



# A redetermination from the original data of the crystal structure of 2-amino-4,6-dimethoxy-pyrimidin-1-ium 4-aminobenzoate

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**Keywords:** crystal structure; redetermination; hydrogen bonding; symmetric hydrogen bonds; refinement constraints; refinement restraints.

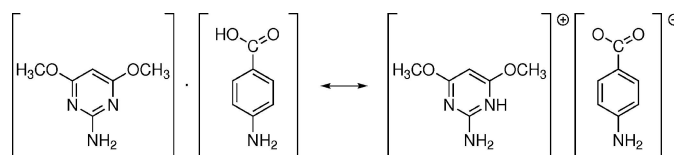
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The title structure,  $C_6H_9.5N_3O_2^{0.5+} \cdot C_7H_6.5NO_2^{0.5-}$ , which might be named schematically as 2-amino-4,6-dimethoxypyrimidine-( $\mu_2$ -hydrogen)-4-aminobenzoate to indicate a bridging H atom, has been redetermined from the data published by Thanigaimani, Muthiah & Lynch [*Acta Cryst.* (2006), E62, o2976–o2978]. The improvement of the present redetermination consists in a released geometry of the primary amine groups, which were originally assumed to be planar, as well as in a redetermination of the position of the hydroxy H atom. This H atom, whose parameters were originally constrained, turns out to be situated about the centre of the O...N hydrogen bond in two disordered positions with occupancies of 0.5 each.

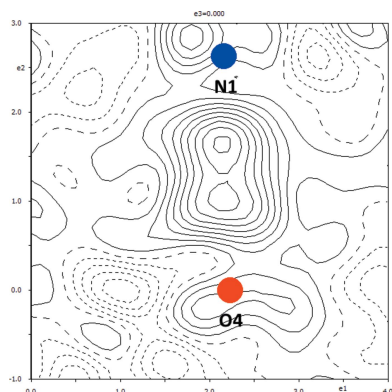
## 1. Chemical context

Structures which contain hydroxyl, secondary and primary amine groups are often determined incorrectly because of an assumed geometry of these groups from which the applied constraints or restraints were inferred. In such cases, the correct geometry is missed as it is not verified by inspection of the difference electron-density maps. Thus, a considerable number of structures could have been determined more correctly – cf. Figs. 1 and 2 in Fábry *et al.* (2014). The inclusion of such structures causes bias in crystallographic databases such as the Cambridge Structural Database (CSD; Groom & Allen, 2014).

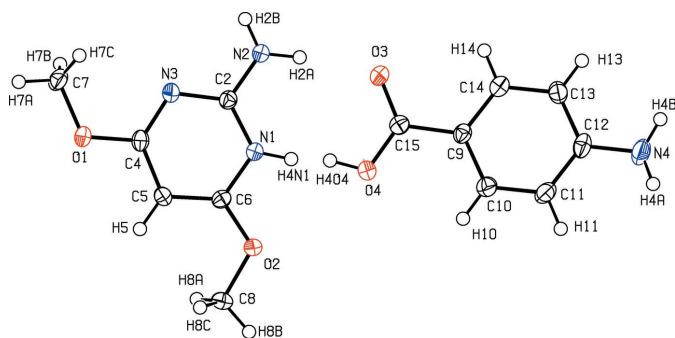


In the course of recalculation of suspect structures which were retrieved from the CSD, defects in the structure determination of 2-amino-4,6-dimethoxypyrimidine-4-aminobenzoic acid (1/1) by Thanigaimani *et al.* (2006) have been found; the pertinent CSD refcode is *IFACUO*.

The defects in the original structure concern positional parameters both of the hydroxyl and the primary amine hydrogen atoms, which follow from unsubstantiated constraints of these hydrogen atoms. This means that the amine groups were assumed to be planar while the disorder regarding atom H4 was neglected because atom H4 was forced to be situated at atom O4.



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**Figure 1**  
View of the constituent molecules of the title structure after the improved refinement. The displacement ellipsoids are depicted at the 50% probability level. The occupancies of atoms H4N1 and H4O4 are each equal to 0.5.

The aim of the present article is to demonstrate how the original structure determination can be improved.

