

## Hydrogen-bonding patterns in 2-amino-4,6-dimethoxypyrimidinium salicylate

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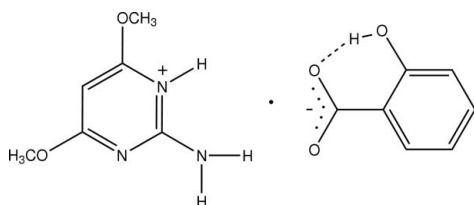
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Key indicators: single-crystal X-ray study;  $T = 120$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.054;  $wR$  factor = 0.137; data-to-parameter ratio = 16.2.

The asymmetric unit of the title compound,  $\text{C}_6\text{H}_{10}\text{N}_3\text{O}_2^+\text{-C}_7\text{H}_5\text{O}_3^-$ , contains one 2-amino-4,6-dimethoxypyrimidinium cation and a salicylate anion. The 2-amino-4,6-dimethoxypyrimidinium cation interacts with the carboxylate group of the salicylate anion through a pair of nearly parallel  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds, forming an  $R_2^2(8)$  ring motif. These motifs are centrosymmetrically paired *via*  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds, forming a complementary *DDAA* array. The typical intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond is observed in the anion. The salicylate ions form a hydrogen-bonded supramolecular chain along the  $c$  axis *via*  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds involving a benzene hydrogen and one of the O atoms of the carboxylate group.

### Related literature

For related literature, see: Baker & Santi (1965); Bernstein *et al.* (1995); Chinnakali *et al.* (1999); Cochran (1953); Desiraju (1989); Etter (1990); Etter & Adsmund (1990); Hunt *et al.* (1980); Hunter (1994); Low *et al.* (2002); Lynch & Jones (2004); Muthiah, Balasubramani *et al.* (2006); Muthiah, Francis *et al.* (2006); Raj *et al.* (2003); Robert *et al.* (2001); Scheinbeim & Schempp (1976); Schwalbe & Williams (1982); Singh & Vijayan (1974); Subashini *et al.* (2007); Thanigaimani *et al.* (2006, 2007*a,b*); Umadevi *et al.* (2002); Varughese & Kartha (1982).



### Experimental

#### Crystal data

$\text{C}_6\text{H}_{10}\text{N}_3\text{O}_2^+\text{-C}_7\text{H}_5\text{O}_3^-$   
 $M_r = 293.28$   
 Monoclinic,  $P2_1/c$   
 $a = 9.1071$  (3) Å  
 $b = 14.7657$  (6) Å  
 $c = 12.2829$  (6) Å  
 $\beta = 123.465$  (3)°

$V = 1377.90$  (11) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 120$  K  
 $0.30 \times 0.30 \times 0.08$  mm

#### Data collection

Bruker–Nonius KappaCCD area-detector diffractometer  
 Absorption correction: none  
 14310 measured reflections

3136 independent reflections  
 2465 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.034$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.137$   
 $S = 1.11$   
 3136 reflections

194 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.66$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.72$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O3}$	0.86	1.81	2.675 (2)	178
$\text{N2}-\text{H2A}\cdots\text{O4}^i$	0.86	2.00	2.8216 (16)	159
$\text{N2}-\text{H2B}\cdots\text{O4}$	0.86	1.97	2.822 (2)	173
$\text{O5}-\text{H5A}\cdots\text{O3}$	0.82	1.82	2.5486 (17)	147
$\text{C11}-\text{H11}\cdots\text{O4}^i$	0.93	2.58	3.4753 (19)	161

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

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2576).

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**supplementary materials**

*Acta Cryst.* (2007). E63, o4555-o4556 [ doi:10.1107/S1600536807054621 ]

