

## 2-Aminopyridinium 2-methoxycarbonyl-4,6-dinitrophenolate

Dong-Liang Wu and Zi-Jing Xiao\*

College of Materials Science & Engineering, Huaqiao University, Xiamen 361021, People's Republic of China

Correspondence e-mail: xzj@hqu.edu.cn

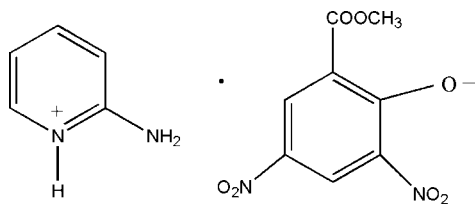
Received 18 October 2011; accepted 8 December 2011

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.040;  $wR$  factor = 0.111; data-to-parameter ratio = 14.5.

In the title molecular salt,  $\text{C}_5\text{H}_7\text{N}_2^+\cdot\text{C}_8\text{H}_5\text{N}_2\text{O}_7^-$ , the 2-aminopyridinium cation is essentially planar, with a maximum deviation of 0.015 (1) Å, while the 2-methoxycarbonyl-4,6-dinitrophenolate anion is slightly twisted away from planarity, with a maximum deviation of 0.187 (1) Å. Deprotonation of the hydroxy O atom was observed. The cation and anion are connected by four bifurcated  $\text{N}-\text{H}\cdots(\text{O},\text{O})$  hydrogen bonds, forming a molecular proton-transfer adduct. The dihedral angle between the pyridinium ring in the cation and the benzene ring in the anion is 3.65 (6)°. Every adduct connects to six neighboring adducts by  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, yielding extended layers parallel to the  $bc$  plane. There is a weak  $\pi-\pi$  interaction between the benzene rings of two neighboring anions; the interplanar spacing and the centroid-centroid separation are 3.309 (1) and 3.69 (1) Å, respectively.

### Related literature

For the structures of molecular proton-transfer adducts containing substituted pyridinium and an acid anion, see Gellert & Hsu (1988); Smith *et al.* (2000); Jebas *et al.* (2006); Rademeyer (2007); Hemamalini & Fun (2010*a,b,c*); Perpétuo & Janczak (2010). For comparable structures, see: Jebas *et al.* (2006); Perpétuo & Janczak (2010); Hemamalini & Fun (2010*a*). For the synthesis of 3,5-dinitromethyl salicylate, see: Bartlett & Trachten (1958).



### Experimental

#### Crystal data

$\text{C}_5\text{H}_7\text{N}_2^+\cdot\text{C}_8\text{H}_5\text{N}_2\text{O}_7^-$

$M_r = 336.27$

Monoclinic,  $P2_1/n$

$a = 7.4088$  (3) Å

$b = 19.1779$  (6) Å

$c = 9.9784$  (4) Å

$\beta = 98.2825$  (15)°

$V = 1403.00$  (9) Å<sup>3</sup>

$Z = 4$

Mo  $K\alpha$  radiation

$\mu = 0.13$  mm<sup>-1</sup>

$T = 293$  K

0.35 × 0.35 × 0.26 mm

#### Data collection

Rigaku R-Axis SPIDER IP diffractometer

Absorption correction:  $\psi$  scan (TEXRAY; Molecular Structure Corporation, 1999)

$T_{\min} = 0.951$ ,  $T_{\max} = 0.969$

21789 measured reflections

3200 independent reflections

2760 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.111$

$S = 1.09$

3200 reflections

221 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.32$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.30$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H01A}\cdots\text{O3}$	0.90	1.88	2.6864 (13)	148
$\text{N1}-\text{H01A}\cdots\text{O2}$	0.90	2.23	2.8783 (14)	130
$\text{N2}-\text{H02A}\cdots\text{O3}$	0.88	2.01	2.7592 (14)	142
$\text{N2}-\text{H02A}\cdots\text{O4}$	0.88	2.45	3.2082 (15)	144
$\text{N2}-\text{H02B}\cdots\text{O6}^i$	0.87	2.24	3.0537 (14)	155
$\text{C4}-\text{H4A}\cdots\text{O7}^{ii}$	0.93	2.57	3.2052 (16)	126
$\text{C5}-\text{H5A}\cdots\text{O5}^{iii}$	0.93	2.42	3.2604 (17)	151

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

Data collection: *RAPID-AUTO* (Rigaku, 2008); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*.