## 2. Structural commentary

The structure of the title compound has been described by Thanigaimani *et al.* (2006) as 2-amino-4,6-dimethoxy-pyrimidine/4-aminobenzoic acid (1/1). In that article, the amine groups (centred on atoms N2 and N4) were assumed to be planar and were refined with distance constraints of N—H = 0.86 Å. For the hydroxyl group O4—H4, atom H4 was refined with a distance constraint of O4—H4 = 0.82 Å [ $U_{\text{iso}}(\text{H}_{\text{primary amine}}) = 1.2U_{\text{eq}}(\text{N}_{\text{primary amine}})$  while  $U_{\text{iso}}(\text{H4}) = 1.5U_{\text{eq}}(\text{O4})$ ].

The improved refinement by JANA2006 (Petříček *et al.*, 2014) yielded a non-planar geometry of the primary amine groups and a considerably different position for the hydrogen atom H4. This atom turns out to be disordered over two positions at about the centre of the hydrogen bond O4...N1 (Fig. 1). Thus, the title structure can be envisaged as an example of a structure with a symmetric hydrogen bond where the bridging hydrogen atom is disordered over two positions (see: for example Olovsson *et al.*, 2002). One of these positions is closer to atom N1 while the other is closer to atom O4, and correspondingly they were labelled as H4*n*1 and H4*o*4. Each of the occupancies of H4*n*1 and H4*o*4 turned out to be equal to 0.5 within the interval given by the refined standard uncertainties; *cf.* the section of the electron density map in Fig. 2. The  $pK_a$  of the conjugate acid to 2-amino-4,6-dimethoxy-pyrimidine is equal to 3.36 (Baldwin & van den Broek, 1975), while  $pK_{a1}$  and  $pK_{a2}$  of 4-aminobenzoic acid are equal to 2.50 and 4.87, respectively (CRC Handbook of Chemistry and Physics, 2009).  $pK_{a1}$  refers to the deprotonation of the hydrogen carboxylate into the carboxylate group, while  $pK_{a2}$  refers to the deprotonation of the ammonium group into the primary amine group in the solution (*cf.*  $pK_a$  for benzoic acid and aniline are equal to 4.20 and 4.87, respectively; CRC Handbook of Chemistry and Physics, 2009). Thus, 2-amino-4,6-dimethoxy-pyrimidine is a weaker acid while 4-aminobenzoic acid is a weaker base. These values favour the

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

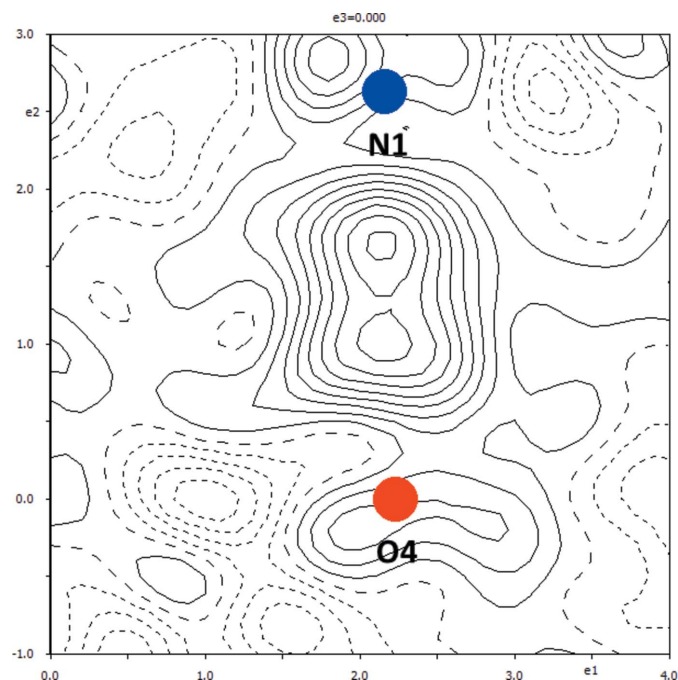
Cg1 is the centroid of the C9–C14 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H4N1...O4	0.86 (3)	1.78 (3)	2.6459 (14)	176 (2)
O4—H4O4...N1	0.89 (3)	1.77 (3)	2.6459 (14)	170 (3)
N2—H2A...O3	0.92 (1)	1.91 (1)	2.8163 (14)	172 (1)
N2—H2B...O3 <sup>i</sup>	0.88 (1)	2.04 (1)	2.8544 (14)	154 (1)
N4—H4A...O4 <sup>ii</sup>	0.92 (2)	2.27 (2)	3.1625 (15)	164 (1)
C7—H7B...O2 <sup>iii</sup>	0.96	2.59	3.4571 (15)	150
N4—H4 <i>b</i> ...Cg1 <sup>iv</sup>	0.89 (2)	2.724 (15)	3.5472 (14)	154.7 (12)