## Hydrogen-bonding patterns in 2-amino-4,6-dimethoxypyrimidinium salicylate

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### Comment

Aminopyrimidine-carboxylate interactions are of fundamental importance since they are involved in protein-nucleic acids recognition and protein-drug binding (Hunt *et al.*, 1980; Baker & Santi, 1965). Hydrogen bonding plays a key role in molecular recognition and crystal engineering research (Desiraju, 1989). 2-Aminopyrimidine forms 1:1 adduct with different mono and dicarboxylic acids (Etter & Adson, 1990) rather than individual self-assembly compounds (Scheinbeim & Schempp, 1976). The adducts of carboxylic acid with 2-amino heterocyclic ring system have a graph-set motif [ $R_2^2(8)$ ] (Lynch & Jones, 2004). This motif is very robust in aminopyrimidine- carboxylic acid/ carboxylate systems. The crystal structures of aminopyrimidine derivatives (Schwalbe & Williams, 1982), aminopyrimidine carboxylates (Muthiah, Francis *et al.*, 2006) and co-crystals (Chinnakali *et al.*, 1999) have been reported. Salicylic acid (Cochran *et al.*, 1953) and its derivatives are widely used as analgesic. They are also used for various gastric tympany and also used externally as antiseptic and antifungal agents for various skin conditions. The crystal structure of salicylic acid and its complexes, for example, antipyrine-salicylic acid (salipyrine) (Singh & Vijayan, 1974) and piperazinedione-salicylic acid (1:2) (Varughese & Kartha, 1982) have been reported in literature. The crystal structure of 2-amino-4,6-dimethoxy pyrimidine has also been reported (Low *et al.*, 2002). The crystal structures of 2-amino-4,6-dimethylpyrimidinium salicylate (Muthiah, Balasubramani *et al.* 2006), 2-amino-4,6-dimethoxy pyrimidine-4-aminobenzoic acid (1/1) (Thanigaimani *et al.*, 2006) and 2-amino-4,6-dimethoxy pyrimidine phthalic acid (1/1) (Thanigaimani *et al.*, 2007a) and 2-amino-4,6- dimethoxypyrimidinium 4-hydroxybenzoate monohydrate, 2-amino-4,6- dimethoxypyrimidinium 6-carboxypyridine-2-carboxylate monohydrate and 2-amino-4,6-dimethoxypyrimidinium hydrogen (2*R*, 3*R*)-tartrate 2-amino-4,6-dimethoxypyrimidine (Thanigaimani *et al.*, 2007b) have been recently reported from our laboratory. The present study investigates the hydrogen bonding patterns in 2-amino-4,6-dimethoxy pyrimidinium salicylate (I).

The asymmetric unit (Fig 1) contains one 2-amino-4,6-dimethoxypyrimidinium cation and a salicylate anion, The 2-amino-4,6-dimethoxy pyrimidinium cation is protonated at N1. Protonation of the pyrimidine base on the N1 site is reflected by an increase in bond angle. The C2—N3—C4 angle of the unprotonated atom N3 is 116.08 (13)° while for protonated atom N1, the C2—N1—C6 angle is 120.19 (15)°. The carboxylate group of the salicylate anion interacts with the protonated atom N1 and the 2-amino group of the pyrimidine moiety through a pair of N—H···O hydrogen bonds, forming an eight membered  $R_2^2(8)$  ring motif (Etter, 1990; Bernstein *et al.*, 1995). These motifs are centrosymmetrically paired *via* N—H···O hydrogen bonds to produce the DDAA (D=donor in hydrogen bonds, A=acceptor in hydrogen bonds) array of quadruple hydrogen bonds. This can be represented by the graph-set notation  $R_2^2(8)$ ,  $R_4^2(8)$  and  $R_2^2(8)$  (Fig. 2). This type of array has also been identified in trimethoprim hydrogen glutarate (Robert *et al.*, 2001), trimethoprim formate (Umadevi *et al.*, 2002), trimethoprim- *m*-chlorobenzoate (Raj *et al.*, 2003) and pyrimethaminium 3,5-dinitrobenzoate (Subashini *et al.*, 2007). But this array is absent in the crystal structure of a related compound, 2-amino-4,6-dimethylpyrimidinium salicylate (Muthiah, Balasubramani *et al.* 2006) where the bases are paired. In the title compound, these arrays are further connected *via* C—H···O hydrogen bonds. The salicylate ions form a hydrogen-bonded supramolecular chain along the *c* axis, *via* C—H···O hydrogen bonds involving benzene hydrogen (C11) and one of the oxygen atoms of the carboxylate group, as

## supplementary materials

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shown in Fig 3. There is a typical intramolecular hydrogen bond between the phenolic –OH group and the carboxylate group of the salicylate anion [S(6)].  $\pi$ - $\pi$  stacking interactions between the aromatic rings are also observed. The pyrimidine ring of 2-amino-4,6-dimethoxy pyrimidinium cation has stacking interactions with the benzene rings of salicylate anion, with a perpendicular separation of 3.280 Å, a centroid-to-centroid distance of 3.6363 (8) and slip angle (the angle between the centroid vector and the normal to the plan) of 21.03°. These are typical aromatic stacking values (Hunter, 1994).