This project was supported financially by the Natural Science Foundation of China (No. 50971063) and the Natural Science Foundation of Fujian Province (Nos. E0640006, 2003F006, 2010J01042).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2268).

### References

- Bartlett, P. D. & Trachten, E. N. (1958). *J. Am. Chem. Soc.* **80**, 5808–5812.  
 Gellert, R. W. & Hsu, I.-N. (1988). *Acta Cryst.* **C44**, 311–313.  
 Hemamalini, M. & Fun, H.-K. (2010*a*). *Acta Cryst.* **E66**, o691–o692.  
 Hemamalini, M. & Fun, H.-K. (2010*b*). *Acta Cryst.* **E66**, o1418–o1419.  
 Hemamalini, M. & Fun, H.-K. (2010*c*). *Acta Cryst.* **E66**, o2323–o2324.  
 Jebas, S. R., Balasubramanian, T., Peschar, R. & Fraanje, J. (2006). *Acta Cryst.* **E62**, o2606–o2607.

- McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
- Molecular Structure Corporation (1999). *TEXRAY*. MSC, The Woodlands, Texas, USA.
- Perpétuo, G. J. & Janczak, J. (2010). *Acta Cryst.* **C66**, o225–o228.
- Rademeyer, M. (2007). *Acta Cryst.* **E63**, o545–o546.
- Rigaku (2008). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Smith, G., Bott, R. C. & Wermuth, U. D. (2000). *Acta Cryst.* **C56**, 1505–1506.

**supplementary materials**

*Acta Cryst.* (2012). E68, o124-o125 [ doi:10.1107/S160053681105286X ]

## 2-Aminopyridinium 2-methoxycarbonyl-4,6-dinitrophenolate

D.-L. Wu and Z.-J. Xiao

### Comment

The structures of many molecular proton transfer adducts containing substituted pyridinium and an acid anion have been reported in the past decades (Gellert & Hsu, 1988; Smith *et al.*, 2000; Jebas *et al.*, 2006; Rademeyer, 2007; Hemamalini & Fun, 2010*a,b,c*). As a substituted pyridinium, 2-aminopyridine has attracted great attention due to its various hydrogen bonds (Gellert & Hsu, 1988; Jebas *et al.*, 2006; Perpétuo & Janczak, 2010; Hemamalini & Fun, 2010*a*). We report here the synthesis and crystal structure of 2-aminopyridinium 3,5-dinitromethyl salicylate (I).

In the title compound, proton transfer has occurred from the hydroxyl group. As illustrated in Figure 1, the title molecule consists of a protonated 2-aminopyridinium cation and a 3,5-dinitromethyl salicylate anion. The cation and the anion are linked *via* two N—H $\cdots$ O(hydroxy), one N—H $\cdots$ O(carboxy) and one N—H $\cdots$ O(nitro group) hydrogen bonds to form an ion pair. The dihedral angle between the pyridinium ring in the cation and the benzene ring in the anion is 3.65 (6) $^\circ$ .

The bond lengths and angles in (I) are similar to those in other 2-aminopyridinium complexes (Jebas *et al.*, 2006; Perpétuo & Janczak, 2010; Hemamalini & Fun, 2010*a*).

