

Crystal structure and Hirshfeld surface analysis of (*E*)-4-[[2-(4-hydroxybenzoyl)hydrazin-1-ylidene]methyl]pyridin-1-ium nitrate

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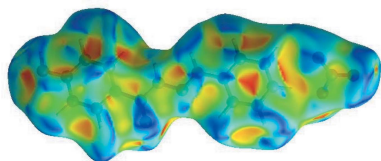
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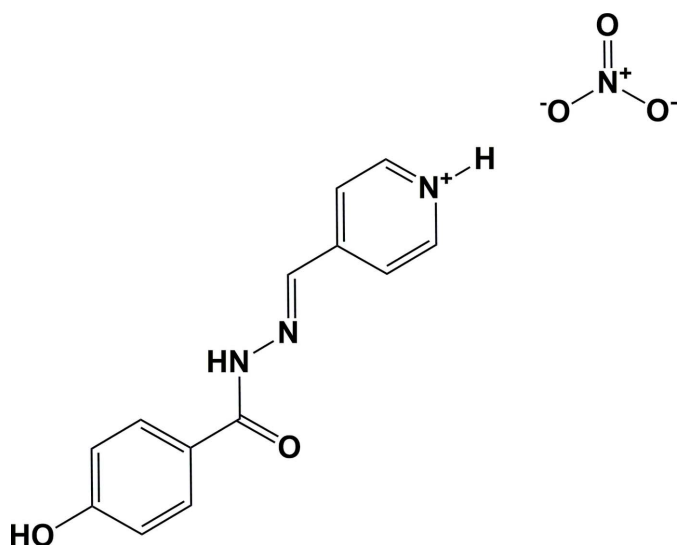
Supporting information: this article has supporting information at journals.iucr.org/e

The asymmetric unit of the title aroyl hydrazone Schiff base salt, $C_{13}H_{12}N_3O_2^+ \cdot N O_3^-$, consists of one molecular cation in the keto tautomeric form, adopting an *E* configuration with respect to the azomethine bond, and one nitrate anion. The two units are linked *via* an $N-H \cdots O$ hydrogen bond. The molecule overall is non-planar, with the pyridinium and benzene rings being inclined to each other by $4.21(4)^\circ$. In the crystal, cations and anions are linked *via* intermolecular $O-H \cdots O$ and bifurcated $N-H \cdots O$ hydrogen bonds, forming a two-dimensional network parallel to (101). These networks are further linked by $C-H \cdots O$ hydrogen bonds, forming slabs parallel to (101). The slabs are linked by offset π - π interactions, involving the benzene and pyridinium rings of adjacent slabs [intercentroid distance = $3.610(2) \text{ \AA}$], forming a three-dimensional structure. The Hirshfeld surface analysis of the crystal structure indicates that the most important contributions for the crystal packing are from $H \cdots O/O \cdots H$ (45.1%), $H \cdots H$ (19.3%), $H \cdots C/C \cdots H$ (14.5%), $H \cdots N/N \cdots H$ (7.9%) and $C \cdots C$ (6.0%) interactions.

1. Chemical context

Hydrazone Schiff bases and their coordination compounds have gained importance recently because of their application as models in biological, analytical and antimicrobial systems, and also due to their anticancer, antibacterial as well as anti-fungal activities (Ruben *et al.*, 2003). Aroyl hydrazones are a class of versatile ligands, capable of generating various molecular architectures and coordination polyhedra (Ruben *et al.*, 2003; Uppadine Gisselbrecht & Lehn, 2004; Uppadine & Lehn, 2004; Wood *et al.*, 2004). Aroyl hydrazones are obtainable through hydrazide-ketone/aldehyde condensation, and they exhibit flexible metal-chelating capabilities through their keto-enol tautomerism and possible reversible deprotonation. The empty N,O-donor chelating pockets of aroyl hydrazones that are incorporated into frameworks can potentially make them amenable to post-synthetic metalation (Evans *et al.*, 2014). The structure determination of the title aroyl hydrazone Schiff base salt was undertaken in order to compare the results obtained with those reported previously. In this context, we synthesized the title compound, (*E*)-4-[[2-(4-hydroxybenzoyl)hydrazin-1-ylidene]methyl]pyridin-1-ium nitrate, and report herein on its crystal and molecular structures along with the Hirshfeld surface analysis.