### Experimental

A hot methanolic solution (20 ml) of 2-amino-4,6-dimethoxy pyrimidine (38 mg, Aldrich) and salicylic acid (34 mg, Loba chemie) was warmed for half an hour over a water bath. The mixture was cooled slowly and kept at room temperature. After a few days colourless plate-like crystals were obtained.

### Refinement

All H atoms were positioned geometrically and were refined using a riding model. The C—H, O—H and N—H bond lengths are 0.93–0.96, 0.82 and 0.86 Å, respectively [ $U_{\text{iso}}(\text{H})=1.2 U_{\text{eq}}(\text{parent atom})$ ]. The highest peak in the final difference map ( $0.66 \text{ e } \text{Å}^{-3}$ ) is at 1.55Å from N1, the deepest hole ( $-0.72 \text{ e } \text{Å}^{-3}$ ) is at 0.75Å from N2.

### Figures

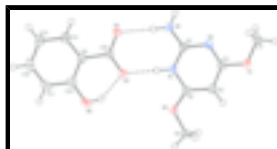


Fig. 1. An *ORTEP* view of the asymmetric unit of (I) showing 50% probability displacement ellipsoids.

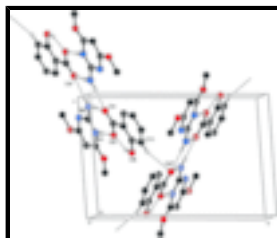


Fig. 2. Hydrogen bonding patterns in compound (I). [symmetry code: (i)  $-x + 2, -y, -z + 2$   
(ii)  $x, -y + 1/2, z - 1/2$ ]

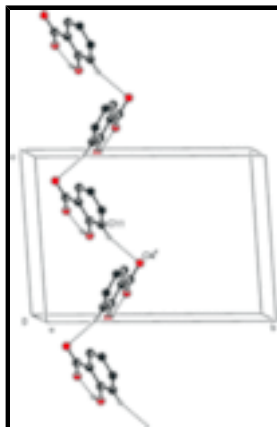


Fig. 3. Hydrogen-bonding (dashed lines) patterns in the supramolecular chain in compound (I) [symmetry code: (ii)  $x, -y + 1/2, z - 1/2$ ]

**2-amino-4,6-dimethoxypyrimidinium salicylate**

*Crystal data*

$C_6H_{10}N_3O_2^+ \cdot C_7H_5O_3^-$	$F_{000} = 616$
$M_r = 293.28$	$D_x = 1.414 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P 2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 9.1071 (3) \text{ \AA}$	Cell parameters from 25 reflections
$b = 14.7657 (6) \text{ \AA}$	$\theta = 3.8\text{--}27.5^\circ$
$c = 12.2829 (6) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$\beta = 123.465 (3)^\circ$	$T = 120 \text{ K}$
$V = 1377.90 (11) \text{ \AA}^3$	Plate-like, colourless
$Z = 4$	$0.30 \times 0.30 \times 0.08 \text{ mm}$

*Data collection*

Bruker–Nonius Kappa CCD area-detector diffractometer	2465 reflections with $I > 2\sigma(I)$
Radiation source: Bruker–Nonius FR591 rotating anode	$R_{\text{int}} = 0.034$
Monochromator: graphite	$\theta_{\text{max}} = 27.5^\circ$
$T = 120 \text{ K}$	$\theta_{\text{min}} = 3.9^\circ$
$\varphi$ and $\omega$ scans	$h = -11 \rightarrow 11$
Absorption correction: none	$k = -17 \rightarrow 19$
14310 measured reflections	$l = -15 \rightarrow 15$
3136 independent reflections	

*Refinement*

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2 + 0.2362P]$
$wR(F^2) = 0.137$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3136 reflections	$\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
194 parameters	$\Delta\rho_{\text{min}} = -0.72 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: shelxl,
Secondary atom site location: difference Fourier map	$FC^* = KFC[1 + 0.001XFC^2\Lambda^3/\text{SIN}(2\Theta)]^{-1/4}$
	Extinction coefficient: 0.068 (6)

