0.0157 (13) and 0.0039 (13) Å. The nitro groups are almost coplanar with the aromatic ring plane; the dihedral angles between the planes of the nitro group and the attached benzene rings are 4.04 (17) and 5.79 (17)°. The coplanarity of the nitro groups with the aromatic rings is stabilized by weak C—H···O hydrogen bonds between the nitro O atoms and the H atoms of neighbouring structures (Table 1). In addition, the two of the hydroxy substituents C—O bonds are similar in length, but are somewhat longer than the normal value for a OH group bound to an aromatic ring (1.362Å; Allen *et al.*, 1987).

3. Supramolecular features

In the crystal structure of (I), two 1:2 adducts are linked to one another by C26—H26···O13^i bond pairs (Table 1) so that an inversion dimer is formed (Table 1 and Fig. 2), which displays an $R_6^6(32)$ motif (Bernstein *et al.*, 1995). The hydrogen bond with atom C6 as the donor firms an inversion dimer, generating forming a zigzag chain running parallel to [111] through a second C6—H6A···O23^{iv} hydrogen bond (Table 1 and Fig. 4). Additional C5—H5A···O11^{ii} intermolecular hydrogen-bonding interactions form a second supramolecular inversion dimer with an $R_2^2(10)$ motif (Fig. 3). Both dimers are further linked by a weak intermolecular C25—H25···N2^v hydrogen bond (Table 1). These contacts combine to generate a three-dimensional network structure.

4. Database survey

Up to now, there are only four structures of 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]undecane derivatives in the Cambridge Structural Database (CSD, Version 5.36; Groom & Allen, 2014), namely hexaaquamagnesium dibromide 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]undecane tetrahydrate (Rivera *et al.*, 2014), 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]undecane hydroquinone (Rivera *et al.* 2007) and 3,6,8-triaza-1-azoniatricyclo[4.3.1.1^{3,8}]undecane pentachlorophenolate monohydrate (Rivera *et al.*, 2011). Since 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]-undecane is a rigid molecule, the torsion angles do not vary considerably even though the C—N bond lengths do.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_{14}N_4 \cdot 2C_6H_5NO_3$
M_r	432.44
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	5.8818 (2), 11.9426 (4), 28.7820 (13)
β (°)	94.252 (3)
V (Å^3)	2016.20 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.11
Crystal size (mm)	$0.29 \times 0.28 \times 0.26$
Data collection	
Diffractometer	Stoe IPDS II two-circle
Absorption correction	Multi-scan (*X-AREA*; Stoe & Cie, 2001)
T_{min}, T_{max}	0.871, 0.896
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32192, 4379, 4086
R_{int}	0.066
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.640
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.039, 0.101, 1.05
No. of reflections	4379
No. of parameters	288
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.28, −0.18

Computer programs: *X-AREA* (Stoe & Cie, 2001), *SHELXS97* and *XP* in *SHELXTL-Plus* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

5. Synthesis and crystallization

Solvent-free direct preparation of the title compound from 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]dodecane (TATU) (0.15 g, 1.00 mmol) and 4-nitrophenol (0.21 g, 1.5 mmol) was carried out by a mechanochemical interaction in a mortar at room temperature. 30 min were required to complete the reaction. The mixture was then dissolved in a minimum amount of methanol and left to crystallize at room temperature. Subsequent recrystallization with MeOH gave the title compound as colourless crystals in 70% yield (m.p. 388–389 K).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were located in a difference map. Those bound to C atoms were positioned geometrically and refined using a riding model with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C)$] and with aromatic C—H = 0.95 Å and methylene C—H = 0.95 Å. H atoms bound to O atoms were refined freely.