2. Structural commentary

The asymmetric unit of the title aroyl hydrazone Schiff base salt contains one molecular cation and one nitrate anion, which are linked *via* an $N^+ - H \cdots O$ hydrogen bond (Fig. 1, Table 1). The organic cation is in the keto tautomeric form, which can be verified from the $C=O$ and $C-NH$ bond lengths of the amide unit: $O2=C7$ is 1.228 (2) Å and $N1-C7$ is 1.359 (2) Å. Amide unit bond lengths for aroyl hydrazones are in the ranges 1.218–1.292 Å for $C=O$ bonds and 1.313–1.365 Å for $C-N$ bonds in the keto tautomeric form, and 1.284–1.314 Å for $C=O$ bonds and 1.291–1.331 Å for $C-N$ bonds in the enol tautomeric form (Hosseini-Monfared *et al.*, 2013). The three bond angles around atom $C7$, *viz.* $O2-C7-$

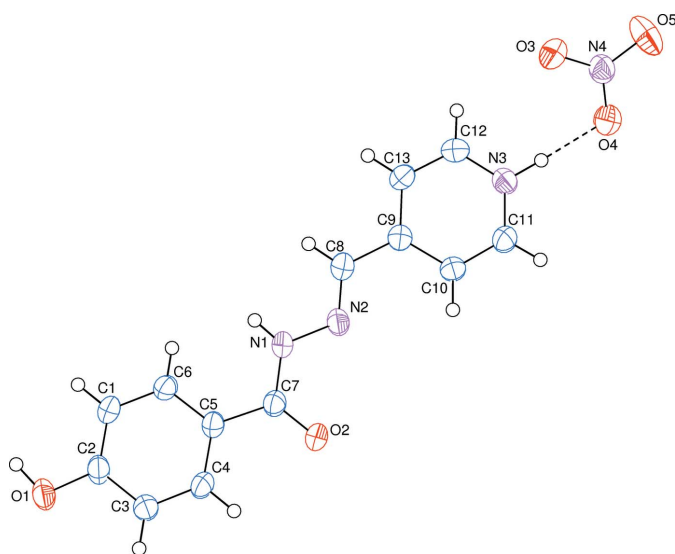


Figure 1

The molecular structure of the title aroyl hydrazone Schiff base salt, with the atom-numbering scheme. The $N-H_{Pym} \cdots O_N$ (Pym = pyridinium and N = nitrate) hydrogen bond (see Table 1) is shown as a dashed line. Displacement ellipsoids are drawn at the 50% probability level.

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H1A \cdots O2^i$	0.96 (2)	1.79 (2)	2.742 (2)	170 (2)
$N1-H1B \cdots O4^{iii}$	0.84 (2)	2.25 (2)	3.057 (2)	161 (2)
$N1-H1B \cdots O5^{iii}$	0.84 (2)	2.47 (2)	3.174 (3)	141 (2)
$N3-H3A \cdots O4$	0.97 (2)	1.80 (2)	2.763 (2)	178 (2)
$C1-H1 \cdots O2^i$	0.93	2.58	3.258 (2)	130
$C8-H8 \cdots O4^{iii}$	0.93	2.42	3.243 (2)	148
$C10-H10 \cdots O1^{ii}$	0.93	2.48	3.375 (2)	162
$C11-H11 \cdots O5^{iv}$	0.93	2.42	3.104 (3)	130
$C12-H12 \cdots O3^v$	0.93	2.34	3.191 (2)	152

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

Table 2

Selected interatomic distances (Å).

$O1 \cdots H10^i$	2.48	$C7 \cdots H1A^{ii}$	2.72 (2)
$O2 \cdots H1^{ii}$	2.58	$H1 \cdots H1A$	2.28
$O2 \cdots H1A^{ii}$	1.79 (2)	$H1B \cdots O4^{iii}$	2.25 (2)
$O2 \cdots H4$	2.52	$H1B \cdots O5^{iii}$	2.47 (2)
$O3 \cdots H3A$	2.48 (2)	$H1B \cdots N4^{iii}$	2.73 (2)
$O3 \cdots H12$	2.59	$H6 \cdots O4^{iii}$	2.71
$O4 \cdots H3A$	1.80 (2)	$H6 \cdots O5^{iii}$	2.75
$N1 \cdots H6$	2.59	$H6 \cdots N4^{iii}$	2.81
$N2 \cdots H1A^{ii}$	2.56 (2)	$H6 \cdots H1B$	2.11
$N2 \cdots H10$	2.62	$H8 \cdots O4^{iii}$	2.42
$N4 \cdots H3A$	2.47 (2)	$H8 \cdots H1B$	2.12
$C6 \cdots H1B$	2.61 (2)	$H8 \cdots H13$	2.46

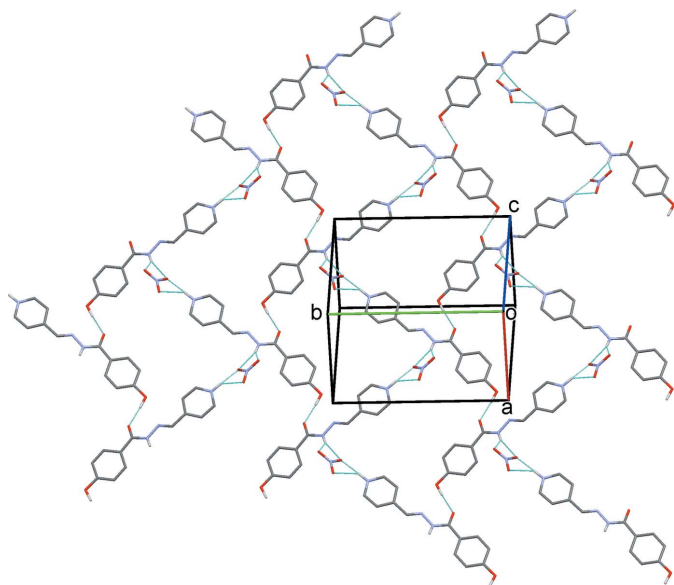
Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.