As shown in Figure 2, the adduct at  $(x, y, z)$  connects to two neighboring adducts [at  $(0.5-x, 0.5+y, 0.5-z)$  and at  $(0.5-x, -0.5+y, 0.5-z)$ ] through two N2-H $\cdots$ O6A (symmetry code A,  $0.5-x, 0.5+y, 0.5-z$ ) hydrogen bonds, forming a spiral chain. At the same time, the adduct at  $(x, y, z)$  interacts with two neighboring adducts *via* two C4-H $\cdots$ O7B (symmetry code B,  $0.5-x, 0.5+y, 1.5-z$ ) hydrogen bonds, also resulting in a spiral chain. A further C5-H $\cdots$ O5D (symmetry code D,  $x, y, 1+z$ ) hydrogen bond connects the adduct to another two adducts. Therefore, every adduct connects to six neighboring adducts by these N-H $\cdots$ O and C<sub>aryl</sub>-H $\cdots$ O hydrogen bonds to yield an extended undulating two-dimensional network (Figure 2).

The benzene ring of the anion at  $(x, y, z)$  and the benzene ring in the anion at  $(1-x, 1-y, 1-z)$  are almost parallel, with a dihedral angle of 0.00 (6) $^\circ$  between them. The interplanar spacing is about 3.309 (1) Å, the centroid-centroid separation is 3.69 (1) Å, indicating a weak  $\pi$ - $\pi$  interaction between these rings (Figure 3).

### Experimental

Reagents and solvents were used as obtained without further purification. 3,5-dinitromethyl salicylate was synthesized according to literature methods (Bartlett & Trachten, 1958). Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.0498g, 0.2 mmol) was dissolved in 10 mL of methanol to yield solution A. 3,5-dinitromethyl salicylate (0.0484 g, 0.2 mmol) and 2-aminopyridine (0.0188 g, 0.2 mmol) were dissolved in 10 mL of acetone to yield solution B. Solution A was slowly added to solution B. The mixture was stirred for 4 h at room temperature. After filtration, the green filtrate was allowed to stand at room temperature for several days. The yellow block crystals of the title compound (I) were obtained by slow evaporation.

## Refinement

The pyridinium H atom and H atoms in the NH<sub>2</sub> group were located in a Fourier map and their positions refined. This resulted in the best placement of these atoms in the hydrogen-bonding network. All other H atoms were placed in calculated positions and refined using a riding model [C-H = 0.93 Å and U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(C) for aromatic H atoms, C-H = 0.96 Å and U<sub>iso</sub>(H) = 1.5U<sub>eq</sub>(C) for methyl H atoms].

## Figures

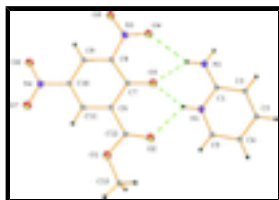


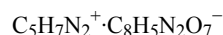
Fig. 1. The molecular components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines



Fig. 2. The extended 2D network of compound (I) formed by N-H...O and C-H...O hydrogen bonds

## 2-Aminopyridinium 2-methoxycarbonyl-4,6-dinitrophenolate

### Crystal data



$$M_r = 336.27$$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$$a = 7.4088 (3) \text{ \AA}$$

$$b = 19.1779 (6) \text{ \AA}$$

$$c = 9.9784 (4) \text{ \AA}$$

$$\beta = 98.2825 (15)^\circ$$

$$V = 1403.00 (9) \text{ \AA}^3$$

$$Z = 4$$

$$F(000) = 696$$

$$D_x = 1.592 \text{ Mg m}^{-3}$$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3200 reflections

$$\theta = 3.2\text{--}27.5^\circ$$

$$\mu = 0.13 \text{ mm}^{-1}$$

$$T = 293 \text{ K}$$

Block, pale yellow

$$0.35 \times 0.35 \times 0.26 \text{ mm}$$

### Data collection

Rigaku R-Axis SPIDER IP  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\phi$  and  $\omega$  scan