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Crystal structure of the 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]undecane (TATU)–4-nitrophenol (1/2) adduct: the role of anomeric effect in the formation of a second hydrogen-bond interaction

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA* (Stoe & Cie, 2001); data reduction: *X-AREA* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]dodecane; 4-nitrophenol

Crystal data

$C_7H_{14}N_4 \cdot 2C_6H_5NO_3$	$F(000) = 912$
$M_r = 432.44$	$D_x = 1.425$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.8818$ (2) Å	Cell parameters from 38374 reflections
$b = 11.9426$ (4) Å	$\theta = 1.9$–$27.5°$
$c = 28.7820$ (13) Å	$\mu = 0.11$ mm^{-1}
$\beta = 94.252$ (3)°	$T = 173$ K
$V = 2016.20$ (13) Å^3	Block, colourless
$Z = 4$	$0.29 \times 0.28 \times 0.26$ mm

Data collection

Stoe IPDS II two-circle diffractometer	32192 measured reflections
	4379 independent reflections
Radiation source: Genix 3D IμS microfocus X-ray source	4086 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.066$
ω scans	$\theta_{max} = 27.1°$, $\theta_{min} = 1.9°$
Absorption correction: multi-scan (X-AREA; Stoe & Cie, 2001)	$h = -7 \rightarrow 7$
	$k = -15 \rightarrow 15$
$T_{min} = 0.871$, $T_{max} = 0.896$	$l = -36 \rightarrow 36$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.039$	
$wR(F^2) = 0.101$	$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 0.6818P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
4379 reflections	$(\Delta/\sigma)_{max} = 0.001$
288 parameters	$\Delta\rho_{max} = 0.28$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.18$ 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 ($Å^2$)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
N1	0.53235 (16)	0.54216 (8)	0.36281 (3)	0.0257 (2)
N2	0.53803 (16)	0.30513 (9)	0.34430 (4)	0.0287 (2)
N3	0.50006 (16)	0.39145 (8)	0.42185 (3)	0.0255 (2)
N4	0.85374 (16)	0.41212 (8)	0.38454 (3)	0.0259 (2)
C1	0.4260 (2)	0.37586 (12)	0.30852 (5)	0.0352 (3)
H1A	0.2678	0.3486	0.3022	0.042*
H1B	0.5046	0.3656	0.2796	0.042*
C2	0.4162 (2)	0.50300 (11)	0.31888 (4)	0.0329 (3)
H2A	0.4823	0.5433	0.2930	0.039*
H2B	0.2538	0.5251	0.3186	0.039*
C3	0.42828 (19)	0.50365 (10)	0.40489 (4)	0.0259 (2)
H3A	0.2606	0.5034	0.3984	0.031*
H3B	0.4651	0.5585	0.4301	0.031*
C4	0.43109 (19)	0.30056 (10)	0.38813 (4)	0.0281 (2)
H4A	0.4678	0.2275	0.4031	0.034*
H4B	0.2637	0.3038	0.3814	0.034*
C5	0.75221 (19)	0.39112 (10)	0.42864 (4)	0.0272 (2)
H5A	0.8027	0.4496	0.4515	0.033*
H5B	0.8049	0.3177	0.4413	0.033*
C6	0.78086 (18)	0.52223 (10)	0.36721 (4)	0.0265 (2)
H6A	0.8402	0.5333	0.3362	0.032*
H6B	0.8524	0.5797	0.3883	0.032*
C7	0.78366 (19)	0.32159 (10)	0.35191 (4)	0.0289 (2)
H7A	0.8454	0.3377	0.3215	0.035*
H7B	0.8535	0.2508	0.3638	0.035*
N11	0.0449 (2)	−0.02774 (10)	0.57131 (4)	0.0378 (3)
O11	0.24196 (16)	0.38395 (7)	0.49365 (3)	0.0338 (2)
H11	0.351 (3)	0.3797 (17)	0.4697 (7)	0.063 (6)*
O12	0.1721 (2)	−0.10676 (9)	0.56483 (4)	0.0520 (3)
O13	−0.1284 (2)	−0.03768 (10)	0.59193 (4)	0.0582 (3)
C11	0.20153 (19)	0.28382 (10)	0.51277 (4)	0.0270 (2)
C12	0.3496 (2)	0.19295 (12)	0.50991 (4)	0.0336 (3)
H12	0.4853	0.2008	0.4942	0.040*
C13	0.2988 (2)	0.09208 (11)	0.52981 (5)	0.0357 (3)
H13	0.3992	0.0302	0.5280	0.043*
C14	0.1002 (2)	0.08132 (10)	0.55258 (4)	0.0299 (3)
C15	−0.0455 (2)	0.17094 (11)	0.55729 (4)	0.0298 (2)
H15	−0.1783	0.1630	0.5739	0.036*
C16	0.0062 (2)	0.27210 (11)	0.53735 (4)	0.0292 (2)