$N1$ [121.65 (15)°], $O2-C7-C5$ [122.00 (15)°] and $N1-C7-C5$ [116.35 (14)°], differ from 120°, probably in order to decrease the repulsion between the lone pairs present on atoms $N1$ and $O2$.

The configuration at the $N2=C8$ [1.276 (2) Å] bond is *E*, where torsion angle $N1-N2-C8-C9$ is -177.58 (14)°. On the other hand, torsion angles $N2-N1-C7-C5$ and $C8-N2-N1-C7$ are -179.66 (13) and -178.09 (15)°, respectively, and the benzene ($C1-C6$) and pyridinium ($N3/C9-C13$) rings are oriented at a dihedral angle of 4.21 (4)°, probably due to the steric interactions between the hydrogen atoms (Table 2). Thus, the molecule is non-planar as a whole. The central $C9-C8=N2-N1-C7=O2$ moiety of the molecular cation adopts an extended double-bonded conformation and has a maximum deviation of 0.0331 (18) Å for atom $C8$, from the mean plane.

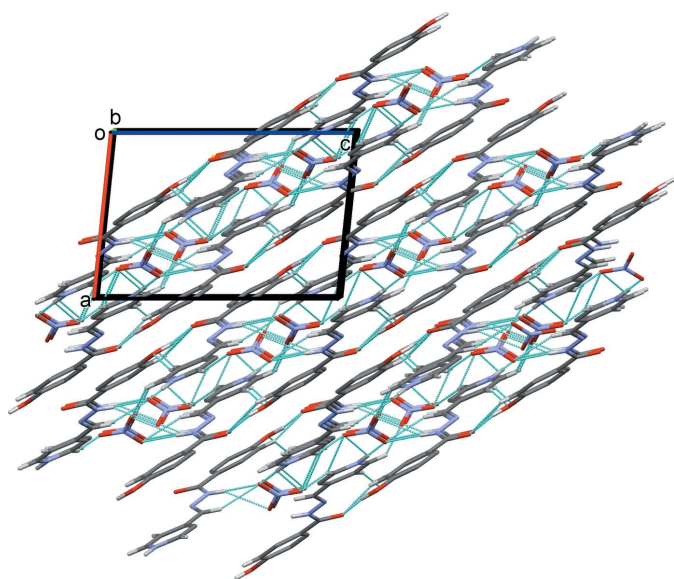
3. Supramolecular features

Hydrogen bonding and van der Waals contacts are the dominant interactions in the crystal packing. In the crystal, $O-H_{Hydr} \cdots O_{Hydrz}$, $N-H_{Pym} \cdots O_N$ and bifurcated $N-H_{Hydrz} \cdots O_N$ ($Hydr$ = hydroxy, $Hydrz$ = hydrazide, Pym = pyridinium and N = nitrate) hydrogen bonds (Table 1) link the cations and anions into a two-dimensional network parallel to (101), as illustrated in Fig. 2. A series of $C-H \cdots O$ hydrogen bonds [$C-H_{Bnz} \cdots O_{Hydrz}$, $C-H_{Pym} \cdots O_N$, $C-H_{Pym} \cdots O_{Hydr}$ and $C-H_{Meth} \cdots O_N$ (Bnz = benzene and $Meth$ = methine)]


Figure 2

Part of the crystal structure, viewed normal to (101). The O—H...O and N—H...O hydrogen bonds (see Table 1) are shown as dashed lines, and C-bound H atoms have been omitted for clarity.

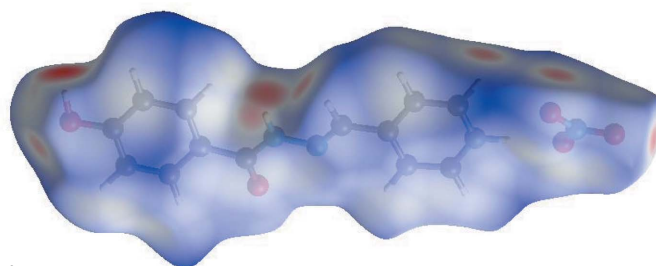
link adjacent layers, forming slabs parallel to (101); see Fig. 3. The slabs are linked by offset π - π interactions, forming a three-dimensional structure. The offset π - π interaction between the benzene ($Cg1$ is the centroid of atoms C1–C6) and pyridinium ($Cg2$ is the centroid of atoms N3/C9–C13) rings of adjacent slabs has an intercentroid $Cg1 \cdots Cg2(-x + 2, -y + 1, -z + 1)$ distance of 3.610 (2) Å, while α is 4.2 (1)°, and the interplanar distances are 3.263 (7) and 3.366 (7) Å, with an offset distance of 1.303 Å.