Absorption correction:  $\psi$  scan  
(*TEXRAY*; Molecular Structure Corporation, 1999)

$$T_{\min} = 0.951, T_{\max} = 0.969$$

21789 measured reflections

3200 independent reflections

2760 reflections with  $I > 2\sigma(I)$

$$R_{\text{int}} = 0.024$$

$$\theta_{\text{max}} = 27.5^\circ, \theta_{\text{min}} = 3.2^\circ$$

$$h = -9 \rightarrow 9$$

$$k = -24 \rightarrow 24$$

$$l = -12 \rightarrow 12$$

*Refinement*

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.111$	H-atom parameters constrained
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 0.3452P]$
3200 reflections	where $P = (F_o^2 + 2F_c^2)/3$
221 parameters	$(\Delta/\sigma)_{\max} = 0.001$
0 restraints	$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$

*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.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and goodness 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 threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.02842 (16)	0.69774 (6)	0.60013 (13)	0.0241 (3)
C2	-0.11062 (17)	0.75222 (6)	0.66522 (14)	0.0289 (3)
H2A	-0.1639	0.7897	0.6151	0.035*
C3	-0.11154 (18)	0.74967 (7)	0.80192 (14)	0.0311 (3)
H3A	-0.1657	0.7856	0.8445	0.037*
C4	-0.03148 (18)	0.69327 (7)	0.87924 (13)	0.0307 (3)
H4A	-0.0299	0.6919	0.9726	0.037*
C5	0.04326 (17)	0.64096 (7)	0.81366 (12)	0.0267 (3)
H5A	0.0952	0.6029	0.8625	0.032*
C6	0.29417 (15)	0.45835 (6)	0.52321 (11)	0.0210 (2)
C7	0.22285 (16)	0.51541 (6)	0.43454 (12)	0.0222 (2)
C8	0.25155 (16)	0.50645 (6)	0.29470 (12)	0.0228 (2)
C9	0.34193 (16)	0.45058 (6)	0.24919 (11)	0.0232 (2)
H9A	0.3571	0.4473	0.1585	0.028*
C10	0.41023 (15)	0.39918 (6)	0.34032 (12)	0.0215 (2)
C11	0.38567 (16)	0.40290 (6)	0.47609 (12)	0.0214 (2)
H11A	0.4314	0.3676	0.5355	0.026*
C12	0.27237 (16)	0.46104 (6)	0.66889 (12)	0.0237 (2)