H16	−0.0920	0.3345	0.5404	0.035*
N21	0.9793 (2)	1.06407 (10)	0.27085 (4)	0.0391 (3)
O21	0.44401 (17)	0.76721 (8)	0.36343 (4)	0.0410 (2)
H21	0.490 (3)	0.6929 (19)	0.3610 (7)	0.065 (6)*
O22	0.9280 (3)	1.16343 (9)	0.27052 (5)	0.0697 (4)
O23	1.13483 (19)	1.02708 (10)	0.24912 (4)	0.0512 (3)
C21	0.5798 (2)	0.83634 (10)	0.34109 (4)	0.0313 (3)
C22	0.7709 (2)	0.79931 (11)	0.31941 (5)	0.0358 (3)
H22	0.8091	0.7220	0.3200	0.043*
C23	0.9043 (2)	0.87407 (11)	0.29716 (4)	0.0346 (3)
H23	1.0354	0.8491	0.2828	0.042*
C24	0.8445 (2)	0.98616 (10)	0.29611 (4)	0.0306 (3)
C25	0.6549 (2)	1.02526 (10)	0.31720 (5)	0.0346 (3)
H25	0.6164	1.1025	0.3161	0.042*
C26	0.5237 (2)	0.94998 (11)	0.33973 (5)	0.0350 (3)
H26	0.3941	0.9756	0.3545	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0219 (4)	0.0270 (5)	0.0285 (5)	0.0018 (4)	0.0044 (4)	0.0031 (4)
N2	0.0257 (5)	0.0298 (5)	0.0305 (5)	−0.0023 (4)	0.0029 (4)	−0.0042 (4)
N3	0.0242 (5)	0.0247 (5)	0.0280 (5)	0.0003 (4)	0.0043 (4)	0.0014 (4)
N4	0.0209 (4)	0.0249 (5)	0.0321 (5)	0.0007 (4)	0.0025 (4)	−0.0009 (4)
C1	0.0324 (6)	0.0422 (7)	0.0305 (6)	−0.0025 (5)	−0.0016 (5)	−0.0024 (5)
C2	0.0281 (6)	0.0403 (7)	0.0299 (6)	0.0022 (5)	0.0000 (5)	0.0045 (5)
C3	0.0238 (5)	0.0253 (5)	0.0294 (6)	0.0028 (4)	0.0069 (4)	0.0010 (4)
C4	0.0243 (5)	0.0257 (5)	0.0345 (6)	−0.0033 (4)	0.0040 (4)	−0.0004 (4)
C5	0.0248 (5)	0.0277 (6)	0.0287 (5)	0.0015 (4)	−0.0006 (4)	0.0007 (4)
C6	0.0220 (5)	0.0253 (5)	0.0326 (6)	−0.0011 (4)	0.0052 (4)	0.0006 (4)
C7	0.0247 (5)	0.0277 (6)	0.0349 (6)	0.0016 (4)	0.0064 (4)	−0.0043 (5)
N11	0.0488 (7)	0.0338 (6)	0.0318 (5)	0.0017 (5)	0.0095 (5)	0.0019 (4)
O11	0.0399 (5)	0.0307 (5)	0.0321 (4)	0.0000 (4)	0.0112 (4)	0.0006 (3)
O12	0.0651 (7)	0.0342 (5)	0.0579 (7)	0.0130 (5)	0.0134 (5)	0.0087 (5)
O13	0.0711 (8)	0.0441 (6)	0.0646 (7)	−0.0059 (6)	0.0398 (6)	0.0042 (5)
C11	0.0284 (5)	0.0311 (6)	0.0216 (5)	−0.0005 (4)	0.0025 (4)	−0.0016 (4)
C12	0.0281 (6)	0.0415 (7)	0.0326 (6)	0.0059 (5)	0.0112 (5)	0.0033 (5)
C13	0.0368 (7)	0.0374 (7)	0.0342 (6)	0.0124 (5)	0.0121 (5)	0.0035 (5)
C14	0.0348 (6)	0.0311 (6)	0.0244 (5)	0.0023 (5)	0.0055 (4)	0.0007 (4)
C15	0.0272 (5)	0.0367 (6)	0.0264 (5)	0.0011 (5)	0.0072 (4)	−0.0018 (5)
C16	0.0285 (5)	0.0326 (6)	0.0268 (5)	0.0058 (5)	0.0053 (4)	−0.0029 (4)
N21	0.0504 (7)	0.0367 (6)	0.0316 (5)	−0.0106 (5)	0.0114 (5)	−0.0037 (4)
O21	0.0439 (5)	0.0282 (5)	0.0538 (6)	0.0033 (4)	0.0227 (4)	0.0059 (4)
O22	0.1072 (11)	0.0299 (6)	0.0785 (9)	−0.0138 (6)	0.0509 (8)	−0.0044 (5)
O23	0.0515 (6)	0.0554 (7)	0.0498 (6)	−0.0025 (5)	0.0240 (5)	0.0062 (5)
C21	0.0353 (6)	0.0284 (6)	0.0309 (6)	0.0009 (5)	0.0070 (5)	0.0021 (5)
C22	0.0416 (7)	0.0280 (6)	0.0391 (7)	0.0068 (5)	0.0120 (5)	0.0042 (5)
C23	0.0367 (6)	0.0357 (7)	0.0326 (6)	0.0038 (5)	0.0102 (5)	0.0006 (5)