Figure 3

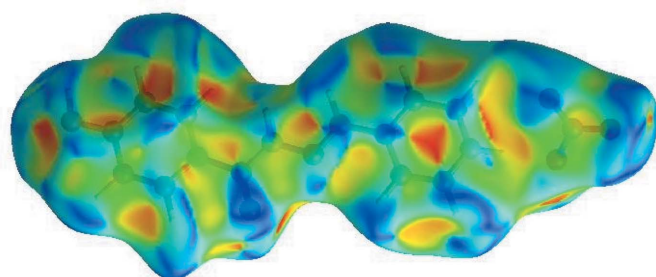
A view along the b axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1), and only H atoms involved in these interactions have been included.

4. Hirshfeld surface analysis

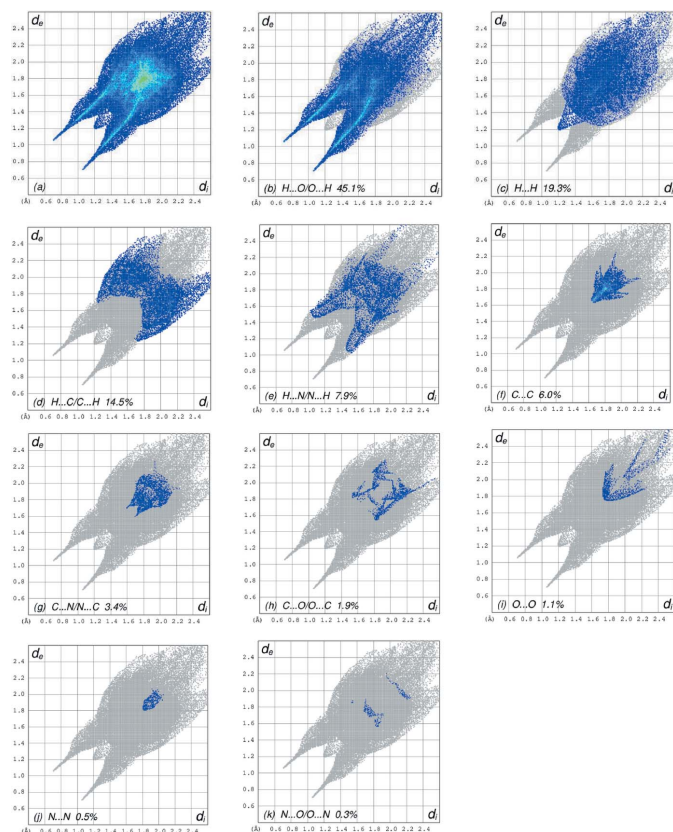
In order to visualize the intermolecular interactions in the crystal of the title aroyl hydrazone Schiff base salt, a Hirshfeld surface (HS) analysis (Hirshfeld, 1977; Spackman & Jayatilaka, 2009) was carried out by using *Crystal Explorer 17.5* (Turner *et al.*, 2017). In the HS plotted over d_{norm} (Fig. 4), the white surfaces indicate contacts with distances equal to the sum of van der Waals radii, and the red and blue colours indicate distances shorter (in close contact) or longer (distinct contact) than the van der Waals radii, respectively (Venkatesan *et al.*, 2016). The bright-red spots appearing near N—O4, N—O5 and hydrogen atoms H1A, H1B and H3A indicate their role as the respective donors and acceptors in the dominant O—H...O and N—H...O hydrogen bonds (Spackman *et al.*, 2008; Jayatilaka *et al.*, 2005). The shape-index of the HS is a tool to visualize the π - π stacking by the presence of adjacent red and blue triangles; if there are no adjacent red and/or blue triangles, then there are no π - π interactions. Fig. 5 clearly suggest that there are π - π interactions in (I). The overall two-dimensional fingerprint plot and those delineated into H...O/O...H, H...H, H...C/C...H, H...N/N...H, C...C, C...N/N...C, C...O/O...C, O...O, N...N and N...O/O...N contacts (McKinnon *et al.*, 2007) are illustrated in Fig. 5 *a–k*, respectively, together with their relative contributions to the Hirshfeld surface. The most important interaction is H...O/O...H contributing 45.1% to the overall crystal packing, which is reflected in Fig. 6*b* as pair of spikes with the tips at $d_e + d_i \sim 1.75$ Å. The short H...O/O...H contacts are masked by strong O—H...O hydrogen bonding in this plot. In the fingerprint plot delineated into


Figure 4

View of the three-dimensional Hirshfeld surface of the title aroyl hydrazone Schiff base salt plotted over d_{norm} in the range -0.6521 to 1.7041 a.u.