## supplementary materials

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### Special details

**Geometry.** Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All e.s.d.'s are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**Refinement.** Refinement on  $F^2$  for ALL reflections except those flagged by the user for potential systematic errors. Weighted  $R$ -factors  $wR$  and all goodnesses of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The observed criterion of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $-R$ -factor-obs *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.20130 (12)	-0.06793 (7)	0.72454 (10)	0.0246 (3)
O2	0.37869 (12)	0.09584 (7)	0.48494 (10)	0.0217 (3)
N1	0.56670 (15)	0.04949 (8)	0.68864 (12)	0.0189 (3)
N2	0.77862 (15)	0.00635 (9)	0.89739 (12)	0.0250 (4)
N3	0.49174 (15)	-0.03420 (8)	0.81536 (12)	0.0199 (4)
C2	0.61084 (17)	0.00665 (9)	0.80033 (14)	0.0192 (4)
C4	0.32600 (18)	-0.03031 (10)	0.71396 (14)	0.0194 (4)
C5	0.26878 (18)	0.01071 (10)	0.59397 (14)	0.0206 (4)
C6	0.39631 (17)	0.05140 (9)	0.58543 (14)	0.0184 (4)
C7	0.2563 (2)	-0.11184 (12)	0.84644 (17)	0.0301 (5)
C8	0.20153 (17)	0.10678 (10)	0.37204 (14)	0.0216 (4)
O3	0.81007 (12)	0.13044 (7)	0.66450 (10)	0.0246 (3)
O4	1.03098 (13)	0.07809 (7)	0.85566 (10)	0.0238 (3)
O5	0.86976 (14)	0.22213 (8)	0.51703 (11)	0.0291 (3)
C9	1.10073 (18)	0.16797 (9)	0.72967 (14)	0.0189 (4)
C10	1.04166 (19)	0.21540 (10)	0.61315 (15)	0.0223 (4)
C11	1.1641 (2)	0.25754 (10)	0.59510 (17)	0.0275 (5)
C12	1.3417 (2)	0.25220 (11)	0.69058 (17)	0.0292 (5)
C13	1.4024 (2)	0.20592 (11)	0.80650 (17)	0.0281 (5)
C14	1.28197 (18)	0.16428 (10)	0.82527 (15)	0.0229 (4)
C15	0.97425 (18)	0.12227 (9)	0.75325 (14)	0.0187 (4)
H1	0.64680	0.07550	0.68300	0.0230*
H2A	0.81090	-0.02000	0.96980	0.0300*
H2B	0.85550	0.03250	0.88820	0.0300*
H5	0.15130	0.01020	0.52460	0.0250*
H7A	0.32260	-0.16530	0.85630	0.0450*
H7B	0.15440	-0.12830	0.84660	0.0450*
H7C	0.32830	-0.07110	0.91750	0.0450*
H8A	0.14990	0.04830	0.33880	0.0320*
H8B	0.20420	0.13990	0.30590	0.0320*
H8C	0.13260	0.13940	0.39630	0.0320*
H5A	0.81080	0.19490	0.53830	0.0440*