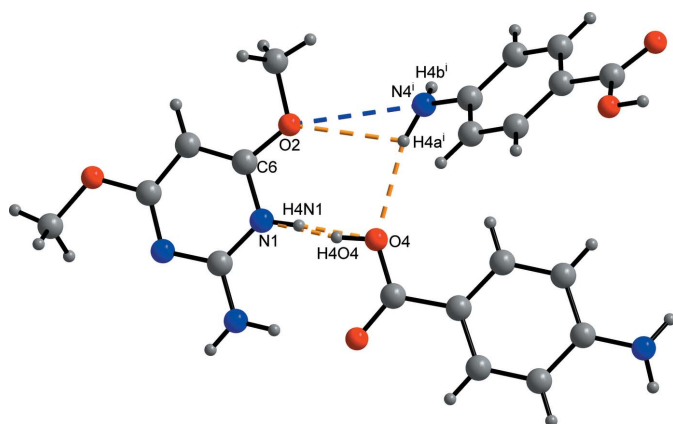
Symmetry codes: (i)  $-x + 1, -y + 2, -z$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x, -y + 1, -z$ ; (iv)  $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$ .

formation of the salt rather than of the co-crystal. Since differences in the dissociation constants are relatively mild, the hydrogen atom is situated about the centre of the hydrogen bond N1...O4 and the structure in the solid state can be envisaged as a mixture of a co-crystal 2-amino-4,6-dimethoxy-pyrimidine–4-aminobenzoic acid (1:1) with a salt 2-amino-4,6-dimethoxy-pyrimidin-1-ium 4-aminobenzoate in a 1:1 proportion. Alternatively – as has been stated above – it can be assumed to be a structure with a disordered bridging hydrogen involved in a symmetric hydrogen bond (Olovsson *et al.*, 2002).

In the recalculated structure determination, the deviation from planarity of the primary amine groups (including the C atoms to which they are attached) is larger for the one that is



**Figure 2**  
A section of the difference electron-density map for the present redetermined title structure, which shows the build-up of the electron density between the atom O4 (red) and N1 (blue). Positive and negative electron densities are indicated by continuous and dashed lines, respectively. The increment of electron density between neighbouring contours is 0.05 e Å<sup>-3</sup> (JANA2006; Petříček *et al.*, 2014).


**Figure 3**

The section of the title structure which shows the graph-set motifs  $R(7)_2^3$   $O4-H4a^1 \cdots N1-C6-O2 \cdots H4a^1 \cdots N4^i$  and  $O4 \cdots H4N1-N1-C6-O2 \cdots H4a^1 \cdots N4^i$  [symmetry code: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ; colour code for atoms: grey – C and H, blue – N; red – O; colour code for bonds: black: covalent bonds, dashed orange: H...hydrogen-bond acceptor; blue  $O2-N4$ : inclusion into the graph-set motif  $R(7)_2^3$ ].

centred on N4 [C12–N4–H4a 115.4 (9), C12–N4–H4a 114.5 (9), H4a–N4–H4b 119.5 (13) $^\circ$ ] than on N2 [C2–N2–H2a 119.5 (8), C2–N2–H2b 119.7 (8), H2a–N2–H2b 120.7 (12) $^\circ$ ]. This is in agreement with the longer bond length for C12–N4 [1.3786 (17) Å] compared to C2–N2 [1.3253 (16) Å].

In a broader sense, the present redetermination emphasizes the importance of careful examination of the difference electron-density maps during structure determinations.

### 3. Supramolecular features

The details of the hydrogen bonding and the N–H... $\pi$ -electron ring interaction involving N4–H4b are given in Table 1. The graph-set motifs (Etter *et al.*, 1990) were described by Thanigaimani *et al.* (2006) for the title structure. The graph-set motif  $R_2^3(7)$  (Fig. 3) is shown in Fig. 2 of the article by Thanigaimani *et al.* (2006) and described there as  $R_2^3(6)$ .

In the present article, the graph-set motif  $R_2^3(7)$  includes the atoms  $O4-H4a^1 \cdots N1-C6-O2 \cdots H4a^1-N4^i$  or  $O4 \cdots H4N1-N1-C6-O2 \cdots H4a^1-N4^i$  on a local scale [Fig. 3; symmetry code (i):  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ].