Figure 5

Hirshfeld surface of the title aroyl hydrazone Schiff base salt plotted over shape-index.


Figure 6

The full two-dimensional fingerprint plots for the title aroyl hydrazone Schiff base salt, showing (a) all interactions, and delineated into (b) $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, (c) $\text{H}\cdots\text{H}$, (d) $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$, (e) $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$, (f) $\text{C}\cdots\text{C}$, (g) $\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$, (h) $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$, (i) $\text{O}\cdots\text{O}$, (j) $\text{N}\cdots\text{N}$ and (k) $\text{N}\cdots\text{O}/\text{O}\cdots\text{N}$ interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

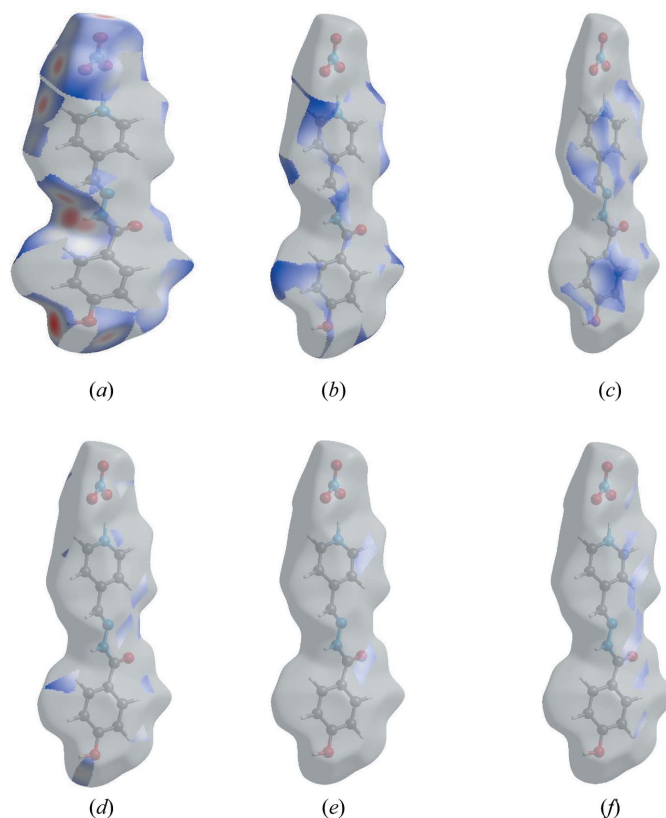
$\text{H}\cdots\text{H}$ contacts (Fig. 6c), the 19.3% contribution to the overall crystal packing is reflected as widely scattered points of high density due to the large hydrogen content of the molecule. The single spike in the centre at $d_e = d_i = 1.2$ Å in Fig. 5c is due to the short interatomic $\text{H}\cdots\text{H}$ contacts (Table 2). In the absence of $\text{C}-\text{H}\cdots\pi$ interactions in the crystal, the pair of characteristic wings resulting in the fingerprint plot delineated into $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ contacts with 14.5% contribution to the HS, Fig. 6d, and the pair of thin edges at $d_e + d_i \sim 1.93$ Å result from short interatomic $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ contacts (Table 2). The $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$ contacts in the structure with 7.9% contribution to the HS has a symmetrical distribution of points, Fig. 5e, with the tips at $d_e + d_i \sim 1.52$ Å arising from the short interatomic $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$ contacts listed in Table 2. The $\text{C}\cdots\text{C}$ contacts assigned to short interatomic $\text{C}\cdots\text{C}$ contacts with 6.0% contribution to the HS appear as an arrow-shaped distribution of points in Fig. 6f, with the vertex at $d_e = d_i \sim 1.65$ Å. Finally, the $\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$ (Fig. 6g) and $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$ (Fig. 6h) contacts in the structure with 3.4% and 1.9% contributions to the HS have nearly symmetrical distributions of points, with the scattered points of low density.

The Hirshfeld surface representations with the function d_{norm} plotted onto the surface are shown for the $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, $\text{H}\cdots\text{H}$, $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$, $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$, $\text{C}\cdots\text{C}$ and $\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$ interactions in Fig. 7a–f, respectively.

The Hirshfeld surface analysis confirms the importance of H-atom contacts in establishing the packing. The large number of $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, $\text{H}\cdots\text{H}$ and $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing (Hathwar *et al.*, 2015).