H11	1.12590	0.28930	0.51850	0.0330*
H12	1.42210	0.28000	0.67710	0.0350*
H13	1.52220	0.20300	0.87050	0.0340*
H14	1.32190	0.13330	0.90270	0.0280*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0199 (5)	0.0316 (6)	0.0247 (6)	-0.0019 (4)	0.0139 (4)	0.0051 (5)
O2	0.0179 (5)	0.0281 (6)	0.0174 (5)	-0.0004 (4)	0.0086 (4)	0.0049 (4)
N1	0.0159 (6)	0.0222 (6)	0.0192 (6)	-0.0008 (4)	0.0101 (5)	0.0018 (5)
N2	0.0186 (6)	0.0342 (8)	0.0209 (7)	0.0001 (5)	0.0100 (5)	0.0089 (5)
N3	0.0193 (6)	0.0209 (6)	0.0210 (7)	0.0020 (5)	0.0120 (5)	0.0025 (5)
C2	0.0197 (7)	0.0185 (7)	0.0209 (7)	0.0027 (5)	0.0121 (6)	0.0018 (5)
C4	0.0221 (7)	0.0175 (7)	0.0227 (8)	0.0006 (5)	0.0150 (6)	-0.0003 (6)
C5	0.0181 (6)	0.0223 (8)	0.0210 (7)	-0.0008 (5)	0.0105 (6)	-0.0002 (6)
C6	0.0194 (7)	0.0185 (7)	0.0167 (7)	0.0019 (5)	0.0096 (6)	-0.0005 (5)
C7	0.0276 (8)	0.0366 (9)	0.0314 (9)	0.0020 (7)	0.0197 (7)	0.0108 (7)
C8	0.0184 (7)	0.0246 (8)	0.0170 (7)	0.0006 (5)	0.0067 (6)	0.0029 (6)
O3	0.0181 (5)	0.0307 (6)	0.0212 (6)	-0.0016 (4)	0.0085 (4)	0.0052 (4)
O4	0.0224 (5)	0.0291 (6)	0.0186 (6)	-0.0017 (4)	0.0105 (4)	0.0045 (4)
O5	0.0305 (6)	0.0311 (6)	0.0234 (6)	-0.0006 (5)	0.0135 (5)	0.0056 (5)
C9	0.0226 (7)	0.0155 (7)	0.0211 (8)	-0.0019 (5)	0.0137 (6)	-0.0029 (5)
C10	0.0283 (8)	0.0184 (7)	0.0231 (8)	-0.0005 (6)	0.0160 (6)	-0.0020 (6)
C11	0.0428 (9)	0.0189 (8)	0.0317 (9)	-0.0017 (6)	0.0274 (8)	0.0008 (6)
C12	0.0364 (8)	0.0213 (8)	0.0456 (10)	-0.0066 (6)	0.0325 (8)	-0.0055 (7)
C13	0.0239 (7)	0.0245 (8)	0.0388 (10)	-0.0025 (6)	0.0191 (7)	-0.0058 (7)
C14	0.0236 (7)	0.0195 (7)	0.0279 (8)	-0.0019 (5)	0.0156 (6)	-0.0029 (6)
C15	0.0212 (7)	0.0164 (7)	0.0186 (7)	-0.0014 (5)	0.0111 (6)	-0.0023 (5)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C4	1.333 (2)	C5—H5	0.9303
O1—C7	1.444 (2)	C7—H7A	0.9601
O2—C6	1.3272 (18)	C7—H7C	0.9604
O2—C8	1.4439 (19)	C7—H7B	0.9604
O3—C15	1.281 (2)	C8—H8B	0.9600
O4—C15	1.2482 (18)	C8—H8C	0.9598
O5—C10	1.348 (2)	C8—H8A	0.9600
O5—H5A	0.8203	C9—C14	1.403 (2)
N1—C2	1.3548 (19)	C9—C15	1.495 (3)
N1—C6	1.359 (2)	C9—C10	1.407 (2)
N2—C2	1.322 (2)	C10—C11	1.397 (3)
N3—C4	1.326 (2)	C11—C12	1.380 (3)
N3—C2	1.340 (2)	C12—C13	1.390 (2)
N1—H1	0.8603	C13—C14	1.383 (3)
N2—H2B	0.8598	C11—H11	0.9302
N2—H2A	0.8605	C12—H12	0.9305
C4—C5	1.401 (2)	C13—H13	0.9297