### 4. Database survey

The structure determination by Thanigaimani *et al.* (2006) has been included in the Cambridge Structural Database (Groom & Allen, 2014) under the refcode *IFACUO*.

### 5. Synthesis and crystallization

The preparation of the title compound has been described by Thanigaimani *et al.* (2006).

**Table 2**

Experimental details.

Crystal data	
Chemical formula	$C_6H_{9.5}N_3O_2^{0.5+} \cdot C_7H_{6.5}NO_2^{0.5-}$
$M_r$	292.30
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
$a, b, c$ (Å)	6.6358 (4), 7.5560 (5), 27.4226 (16)
$\beta$ ( $^\circ$ )	94.418 (2)
$V$ (Å $^3$ )	1370.89 (15)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm $^{-1}$ )	0.11
Crystal size (mm)	0.44 $\times$ 0.32 $\times$ 0.08
Data collection	
Diffractometer	Bruker–Nonius KappaCCD area-detector
No. of measured, independent and observed [ $I > 3\sigma(I)$ ] reflections	14577, 3130, 2302
$R_{int}$	0.032
( $\sin \theta/\lambda$ ) $_{max}$ (Å $^{-1}$ )	0.651
Refinement	
$R[F^2 > 3\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.037, 0.084, 1.91
No. of reflections	3130
No. of parameters	208
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å $^{-3}$ )	0.21, –0.23

Computer programs: *DENZO* (Otwinowski & Minor, 1997), *COLLECT* (Hooft, 1998), *SHELXS97* (Sheldrick, 2008), *PLATON* (Spek, 2009), *DIAMOND* (Brandenburg & Putz, 2005) and *JANA2006* (Petříček *et al.*, 2014).

### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the hydrogen atoms were discernible in the difference electron-density map. The aryl hydrogen atoms were constrained by the constraints  $C_{aryl}-H_{aryl} = 0.93$  Å and  $U_{iso}(H_{aryl}) = 1.2U_{eq}(C_{aryl})$  while the methyl hydrogens were constrained by the constraints  $C_{methyl}-H_{methyl} = 0.96$  Å and  $U_{iso}(H_{methyl}) = 1.5U_{eq}(C_{methyl})$ . The hydrogen atoms of the primary amine group N2 were constrained by  $U_{iso}(H_{N2}) = 1.2U_{eq}(N2)$ . The displacement parameters of the hydroxyl hydrogen H4O4 and of the secondary amine H4N1 were constrained by  $U_{iso}(H4O4) = 1.5U_{eq}(O4)$  and  $U_{iso}(H4N1) = 1.5U_{eq}(N1)$  while their positional parameters were refined freely.

The model with the refinement of the occupational factors of H4N1 and H4O4 under the condition that the sum of these occupational factors should equal to 1 resulted in the values 0.499 (25) and 0.501 (25), respectively. Therefore the occupational parameters were set to 0.5 in the final model and not further refined.

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## supporting information

*Acta Cryst.* (2016). E72, 512-515 [https://doi.org/10.1107/S2056989016004321]

## A redetermination from the original data of the crystal structure of 2-amino-4,6-dimethoxypyrimidin-1-ium 4-aminobenzoate

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### Computing details

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2014); molecular graphics: *PLATON* (Spek, 2009), *DIAMOND* (Brandenburg & Putz, 2005) and *JANA2006* (Petříček *et al.*, 2014); software used to prepare material for publication: *JANA2006* (Petříček *et al.*, 2014).

### 2-Amino-4,6-dimethoxypyrimidin-1-ium 4-aminobenzoate

#### Crystal data

$C_6H_{9.5}N_3O_2 \cdot 0.5 + C_7H_6.5NO_2 \cdot 0.5$

$M_r = 292.30$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 6.6358$  (4) Å

$b = 7.5560$  (5) Å

$c = 27.4226$  (16) Å

$\beta = 94.418$  (2)°

$V = 1370.89$  (15) Å<sup>3</sup>

$Z = 4$

$F(000) = 616$

$D_x = 1.416$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 50 reflections