5. Synthesis and crystallization

The title compound was prepared by the reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.15 g, 0.5 mmol) and 4-[(4-hydroxybenzoyl)hydrazonemethyl]pyridin (0.12 g, 0.5 mmol) in ethanol by using a branched-tube method (Shaabani *et al.*, 2017). After two months, the formation of yellow-coloured crystals was observed. They were filtered off and washed several times with hot ethanol for purification (yield: 0.20 g, 74%, m.p. 613 K). Analysis calculated for $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_5$: C, 51.32; H, 3.98; N, 17.41. Found: C, 51.08; H, 4.14; N, 17.09. Characteristic IR bands (cm^{-1}): 3526 *m*, $\nu(\text{OH})$; 1375 *m*, $\nu(\text{N}-\text{O})$; 1644 *s*, $\nu(\text{C}=\text{N})$; 1501 *s*, $\nu(\text{N}=\text{O})$; 1105 *s*, $\nu(\text{NN})$.


Figure 7

The Hirshfeld surface representations with the function d_{norm} plotted onto the surface for (a) $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, (b) $\text{H}\cdots\text{H}$, (c) $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$, (d) $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$, (e) $\text{C}\cdots\text{C}$ and (f) $\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$ interactions.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms of the OH and NH groups were located in a difference-Fourier map and refined freely. The C-bound H atoms were positioned geometrically with C—H = 0.93 Å, and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest residual electron density was found 2.48 Å from atom H1.

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Table 3

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{13}\text{H}_{12}\text{N}_3\text{O}_2^+\cdot\text{NO}_3^-$
M_r	304.27
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	8.335 (3), 13.929 (5), 12.184 (4)
β (°)	95.902 (10)
V (Å ³)	1407.1 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.15 × 0.14 × 0.12
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2012)
$T_{\text{min}}, T_{\text{max}}$	0.945, 0.976
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	44410, 3499, 2508
R_{int}	0.052
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.049, 0.149, 1.04
No. of reflections	3499
No. of parameters	211
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.75, -0.25

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2015).

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supporting information

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Mir Abolfazl Naziri, Ertan Şahin and Tuncer Hökelek

Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* for Windows (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2015).

(*E*)-4-[[2-(4-Hydroxybenzoyl)hydrazin-1-ylidene]methyl]pyridin-1-ium nitrate

Crystal data

$C_{13}H_{12}N_3O_2^+ \cdot NO_3^-$

$M_r = 304.27$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 8.335$ (3) Å

$b = 13.929$ (5) Å

$c = 12.184$ (4) Å

$\beta = 95.902$ (10)°

$V = 1407.1$ (8) Å³

$Z = 4$

$F(000) = 632$

$D_x = 1.436$ Mg m⁻³

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

Cell parameters from 9700 reflections

$\theta = 3.1$ – 27.5 °

$\mu = 0.11$ mm⁻¹

$T = 296$ K

Block, colourless

$0.15 \times 0.14 \times 0.12$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2012)

$T_{\min} = 0.945$, $T_{\max} = 0.976$

44410 measured reflections

3499 independent reflections

2508 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 28.4$ °, $\theta_{\min} = 2.9$ °

$h = -11 \rightarrow 10$

$k = -18 \rightarrow 18$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.149$

$S = 1.04$

3499 reflections

211 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.4149P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.75 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$$

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 $F^2 > 2\text{sigma}(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	1.15687 (19)	0.08055 (9)	0.24127 (12)	0.0576 (4)
H1A	1.207 (3)	0.1109 (18)	0.183 (2)	0.080 (8)*
O2	0.82328 (18)	0.32288 (9)	0.59284 (11)	0.0549 (4)
O3	0.3316 (2)	0.99298 (10)	0.57667 (11)	0.0619 (4)
O4	0.37385 (19)	0.95570 (10)	0.74819 (11)	0.0595 (4)
O5	0.22205 (19)	1.07556 (11)	0.69841 (15)	0.0730 (5)
N1	0.81569 (17)	0.43407 (10)	0.45738 (12)	0.0392 (3)
H1B	0.830 (3)	0.4512 (15)	0.3928 (19)	0.055 (6)*
N2	0.74051 (16)	0.49881 (10)	0.51883 (11)	0.0368 (3)
N3	0.50122 (17)	0.80177 (10)	0.64341 (12)	0.0408 (3)
H3A	0.456 (3)	0.8548 (17)	0.6811 (19)	0.069 (7)*
N4	0.30832 (18)	1.00915 (10)	0.67253 (13)	0.0438 (4)
C1	1.08209 (19)	0.24460 (12)	0.27240 (13)	0.0367 (4)
H1	1.1286	0.2655	0.2104	0.044*
C2	1.0865 (2)	0.14803 (12)	0.30031 (14)	0.0386 (4)
C3	1.0173 (2)	0.11743 (13)	0.39341 (15)	0.0452 (4)
H3	1.0208	0.0528	0.4129	0.054*
C4	0.9439 (2)	0.18265 (12)	0.45671 (14)	0.0410 (4)
H4	0.8980	0.1616	0.5189	0.049*
C5	0.93716 (18)	0.27990 (11)	0.42900 (13)	0.0334 (3)
C6	1.00883 (18)	0.30970 (12)	0.33645 (13)	0.0353 (4)
H6	1.0073	0.3744	0.3176	0.042*
C7	0.85500 (18)	0.34613 (11)	0.50025 (13)	0.0352 (3)
C8	0.7030 (2)	0.57893 (12)	0.47233 (14)	0.0417 (4)
H8	0.7236	0.5893	0.3997	0.050*
C9	0.62801 (18)	0.65447 (11)	0.53250 (13)	0.0347 (3)
C10	0.56331 (19)	0.63741 (12)	0.63168 (14)	0.0377 (4)
H10	0.5629	0.5758	0.6610	0.045*
C11	0.5004 (2)	0.71264 (12)	0.68521 (15)	0.0402 (4)
H11	0.4565	0.7019	0.7513	0.048*
C12	0.5620 (2)	0.82024 (12)	0.54903 (15)	0.0441 (4)
H12	0.5613	0.8827	0.5221	0.053*