## supplementary materials

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C5—C6	1.362 (3)	C14—H14	0.9298
O1…C8 <sup>i</sup>	3.224 (2)	C11…H8B <sup>x</sup>	2.8439
O2…C6 <sup>ii</sup>	3.410 (2)	C12…H8B <sup>x</sup>	2.8406
O2…N1 <sup>ii</sup>	3.2507 (17)	C13…H8B <sup>x</sup>	2.9028
O3…O5	2.5486 (17)	C14…H8B <sup>x</sup>	2.9551
O3…N1	2.675 (2)	C15…H8A <sup>ii</sup>	2.7368
O4…N2	2.822 (2)	C15…H5A	2.4500
O4…N2 <sup>iii</sup>	2.8216 (16)	C15…H2B	2.7661
O5…O3	2.5486 (17)	C15…H1	2.6975
O1…H8C <sup>i</sup>	2.7542	C15…H11 <sup>iv</sup>	3.0438
O1…H8A <sup>i</sup>	2.8592	H1…O3	1.8147
O3…H5A	1.8221	H1…C15	2.6975
O3…H8A <sup>ii</sup>	2.6676	H1…H2B	2.2550
O3…H1	1.8147	H2A…O4 <sup>iii</sup>	2.0002
O4…H2A <sup>iii</sup>	2.0002	H2A…H2B <sup>iii</sup>	2.5421
O4…H14	2.5159	H2B…H1	2.2550
O4…H8A <sup>ii</sup>	2.7499	H2B…N2 <sup>iii</sup>	2.9478
O4…H11 <sup>iv</sup>	2.5836	H2B…C15	2.7661
O4…H2B	1.9676	H2B…O4	1.9676
O5…H7B <sup>v</sup>	2.8527	H2B…H2A <sup>iii</sup>	2.5421
O5…H13 <sup>vi</sup>	2.8631	H5…H8A	2.3437
N1…O2 <sup>ii</sup>	3.2507 (17)	H5…C8	2.5884
N1…O3	2.675 (2)	H5…H5 <sup>i</sup>	2.4927
N2…O4	2.822 (2)	H5…H8C	2.4199
N2…O4 <sup>iii</sup>	2.8216 (16)	H5A…C15	2.4500
N2…H2B <sup>iii</sup>	2.9478	H5A…O3	1.8221
N3…H7C	2.4791	H7A…N3	2.6883
N3…H12 <sup>vii</sup>	2.8409	H7B…C8 <sup>i</sup>	2.8670
N3…H7A	2.6883	H7B…O5 <sup>xi</sup>	2.8527
C2…C13 <sup>viii</sup>	3.525 (2)	H7C…N3	2.4791
C4…C14 <sup>viii</sup>	3.300 (2)	H8A…C5	2.7498
C5…C14 <sup>viii</sup>	3.585 (2)	H8A…C15 <sup>ii</sup>	2.7368
C6…C13 <sup>viii</sup>	3.524 (2)	H8A…H5	2.3437
C6…O2 <sup>ii</sup>	3.410 (2)	H8A…O1 <sup>i</sup>	2.8592
C6…C12 <sup>viii</sup>	3.379 (2)	H8A…O3 <sup>ii</sup>	2.6676
C7…C8 <sup>i</sup>	3.500 (3)	H8A…O4 <sup>ii</sup>	2.7499
C8…O1 <sup>i</sup>	3.224 (2)	H8B…C10 <sup>vi</sup>	2.9149
C8…C7 <sup>i</sup>	3.500 (3)	H8B…C11 <sup>vi</sup>	2.8439
C8…C14 <sup>vi</sup>	3.572 (2)	H8B…C9 <sup>vi</sup>	2.9732
C12…C6 <sup>ix</sup>	3.379 (2)	H8B…C12 <sup>vi</sup>	2.8406
C13…C6 <sup>ix</sup>	3.524 (2)	H8B…C13 <sup>vi</sup>	2.9028
C13…C2 <sup>ix</sup>	3.525 (2)	H8B…C14 <sup>vi</sup>	2.9551