$\theta = 3.5$ – $27.5$ °

$\mu = 0.11$  mm<sup>-1</sup>

$T = 293$  K

Block, colourless

$0.44 \times 0.32 \times 0.08$  mm

#### Data collection

Bruker–Nonius KappaCCD area-detector diffractometer

Radiation source: Bruker–Nonius FR591

rotating anode

Graphite monochromator

$\varphi$  and  $\omega$  scans

14577 measured reflections

3130 independent reflections

2302 reflections with  $I > 3\sigma(I)$

$R_{int} = 0.032$

$\theta_{max} = 27.5$ °,  $\theta_{min} = 3.5$ °

$h = -8$ → $8$

$k = -9$ → $9$

$l = -35$ → $35$

#### Refinement

Refinement on  $F^2$

$R[F > 3\sigma(F)] = 0.037$

$wR(F) = 0.084$

$S = 1.91$

3130 reflections

208 parameters

0 restraints

50 constraints

H atoms treated by a mixture of independent and constrained refinement

Weighting scheme based on measured s.u.'s  $w = 1/(\sigma^2(I) + 0.0004I^2)$

$$(\Delta/\sigma)_{\max} = 0.021$$

$$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

### Special details

**Refinement.** This part differs from the original article by Thanigaimani *et al.* (2006). It also differs from the refinement by Thanigaimani *et al.* (2006) by a different threshold for the consideration of the observed diffractions:  $F^2 > 3\sigma(F^2)$  has been used as criterion for observed diffractions by *JANA2006* which was used for the calculation of the corrected structural model.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	−0.31928 (12)	0.65273 (11)	−0.06555 (3)	0.0245 (3)	
O2	−0.10295 (12)	0.62305 (10)	0.10293 (3)	0.0220 (3)	
N1	0.08195 (15)	0.75282 (13)	0.04894 (4)	0.0190 (3)	
N2	0.29136 (17)	0.87608 (15)	−0.00426 (4)	0.0257 (4)	
N3	−0.01303 (15)	0.76827 (13)	−0.03671 (3)	0.0195 (3)	
C2	0.11662 (18)	0.79867 (15)	0.00265 (4)	0.0187 (4)	
C4	−0.18261 (18)	0.68662 (15)	−0.02786 (4)	0.0194 (4)	
C5	−0.23220 (18)	0.62937 (15)	0.01815 (4)	0.0201 (4)	
C6	−0.09140 (18)	0.66647 (15)	0.05581 (4)	0.0186 (4)	
C7	−0.26609 (18)	0.70054 (18)	−0.11374 (4)	0.0261 (4)	
C8	−0.26910 (18)	0.51184 (16)	0.11446 (4)	0.0244 (4)	
O3	0.54244 (13)	0.93439 (11)	0.08178 (3)	0.0263 (3)	
O4	0.31630 (13)	0.82158 (12)	0.12916 (3)	0.0258 (3)	
N4	0.9485 (2)	1.16699 (16)	0.28973 (4)	0.0366 (4)	
C9	0.60450 (18)	0.96745 (15)	0.16726 (4)	0.0198 (4)	
C10	0.5334 (2)	0.95948 (16)	0.21374 (5)	0.0252 (4)	
C11	0.6456 (2)	1.02612 (16)	0.25407 (5)	0.0286 (4)	
C12	0.8340 (2)	1.10412 (16)	0.24933 (4)	0.0251 (4)	
C13	0.90630 (19)	1.11079 (16)	0.20281 (5)	0.0254 (4)	
C14	0.79433 (19)	1.04458 (15)	0.16262 (5)	0.0227 (4)	
C15	0.48369 (18)	0.90491 (15)	0.12288 (4)	0.0202 (4)	
H2a	0.3827 (19)	0.8954 (17)	0.0219 (5)	0.0308*	
H2b	0.3152 (19)	0.9139 (17)	−0.0336 (5)	0.0308*	
H5	−0.352188	0.570355	0.022827	0.0241*	
H7a	−0.38336	0.691873	−0.13641	0.0391*	
H7b	−0.163259	0.621794	−0.123627	0.0391*	
H7c	−0.216204	0.819832	−0.113329	0.0391*	
H8a	−0.266284	0.403993	0.096019	0.0365*	
H8b	−0.257451	0.484961	0.148775	0.0365*	
H8c	−0.394276	0.572471	0.106262	0.0365*	
H4a	0.878 (2)	1.1906 (19)	0.3166 (6)	0.0439*	
H4b	1.050 (2)	1.237 (2)	0.2829 (5)	0.0439*	
H10	0.408167	0.908373	0.217631	0.0302*	
H11	0.595299	1.019027	0.284732	0.0344*	
H13	1.032145	1.160827	0.198977	0.0305*	
H14	0.845086	1.051013	0.131987	0.0273*	
H4N1	0.157 (5)	0.771 (4)	0.0756 (12)	0.0285*	0.5