C13	0.6257 (2)	0.74791 (12)	0.49147 (14)	0.0401 (4)
H13	0.6673	0.7610	0.4251	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0805 (10)	0.0412 (7)	0.0580 (9)	−0.0054 (6)	0.0395 (8)	−0.0132 (6)
O2	0.0797 (10)	0.0457 (7)	0.0451 (7)	0.0120 (6)	0.0345 (7)	0.0058 (6)
O3	0.0884 (11)	0.0562 (9)	0.0452 (8)	0.0093 (7)	0.0264 (7)	0.0067 (6)
O4	0.0837 (10)	0.0566 (8)	0.0401 (7)	0.0142 (7)	0.0156 (7)	−0.0006 (6)
O5	0.0723 (10)	0.0593 (9)	0.0875 (12)	0.0217 (8)	0.0090 (9)	−0.0260 (8)
N1	0.0496 (8)	0.0387 (8)	0.0316 (7)	0.0066 (6)	0.0145 (6)	−0.0011 (6)
N2	0.0385 (7)	0.0374 (7)	0.0360 (7)	0.0026 (5)	0.0107 (6)	−0.0047 (6)
N3	0.0446 (8)	0.0330 (7)	0.0466 (8)	0.0026 (6)	0.0132 (6)	−0.0013 (6)
N4	0.0502 (8)	0.0359 (7)	0.0473 (9)	−0.0017 (6)	0.0142 (7)	−0.0056 (6)
C1	0.0379 (8)	0.0441 (9)	0.0296 (8)	−0.0016 (7)	0.0103 (6)	−0.0001 (7)
C2	0.0416 (8)	0.0398 (9)	0.0364 (8)	−0.0050 (7)	0.0134 (7)	−0.0096 (7)
C3	0.0586 (11)	0.0329 (9)	0.0479 (10)	−0.0051 (7)	0.0236 (8)	−0.0023 (7)
C4	0.0500 (9)	0.0389 (9)	0.0373 (9)	−0.0059 (7)	0.0198 (7)	−0.0004 (7)
C5	0.0327 (7)	0.0369 (8)	0.0315 (8)	−0.0005 (6)	0.0080 (6)	−0.0027 (6)
C6	0.0355 (8)	0.0375 (8)	0.0340 (8)	0.0018 (6)	0.0085 (6)	0.0034 (6)
C7	0.0359 (8)	0.0368 (8)	0.0343 (8)	−0.0011 (6)	0.0104 (6)	−0.0018 (6)
C8	0.0496 (9)	0.0437 (9)	0.0333 (8)	0.0058 (8)	0.0110 (7)	−0.0005 (7)
C9	0.0346 (8)	0.0363 (8)	0.0334 (8)	0.0004 (6)	0.0046 (6)	−0.0009 (6)
C10	0.0421 (8)	0.0314 (8)	0.0412 (9)	−0.0028 (6)	0.0113 (7)	0.0022 (7)
C11	0.0434 (9)	0.0373 (9)	0.0422 (9)	−0.0030 (7)	0.0154 (7)	0.0006 (7)
C12	0.0522 (10)	0.0350 (9)	0.0464 (10)	0.0042 (7)	0.0106 (8)	0.0088 (7)
C13	0.0449 (9)	0.0425 (9)	0.0342 (8)	0.0030 (7)	0.0096 (7)	0.0070 (7)

Geometric parameters (Å, °)