## supplementary materials

---

C13	0.3255 (2)	0.40100 (9)	0.87787 (14)	0.0451 (4)
H13A	0.3399	0.3538	0.9098	0.068*
H13B	0.2093	0.4185	0.8942	0.068*
H13C	0.4209	0.4294	0.9250	0.068*
N1	0.04300 (14)	0.64367 (5)	0.67753 (10)	0.0233 (2)
H01A	0.0871	0.6072	0.6366	0.044 (5)*
N2	-0.01983 (16)	0.69663 (6)	0.46755 (11)	0.0301 (3)
H02A	0.0212	0.6592	0.4298	0.043 (5)*
H02B	-0.0560	0.7330	0.4189	0.043 (5)*
N3	0.18614 (16)	0.55870 (6)	0.19326 (11)	0.0312 (3)
N4	0.50832 (14)	0.34132 (5)	0.29295 (10)	0.0241 (2)
O1	0.33525 (16)	0.40289 (5)	0.73434 (9)	0.0380 (3)
O2	0.20907 (15)	0.50859 (5)	0.72572 (9)	0.0361 (2)
O3	0.14378 (14)	0.56716 (5)	0.47530 (9)	0.0347 (2)
O4	0.12739 (17)	0.61428 (5)	0.22518 (11)	0.0425 (3)
O5	0.1928 (3)	0.54493 (9)	0.07588 (12)	0.1015 (8)
O6	0.52421 (14)	0.33865 (5)	0.17125 (9)	0.0329 (2)
O7	0.57286 (14)	0.29666 (5)	0.37464 (10)	0.0342 (2)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0235 (5)	0.0210 (5)	0.0277 (6)	-0.0042 (4)	0.0030 (5)	0.0003 (4)
C2	0.0288 (6)	0.0210 (6)	0.0366 (7)	0.0003 (5)	0.0031 (5)	-0.0011 (5)
C3	0.0305 (6)	0.0267 (6)	0.0367 (7)	-0.0006 (5)	0.0073 (5)	-0.0103 (5)
C4	0.0331 (7)	0.0338 (7)	0.0255 (6)	-0.0029 (5)	0.0057 (5)	-0.0063 (5)
C5	0.0288 (6)	0.0273 (6)	0.0237 (6)	-0.0016 (5)	0.0028 (5)	-0.0001 (5)
C6	0.0221 (5)	0.0229 (6)	0.0181 (5)	-0.0014 (4)	0.0027 (4)	-0.0004 (4)
C7	0.0239 (5)	0.0221 (5)	0.0206 (5)	0.0005 (4)	0.0029 (4)	-0.0010 (4)
C8	0.0257 (6)	0.0229 (6)	0.0194 (5)	-0.0001 (4)	0.0014 (4)	0.0028 (4)
C9	0.0258 (6)	0.0264 (6)	0.0175 (5)	-0.0016 (4)	0.0034 (4)	-0.0008 (4)
C10	0.0226 (5)	0.0203 (5)	0.0219 (6)	-0.0007 (4)	0.0046 (4)	-0.0027 (4)
C11	0.0225 (5)	0.0210 (5)	0.0206 (5)	-0.0017 (4)	0.0028 (4)	0.0012 (4)
C12	0.0248 (6)	0.0258 (6)	0.0206 (5)	0.0007 (4)	0.0034 (4)	0.0004 (4)
C13	0.0604 (10)	0.0566 (10)	0.0200 (7)	0.0201 (8)	0.0117 (6)	0.0107 (6)
N1	0.0261 (5)	0.0209 (5)	0.0233 (5)	0.0003 (4)	0.0053 (4)	-0.0014 (4)
N2	0.0410 (6)	0.0236 (5)	0.0261 (5)	0.0033 (4)	0.0062 (5)	0.0037 (4)
N3	0.0399 (6)	0.0313 (6)	0.0224 (5)	0.0076 (5)	0.0046 (5)	0.0052 (4)
N4	0.0256 (5)	0.0230 (5)	0.0244 (5)	-0.0013 (4)	0.0061 (4)	-0.0022 (4)
O1	0.0586 (7)	0.0379 (5)	0.0194 (4)	0.0191 (5)	0.0117 (4)	0.0066 (4)
O2	0.0546 (6)	0.0321 (5)	0.0237 (4)	0.0117 (4)	0.0125 (4)	-0.0005 (4)
O3	0.0507 (6)	0.0296 (5)	0.0246 (5)	0.0156 (4)	0.0084 (4)	0.0011 (4)
O4	0.0678 (7)	0.0245 (5)	0.0355 (5)	0.0100 (5)	0.0088 (5)	0.0069 (4)
O5	0.1943 (19)	0.0906 (11)	0.0208 (6)	0.0938 (13)	0.0190 (8)	0.0151 (6)
O6	0.0432 (5)	0.0334 (5)	0.0237 (4)	0.0050 (4)	0.0097 (4)	-0.0060 (4)
O7	0.0433 (5)	0.0269 (5)	0.0340 (5)	0.0102 (4)	0.0117 (4)	0.0055 (4)