C24	0.0376 (6)	0.0301 (6)	0.0247 (5)	−0.0060 (5)	0.0056 (5)	−0.0021 (4)
C25	0.0449 (7)	0.0241 (6)	0.0356 (6)	0.0000 (5)	0.0082 (5)	−0.0034 (5)
C26	0.0375 (6)	0.0297 (6)	0.0392 (7)	0.0034 (5)	0.0126 (5)	−0.0023 (5)

Geometric parameters (Å, º)

N1—C2	1.4685 (16)	N11—C14	1.4557 (16)
N1—C3	1.4707 (14)	O11—C11	1.3449 (15)
N1—C6	1.4771 (14)	O11—H11	0.98 (2)
N2—C1	1.4517 (16)	C11—C12	1.3977 (17)
N2—C4	1.4517 (15)	C11—C16	1.4005 (16)
N2—C7	1.4584 (15)	C12—C13	1.3762 (19)
N3—C3	1.4770 (14)	C12—H12	0.9500
N3—C5	1.4815 (14)	C13—C14	1.3872 (17)
N3—C4	1.4920 (15)	C13—H13	0.9500
N4—C6	1.4595 (15)	C14—C15	1.3839 (17)
N4—C5	1.4639 (15)	C15—C16	1.3809 (18)
N4—C7	1.4708 (15)	C15—H15	0.9500
C1—C2	1.5493 (19)	C16—H16	0.9500
C1—H1A	0.9900	N21—O22	1.2242 (17)
C1—H1B	0.9900	N21—O23	1.2280 (16)
C2—H2A	0.9900	N21—C24	1.4518 (16)
C2—H2B	0.9900	O21—C21	1.3451 (15)
C3—H3A	0.9900	O21—H21	0.93 (2)
C3—H3B	0.9900	C21—C26	1.3965 (18)
C4—H4A	0.9900	C21—C22	1.3972 (18)
C4—H4B	0.9900	C22—C23	1.3776 (18)
C5—H5A	0.9900	C22—H22	0.9500
C5—H5B	0.9900	C23—C24	1.3838 (18)
C6—H6A	0.9900	C23—H23	0.9500
C6—H6B	0.9900	C24—C25	1.3899 (18)
C7—H7A	0.9900	C25—C26	1.3777 (18)
C7—H7B	0.9900	C25—H25	0.9500
N11—O13	1.2225 (16)	C26—H26	0.9500
N11—O12	1.2272 (16)		
C2—N1—C3	114.45 (9)	N2—C7—H7A	108.5
C2—N1—C6	114.63 (9)	N4—C7—H7A	108.5
C3—N1—C6	110.41 (9)	N2—C7—H7B	108.5
C1—N2—C4	115.79 (10)	N4—C7—H7B	108.5
C1—N2—C7	114.87 (10)	H7A—C7—H7B	107.5
C4—N2—C7	111.27 (9)	O13—N11—O12	122.61 (12)
C3—N3—C5	107.75 (9)	O13—N11—C14	118.94 (11)
C3—N3—C4	112.82 (9)	O12—N11—C14	118.43 (11)
C5—N3—C4	107.77 (9)	C11—O11—H11	112.8 (12)
C6—N4—C5	108.81 (9)	O11—C11—C12	122.44 (11)
C6—N4—C7	112.51 (9)	O11—C11—C16	118.17 (11)
C5—N4—C7	108.34 (9)	C12—C11—C16	119.37 (11)

N2—C1—C2	117.08 (10)	C13—C12—C11	119.97 (11)
N2—C1—H1A	108.0	C13—C12—H12	120.0
C2—C1—H1A	108.0	C11—C12—H12	120.0