C14...C8 <sup>x</sup>	3.572 (2)	H8C...C11 <sup>viii</sup>	2.8836
C14...C5 <sup>ix</sup>	3.585 (2)	H8C...H5	2.4199
C14...C4 <sup>ix</sup>	3.300 (2)	H8C...O1 <sup>i</sup>	2.7542
C5...H8C	2.7790	H8C...C5	2.7790
C5...H8A	2.7498	H11...O4 <sup>xii</sup>	2.5836
C8...H7B <sup>i</sup>	2.8670	H11...C15 <sup>xii</sup>	3.0438
C8...H5	2.5884	H12...N3 <sup>xiii</sup>	2.8409
C9...H8B <sup>x</sup>	2.9732	H13...O5 <sup>x</sup>	2.8631
C10...H8B <sup>x</sup>	2.9149	H14...O4	2.5159
C11...H8C <sup>ix</sup>	2.8836		
C4—O1—C7	117.45 (13)	O2—C8—H8A	109.49
C6—O2—C8	116.52 (13)	O2—C8—H8C	109.50
C10—O5—H5A	109.45	H8A—C8—H8B	109.47
C2—N1—C6	120.19 (15)	O2—C8—H8B	109.48
C2—N3—C4	116.08 (13)	H8B—C8—H8C	109.46
C2—N1—H1	119.91	H8A—C8—H8C	109.43
C6—N1—H1	119.90	C10—C9—C15	121.24 (15)
H2A—N2—H2B	120.00	C14—C9—C15	119.80 (13)
C2—N2—H2A	119.99	C10—C9—C14	118.96 (16)
C2—N2—H2B	120.01	O5—C10—C11	118.12 (14)
N2—C2—N3	119.69 (13)	C9—C10—C11	119.48 (16)
N1—C2—N3	122.61 (15)	O5—C10—C9	122.40 (17)
N1—C2—N2	117.70 (15)	C10—C11—C12	120.23 (16)
O1—C4—C5	116.09 (15)	C11—C12—C13	121.08 (19)
N3—C4—C5	125.24 (17)	C12—C13—C14	119.03 (18)
O1—C4—N3	118.67 (13)	C9—C14—C13	121.22 (15)
C4—C5—C6	115.68 (15)	O3—C15—C9	117.08 (13)
N1—C6—C5	120.17 (14)	O4—C15—C9	119.75 (15)
O2—C6—C5	128.23 (15)	O3—C15—O4	123.17 (16)
O2—C6—N1	111.60 (15)	C10—C11—H11	119.93
C4—C5—H5	122.19	C12—C11—H11	119.84
C6—C5—H5	122.13	C11—C12—H12	119.47
O1—C7—H7B	109.43	C13—C12—H12	119.45
O1—C7—H7C	109.49	C12—C13—H13	120.49
O1—C7—H7A	109.53	C14—C13—H13	120.48
H7A—C7—H7C	109.49	C9—C14—H14	119.42
H7B—C7—H7C	109.44	C13—C14—H14	119.37
H7A—C7—H7B	109.44		
C7—O1—C4—N3	-0.8 (2)	C15—C9—C10—O5	-0.2 (2)
C7—O1—C4—C5	179.19 (14)	C15—C9—C10—C11	179.72 (14)
C8—O2—C6—N1	-176.54 (12)	C10—C9—C14—C13	-0.3 (2)
C8—O2—C6—C5	3.4 (2)	C15—C9—C14—C13	-179.94 (16)
C2—N1—C6—O2	-179.69 (13)	C10—C9—C15—O3	-1.9 (2)
C2—N1—C6—C5	0.4 (2)	C10—C9—C15—O4	177.55 (14)
C6—N1—C2—N2	179.57 (13)	C14—C9—C15—O3	177.71 (13)
C6—N1—C2—N3	-0.8 (2)	C14—C9—C15—O4	-2.8 (2)
C4—N3—C2—N2	179.46 (14)	C14—C9—C10—C11	0.1 (2)

## supplementary materials

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C4—N3—C2—N1	-0.2 (2)	C14—C9—C10—O5	-179.83 (14)
C2—N3—C4—C5	1.6 (2)	C9—C10—C11—C12	0.4 (2)
C2—N3—C4—O1	-178.40 (13)	O5—C10—C11—C12	-179.73 (15)
O1—C4—C5—C6	178.04 (13)	C10—C11—C12—C13	-0.6 (3)
N3—C4—C5—C6	-2.0 (2)	C11—C12—C13—C14	0.4 (3)
C4—C5—C6—N1	0.9 (2)	C12—C13—C14—C9	0.1 (3)
C4—C5—C6—O2	-179.03 (14)		

Symmetry codes: (i)  $-x, -y, -z+1$ ; (ii)  $-x+1, -y, -z+1$ ; (iii)  $-x+2, -y, -z+2$ ; (iv)  $x, -y+1/2, z+1/2$ ; (v)  $-x+1, y+1/2, -z+3/2$ ; (vi)  $x-1, -y+1/2, z-1/2$ ; (vii)  $-x+2, y-1/2, -z+3/2$ ; (viii)  $x-1, y, z$ ; (ix)  $x+1, y, z$ ; (x)  $x+1, -y+1/2, z+1/2$ ; (xi)  $-x+1, y-1/2, -z+3/2$ ; (xii)  $x, -y+1/2, z-1/2$ ; (xiii)  $-x+2, y+1/2, -z+3/2$ .