H4O4	0.251 (5)	0.797 (4)	0.1004 (12)	0.0387*	0.5
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*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0216 (5)	0.0332 (5)	0.0179 (5)	-0.0044 (4)	-0.0040 (4)	0.0017 (4)
O2	0.0211 (5)	0.0274 (5)	0.0173 (5)	-0.0059 (4)	0.0009 (4)	0.0032 (4)
N1	0.0188 (6)	0.0218 (6)	0.0161 (5)	-0.0025 (5)	0.0004 (4)	-0.0001 (4)
N2	0.0232 (6)	0.0371 (7)	0.0165 (6)	-0.0107 (5)	-0.0004 (5)	0.0015 (5)
N3	0.0190 (6)	0.0212 (5)	0.0179 (5)	-0.0008 (4)	-0.0012 (4)	-0.0006 (4)
C2	0.0203 (7)	0.0184 (6)	0.0173 (6)	-0.0003 (5)	0.0008 (5)	-0.0010 (5)
C4	0.0188 (7)	0.0188 (6)	0.0201 (6)	0.0027 (5)	-0.0026 (5)	-0.0015 (5)
C5	0.0178 (7)	0.0212 (6)	0.0211 (7)	-0.0029 (5)	0.0000 (5)	0.0002 (5)
C6	0.0212 (7)	0.0171 (6)	0.0175 (6)	0.0015 (5)	0.0024 (5)	0.0007 (5)
C7	0.0260 (7)	0.0347 (8)	0.0169 (7)	0.0014 (6)	-0.0024 (6)	0.0022 (5)
C8	0.0228 (7)	0.0268 (7)	0.0239 (7)	-0.0055 (6)	0.0043 (6)	0.0043 (5)
O3	0.0258 (5)	0.0358 (5)	0.0172 (5)	-0.0057 (4)	0.0016 (4)	-0.0019 (4)
O4	0.0243 (5)	0.0324 (5)	0.0204 (5)	-0.0089 (4)	-0.0002 (4)	0.0003 (4)
N4	0.0480 (8)	0.0393 (7)	0.0209 (6)	-0.0112 (6)	-0.0072 (6)	-0.0028 (5)
C9	0.0236 (7)	0.0177 (6)	0.0176 (6)	0.0004 (5)	-0.0009 (5)	0.0006 (5)
C10	0.0294 (8)	0.0246 (7)	0.0214 (7)	-0.0043 (6)	0.0017 (6)	0.0008 (5)
C11	0.0400 (9)	0.0287 (7)	0.0171 (7)	-0.0048 (6)	0.0017 (6)	0.0005 (5)
C12	0.0341 (8)	0.0189 (6)	0.0207 (7)	0.0012 (6)	-0.0076 (6)	-0.0002 (5)
C13	0.0239 (7)	0.0261 (7)	0.0255 (7)	-0.0033 (6)	-0.0031 (6)	0.0001 (5)
C14	0.0252 (7)	0.0240 (7)	0.0189 (7)	0.0016 (6)	0.0004 (6)	0.0002 (5)
C15	0.0211 (7)	0.0196 (6)	0.0199 (7)	0.0019 (5)	0.0017 (5)	0.0010 (5)

*Geometric parameters (Å, °)*

O1—C4	1.3462 (14)	O4—H4O4	0.89 (3)
O1—C7	1.4400 (14)	N4—C12	1.3786 (17)
O2—C6	1.3411 (14)	N4—H4a	0.918 (15)
O2—C8	1.4405 (15)	N4—H4b	0.886 (15)
N1—C2	1.3525 (16)	C9—C10	1.3940 (17)
N1—C6	1.3483 (16)	C9—C14	1.4026 (17)
N1—H4N1	0.86 (3)	C9—C15	1.4821 (16)
N2—C2	1.3253 (16)	C10—C11	1.3799 (17)
N2—H2a	0.914 (13)	C10—H10	0.93
N2—H2b	0.880 (14)	C11—C12	1.3973 (19)
N3—C2	1.3472 (15)	C11—H11	0.93
N3—C4	1.3221 (15)	C12—C13	1.3980 (18)
C4—C5	1.3969 (17)	C13—C14	1.3751 (17)
C5—C6	1.3672 (16)	C13—H13	0.93
C5—H5	0.93	C14—H14	0.93
C7—H7a	0.96	H2a—H2b	1.559 (19)
C7—H7b	0.96	H7a—H7b	1.5677
C7—H7c	0.96	H7a—H7c	1.5677
C8—H8a	0.96	H7b—H7c	1.5677