N2—C1—H1B	108.0	C12—C13—C14	119.62 (12)
C2—C1—H1B	108.0	C12—C13—H13	120.2
H1A—C1—H1B	107.3	C14—C13—H13	120.2
N1—C2—C1	117.14 (10)	C15—C14—C13	121.59 (12)
N1—C2—H2A	108.0	C15—C14—N11	119.91 (11)
C1—C2—H2A	108.0	C13—C14—N11	118.49 (11)
N1—C2—H2B	108.0	C16—C15—C14	118.63 (11)
C1—C2—H2B	108.0	C16—C15—H15	120.7
H2A—C2—H2B	107.3	C14—C15—H15	120.7
N1—C3—N3	115.44 (9)	C15—C16—C11	120.75 (11)
N1—C3—H3A	108.4	C15—C16—H16	119.6
N3—C3—H3A	108.4	C11—C16—H16	119.6
N1—C3—H3B	108.4	O22—N21—O23	122.49 (12)
N3—C3—H3B	108.4	O22—N21—C24	118.80 (12)
H3A—C3—H3B	107.5	O23—N21—C24	118.64 (12)
N2—C4—N3	115.05 (9)	C21—O21—H21	111.1 (13)
N2—C4—H4A	108.5	O21—C21—C26	117.55 (11)
N3—C4—H4A	108.5	O21—C21—C22	123.03 (11)
N2—C4—H4B	108.5	C26—C21—C22	119.42 (12)
N3—C4—H4B	108.5	C23—C22—C21	120.49 (12)
H4A—C4—H4B	107.5	C23—C22—H22	119.8
N4—C5—N3	110.72 (9)	C21—C22—H22	119.8
N4—C5—H5A	109.5	C22—C23—C24	118.98 (12)
N3—C5—H5A	109.5	C22—C23—H23	120.5
N4—C5—H5B	109.5	C24—C23—H23	120.5
N3—C5—H5B	109.5	C23—C24—C25	121.76 (11)
H5A—C5—H5B	108.1	C23—C24—N21	118.93 (11)
N4—C6—N1	115.99 (9)	C25—C24—N21	119.28 (11)
N4—C6—H6A	108.3	C26—C25—C24	118.81 (12)
N1—C6—H6A	108.3	C26—C25—H25	120.6
N4—C6—H6B	108.3	C24—C25—H25	120.6
N1—C6—H6B	108.3	C25—C26—C21	120.54 (12)
H6A—C6—H6B	107.4	C25—C26—H26	119.7
N2—C7—N4	115.00 (9)	C21—C26—H26	119.7
C4—N2—C1—C2	63.86 (14)	C11—C12—C13—C14	0.1 (2)
C7—N2—C1—C2	−68.06 (14)	C12—C13—C14—C15	−2.3 (2)
C3—N1—C2—C1	−67.26 (13)	C12—C13—C14—N11	177.01 (12)
C6—N1—C2—C1	61.78 (14)	O13—N11—C14—C15	−1.58 (19)
N2—C1—C2—N1	3.43 (16)	O12—N11—C14—C15	176.86 (12)
C2—N1—C3—N3	84.49 (12)	O13—N11—C14—C13	179.10 (13)
C6—N1—C3—N3	−46.64 (13)	O12—N11—C14—C13	−2.46 (18)
C5—N3—C3—N1	54.85 (12)	C13—C14—C15—C16	2.17 (19)
C4—N3—C3—N1	−63.99 (12)	N11—C14—C15—C16	−177.13 (11)
C1—N2—C4—N3	−85.86 (12)	C14—C15—C16—C11	0.16 (18)