*Geometric parameters (Å, °)*

C1—N2	1.3338 (16)	C9—C10	1.3864 (16)
C1—N1	1.3543 (16)	C9—H9A	0.9300
C1—C2	1.4136 (17)	C10—C11	1.3945 (15)
C2—C3	1.3659 (19)	C10—N4	1.4429 (15)
C2—H2A	0.9300	C11—H11A	0.9300
C3—C4	1.409 (2)	C12—O2	1.2041 (15)
C3—H3A	0.9300	C12—O1	1.3414 (15)
C4—C5	1.3586 (18)	C13—O1	1.4448 (15)
C4—H4A	0.9300	C13—H13A	0.9600
C5—N1	1.3591 (15)	C13—H13B	0.9600
C5—H5A	0.9300	C13—H13C	0.9600
C6—C11	1.3796 (16)	N1—H01A	0.8952
C6—C7	1.4578 (16)	N2—H02A	0.8838
C6—C12	1.4864 (15)	N2—H02B	0.8702
C7—O3	1.2498 (14)	N3—O5	1.2087 (16)
C7—C8	1.4516 (16)	N3—O4	1.2112 (15)
C8—C9	1.3748 (17)	N4—O7	1.2307 (14)
C8—N3	1.4568 (15)	N4—O6	1.2378 (13)
N2—C1—N1	118.87 (11)	C9—C10—N4	119.04 (10)
N2—C1—C2	123.56 (11)	C11—C10—N4	119.99 (10)
N1—C1—C2	117.56 (11)	C6—C11—C10	120.65 (10)
C3—C2—C1	119.79 (12)	C6—C11—H11A	119.7
C3—C2—H2A	120.1	C10—C11—H11A	119.7
C1—C2—H2A	120.1	O2—C12—O1	122.13 (11)
C2—C3—C4	120.81 (12)	O2—C12—C6	126.26 (11)
C2—C3—H3A	119.6	O1—C12—C6	111.61 (10)
C4—C3—H3A	119.6	O1—C13—H13A	109.5
C5—C4—C3	118.15 (12)	O1—C13—H13B	109.5
C5—C4—H4A	120.9	H13A—C13—H13B	109.5
C3—C4—H4A	120.9	O1—C13—H13C	109.5
C4—C5—N1	120.74 (12)	H13A—C13—H13C	109.5
C4—C5—H5A	119.6	H13B—C13—H13C	109.5
N1—C5—H5A	119.6	C1—N1—C5	122.92 (10)
C11—C6—C7	121.65 (10)	C1—N1—H01A	118.4
C11—C6—C12	119.21 (10)	C5—N1—H01A	118.6
C7—C6—C12	119.11 (10)	C1—N2—H02A	120.2
O3—C7—C8	123.18 (11)	C1—N2—H02B	119.0
O3—C7—C6	122.99 (10)	H02A—N2—H02B	120.7
C8—C7—C6	113.83 (10)	O5—N3—O4	120.90 (12)
C9—C8—C7	123.75 (10)	O5—N3—C8	117.84 (11)
C9—C8—N3	115.83 (10)	O4—N3—C8	121.25 (11)
C7—C8—N3	120.41 (10)	O7—N4—O6	122.57 (10)
C8—C9—C10	119.11 (10)	O7—N4—C10	118.96 (10)
C8—C9—H9A	120.4	O6—N4—C10	118.47 (10)
C10—C9—H9A	120.4	C12—O1—C13	116.11 (10)
C9—C10—C11	120.97 (10)		