C8—H8b	0.96	H8a—H8b	1.5677
C8—H8c	0.96	H8a—H8c	1.5677
O3—C15	1.2409 (15)	H8b—H8c	1.5677
O4—C15	1.2998 (15)	H4a—H4b	1.56 (2)
C4—O1—C7	117.31 (9)	H8a—C8—H8b	109.47
C6—O2—C8	117.11 (8)	H8a—C8—H8c	109.47
C2—N1—C6	117.63 (10)	H8b—C8—H8c	109.47
C2—N1—H4N1	129 (2)	C15—O4—H4O4	110 (2)
C6—N1—H4N1	114 (2)	C12—N4—H4a	115.4 (9)
C2—N2—H2a	119.5 (8)	C12—N4—H4b	114.5 (9)
C2—N2—H2b	119.7 (8)	H4a—N4—H4b	119.5 (13)
H2a—N2—H2b	120.7 (12)	C10—C9—C14	118.07 (11)
C2—N3—C4	115.62 (10)	C10—C9—C15	122.49 (11)
N1—C2—N2	117.46 (11)	C14—C9—C15	119.39 (11)
N1—C2—N3	124.33 (11)	C9—C10—C11	121.15 (12)
N2—C2—N3	118.20 (11)	C9—C10—H10	119.43
O1—C4—N3	118.71 (10)	C11—C10—H10	119.43
O1—C4—C5	116.29 (10)	C10—C11—C12	120.73 (12)
N3—C4—C5	125.00 (10)	C10—C11—H11	119.64
C4—C5—C6	115.08 (11)	C12—C11—H11	119.64
C4—C5—H5	122.46	N4—C12—C11	120.82 (12)
C6—C5—H5	122.46	N4—C12—C13	120.96 (12)
O2—C6—N1	111.45 (10)	C11—C12—C13	118.18 (11)
O2—C6—C5	126.24 (11)	C12—C13—C14	121.08 (12)
N1—C6—C5	122.31 (11)	C12—C13—H13	119.46
O1—C7—H7a	109.47	C14—C13—H13	119.46
O1—C7—H7b	109.47	C9—C14—C13	120.80 (12)
O1—C7—H7c	109.47	C9—C14—H14	119.6
H7a—C7—H7b	109.47	C13—C14—H14	119.6
H7a—C7—H7c	109.47	O3—C15—O4	122.60 (11)
H7b—C7—H7c	109.47	O3—C15—C9	120.04 (11)
O2—C8—H8a	109.47	O4—C15—C9	117.35 (11)
O2—C8—H8b	109.47	N1—H4N1—H4O4	171 (5)
O2—C8—H8c	109.47	O4—H4O4—H4N1	165 (5)

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg1 is the centroid of the C9—C14 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H4N1 $\cdots$ O4	0.86 (3)	1.78 (3)	2.6459 (14)	176 (2)
O4—H4O4 $\cdots$ N1	0.89 (3)	1.77 (3)	2.6459 (14)	170 (3)
N2—H2A $\cdots$ O3	0.92 (1)	1.91 (1)	2.8163 (14)	172 (1)
N2—H2B $\cdots$ O3 <sup>i</sup>	0.88 (1)	2.04 (1)	2.8544 (14)	154 (1)
N4—H4A $\cdots$ O4 <sup>ii</sup>	0.92 (2)	2.27 (2)	3.1625 (15)	164 (1)



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C7—H7B···O2 <sup>iii</sup>	0.96	2.59	3.4571 (15)	150
N4—H4b···Cg1 <sup>iv</sup>	0.89 (2)	2.724 (15)	3.5472 (14)	154.7 (12)

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Symmetry codes: (i)  $-x+1, -y+2, -z$ ; (ii)  $-x+1, y+1/2, -z+1/2$ ; (iii)  $-x, -y+1, -z$ ; (iv)  $-x+2, y+1/2, -z+1/2$ .