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O3	0.86	1.81	2.675 (2)	178
N2—H2A $\cdots$ O4 <sup>iii</sup>	0.86	2.00	2.8216 (16)	159
N2—H2B $\cdots$ O4	0.86	1.97	2.822 (2)	173
O5—H5A $\cdots$ O3	0.82	1.82	2.5486 (17)	147
C11—H11 $\cdots$ O4 <sup>xii</sup>	0.93	2.58	3.4753 (19)	161

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

Fig. 1

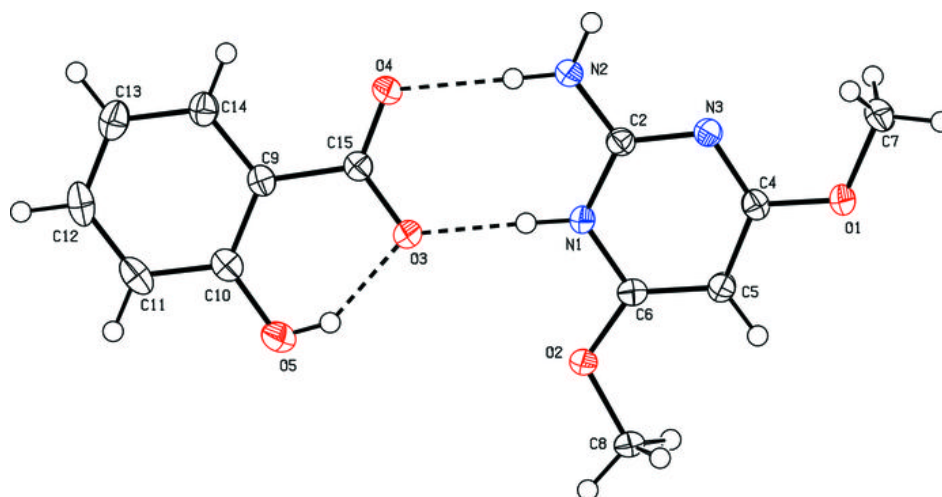


Fig. 2

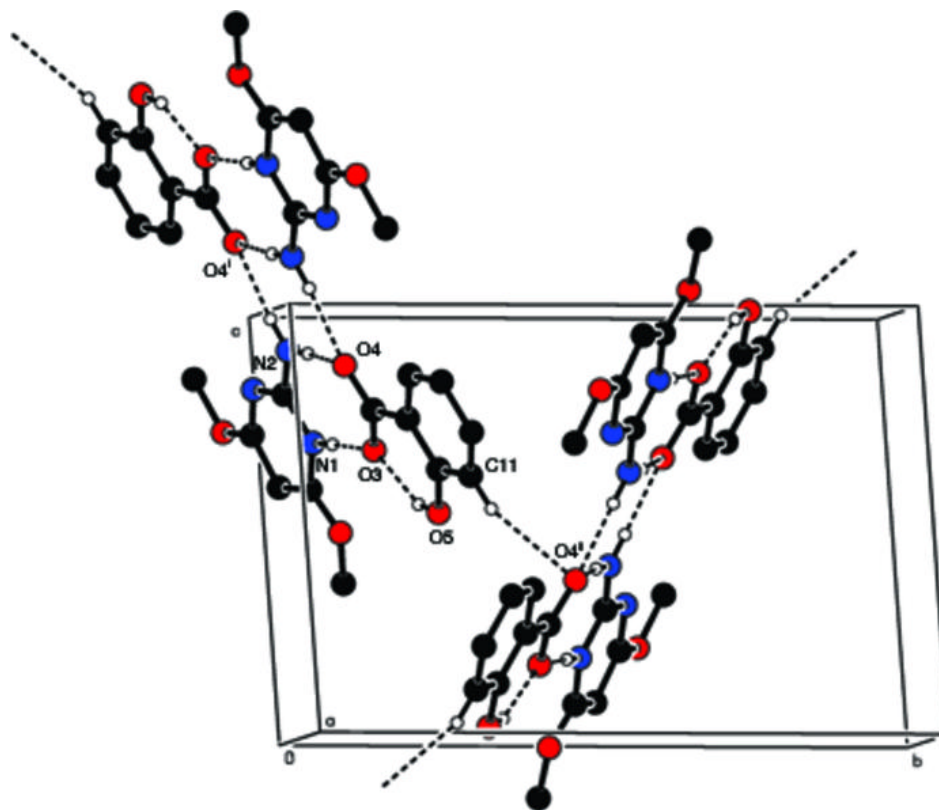


Fig. 3