## supplementary materials

---

N2—C1—C2—C3	-179.20 (12)	C9—C10—C11—C6	-0.67 (17)
N1—C1—C2—C3	1.62 (18)	N4—C10—C11—C6	179.18 (10)
C1—C2—C3—C4	-0.03 (19)	C11—C6—C12—O2	173.68 (12)
C2—C3—C4—C5	-1.28 (19)	C7—C6—C12—O2	-4.57 (18)
C3—C4—C5—N1	0.98 (19)	C11—C6—C12—O1	-5.50 (16)
C11—C6—C7—O3	-178.03 (11)	C7—C6—C12—O1	176.25 (10)
C12—C6—C7—O3	0.17 (18)	N2—C1—N1—C5	178.80 (11)
C11—C6—C7—C8	2.18 (16)	C2—C1—N1—C5	-1.97 (17)
C12—C6—C7—C8	-179.61 (10)	C4—C5—N1—C1	0.68 (18)
O3—C7—C8—C9	178.46 (12)	C9—C8—N3—O5	10.0 (2)
C6—C7—C8—C9	-1.76 (17)	C7—C8—N3—O5	-170.96 (17)
O3—C7—C8—N3	-0.49 (18)	C9—C8—N3—O4	-169.76 (12)
C6—C7—C8—N3	179.30 (10)	C7—C8—N3—O4	9.27 (19)
C7—C8—C9—C10	0.18 (18)	C9—C10—N4—O7	178.17 (11)
N3—C8—C9—C10	179.17 (10)	C11—C10—N4—O7	-1.68 (16)
C8—C9—C10—C11	1.12 (17)	C9—C10—N4—O6	-1.80 (16)
C8—C9—C10—N4	-178.74 (10)	C11—C10—N4—O6	178.35 (10)
C7—C6—C11—C10	-1.09 (17)	O2—C12—O1—C13	-1.0 (2)
C12—C6—C11—C10	-179.29 (10)	C6—C12—O1—C13	178.21 (12)

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

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H01A $\cdots$ O3	0.90	1.88	2.6864 (13)	148.
N1—H01A $\cdots$ O2	0.90	2.23	2.8783 (14)	130.
N2—H02A $\cdots$ O3	0.88	2.01	2.7592 (14)	142.
N2—H02A $\cdots$ O4	0.88	2.45	3.2082 (15)	144.
N2—H02B $\cdots$ O6 <sup>i</sup>	0.87	2.24	3.0537 (14)	155.
C4—H4A $\cdots$ O7 <sup>ii</sup>	0.93	2.57	3.2052 (16)	126.
C5—H5A $\cdots$ O5 <sup>iii</sup>	0.93	2.42	3.2604 (17)	151.

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

Fig. 1

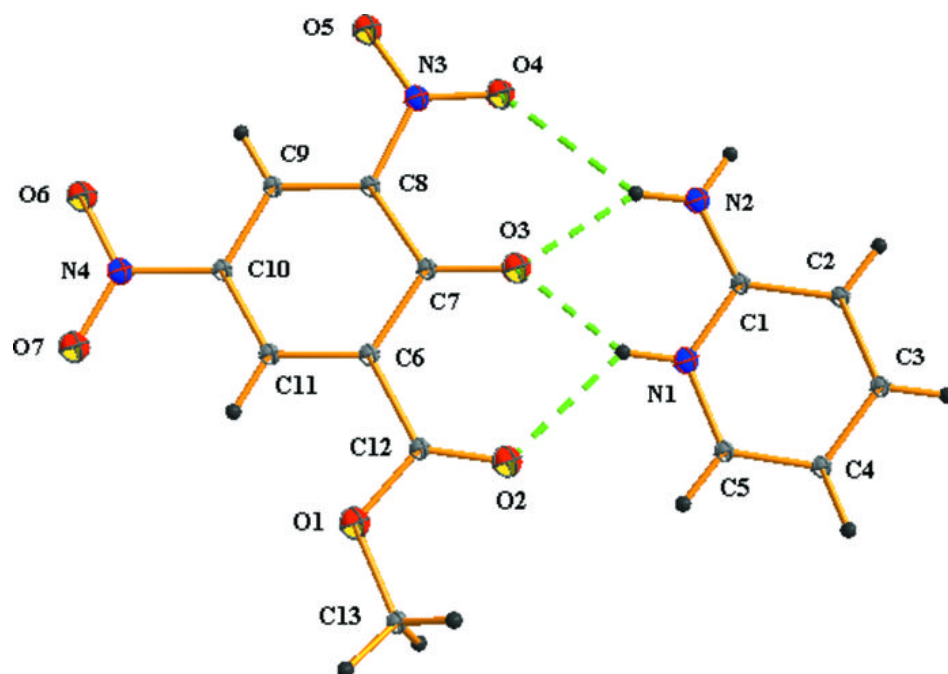


Fig. 2