C7—N2—C4—N3	47.73 (13)	O11—C11—C16—C15	179.27 (11)
C3—N3—C4—N2	64.93 (12)	C12—C11—C16—C15	−2.31 (18)
C5—N3—C4—N2	−53.89 (12)	O21—C21—C22—C23	−179.78 (13)
C6—N4—C5—N3	61.14 (11)	C26—C21—C22—C23	0.5 (2)
C7—N4—C5—N3	−61.47 (11)	C21—C22—C23—C24	−0.8 (2)
C3—N3—C5—N4	−61.52 (11)	C22—C23—C24—C25	0.5 (2)
C4—N3—C5—N4	60.50 (11)	C22—C23—C24—N21	−177.24 (12)
C5—N4—C6—N1	−53.68 (12)	O22—N21—C24—C23	−178.98 (14)
C7—N4—C6—N1	66.39 (12)	O23—N21—C24—C23	3.85 (19)
C2—N1—C6—N4	−85.14 (12)	O22—N21—C24—C25	3.2 (2)
C3—N1—C6—N4	45.89 (13)	O23—N21—C24—C25	−173.99 (13)
C1—N2—C7—N4	85.71 (13)	C23—C24—C25—C26	0.0 (2)
C4—N2—C7—N4	−48.33 (13)	N21—C24—C25—C26	177.83 (12)
C6—N4—C7—N2	−64.98 (13)	C24—C25—C26—C21	−0.4 (2)
C5—N4—C7—N2	55.35 (13)	O21—C21—C26—C25	−179.64 (12)
O11—C11—C12—C13	−179.47 (12)	C22—C21—C26—C25	0.1 (2)
C16—C11—C12—C13	2.18 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H11···N3	0.98 (2)	1.69 (2)	2.6551 (13)	167.4 (19)
O21—H21···N1	0.93 (2)	1.82 (2)	2.7377 (14)	168.6 (19)
C26—H26···O13[i]	0.95	2.39	3.3242 (17)	166
C5—H5*A*···O11[ii]	0.99	2.56	3.4940 (15)	156
C5—H5*B*···O12[iii]	0.99	2.53	3.4284 (16)	151
C6—H6*A*···O23[iv]	0.99	2.47	3.4214 (16)	160
C25—H25···N2[v]	0.95	2.60	3.5117 (16)	160

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