O1—C2	1.354 (2)	C4—C3	1.376 (2)
O1—H1A	0.96 (3)	C4—H4	0.9300
O2—C7	1.228 (2)	C5—C4	1.396 (2)
O3—N4	1.224 (2)	C5—C6	1.393 (2)
O4—N4	1.264 (2)	C5—C7	1.482 (2)
N1—C7	1.359 (2)	C6—C1	1.379 (2)
N1—H1B	0.84 (2)	C6—H6	0.9300
N2—N1	1.3649 (19)	C8—H8	0.9300
N2—C8	1.276 (2)	C9—C8	1.459 (2)
N3—C11	1.342 (2)	C9—C10	1.393 (2)
N3—C12	1.329 (2)	C9—C13	1.394 (2)
N3—H3A	0.97 (2)	C10—C11	1.367 (2)
N4—O5	1.2325 (19)	C10—H10	0.9300
C1—H1	0.9300	C11—H11	0.9300
C2—C1	1.387 (2)	C12—H12	0.9300
C2—C3	1.391 (2)	C13—C12	1.366 (2)
C3—H3	0.9300	C13—H13	0.9300

O1...H10 ⁱ	2.48	C7...H1A ⁱⁱ	2.72 (2)
O2...H1 ⁱⁱ	2.58	H1...H1A	2.28
O2...H1A ⁱⁱ	1.79 (2)	H1B...O4 ⁱⁱⁱ	2.25 (2)
O2...H4	2.52	H1B...O5 ⁱⁱⁱ	2.47 (2)
O3...H3A	2.48 (2)	H1B...N4 ⁱⁱⁱ	2.73 (2)
O3...H12	2.59	H6...O4 ⁱⁱⁱ	2.71
O4...H3A	1.80 (2)	H6...O5 ⁱⁱⁱ	2.75
N1...H6	2.59	H6...N4 ⁱⁱⁱ	2.81
N2...H1A ⁱⁱ	2.56 (2)	H6...H1B	2.11
N2...H10	2.62	H8...O4 ⁱⁱⁱ	2.42
N4...H3A	2.47 (2)	H8...H1B	2.12
C6...H1B	2.61 (2)	H8...H13	2.46
C2—O1—H1A	109.6 (15)	C6—C5—C7	123.46 (15)
N2—N1—H1B	116.3 (15)	C1—C6—C5	120.92 (15)
C7—N1—N2	119.41 (14)	C1—C6—H6	119.5
C7—N1—H1B	124.2 (15)	C5—C6—H6	119.5
C8—N2—N1	116.08 (14)	O2—C7—N1	121.65 (15)
C11—N3—H3A	120.6 (14)	O2—C7—C5	122.00 (15)
C12—N3—C11	121.66 (15)	N1—C7—C5	116.35 (14)
C12—N3—H3A	117.7 (14)	N2—C8—C9	120.38 (15)
O3—N4—O4	119.23 (15)	N2—C8—H8	119.8
O3—N4—O5	122.40 (17)	C9—C8—H8	119.8
O5—N4—O4	118.37 (16)	C10—C9—C8	122.46 (15)
C2—C1—H1	120.0	C10—C9—C13	118.54 (14)
C6—C1—C2	120.06 (14)	C13—C9—C8	118.96 (15)
C6—C1—H1	120.0	C9—C10—H10	120.5
O1—C2—C1	123.03 (15)	C11—C10—C9	119.00 (15)
O1—C2—C3	117.33 (16)	C11—C10—H10	120.5
C1—C2—C3	119.64 (15)	N3—C11—C10	120.71 (16)
C2—C3—H3	120.0	N3—C11—H11	119.6
C4—C3—C2	120.02 (16)	C10—C11—H11	119.6
C4—C3—H3	120.0	N3—C12—C13	120.30 (16)
C3—C4—C5	120.96 (15)	N3—C12—H12	119.9
C3—C4—H4	119.5	C13—C12—H12	119.9
C5—C4—H4	119.5	C9—C13—H13	120.1
C4—C5—C7	118.16 (14)	C12—C13—C9	119.79 (15)
C6—C5—C4	118.38 (14)	C12—C13—H13	120.1
N2—N1—C7—O2	0.7 (2)	C7—C5—C6—C1	-179.26 (15)
N2—N1—C7—C5	-179.66 (13)	C4—C5—C7—O2	15.3 (2)
C8—N2—N1—C7	-178.09 (15)	C4—C5—C7—N1	-164.34 (15)
N1—N2—C8—C9	-177.58 (14)	C6—C5—C7—O2	-164.23 (16)
C12—N3—C11—C10	0.3 (3)	C6—C5—C7—N1	16.1 (2)
C11—N3—C12—C13	0.1 (3)	C5—C6—C1—C2	-0.6 (2)
O1—C2—C1—C6	-179.76 (15)	C10—C9—C8—N2	-13.9 (3)
C3—C2—C1—C6	-0.3 (3)	C13—C9—C8—N2	163.87 (16)

O1—C2—C3—C4	-179.94 (17)	C8—C9—C10—C11	177.61 (16)
C1—C2—C3—C4	0.6 (3)	C13—C9—C10—C11	-0.1 (2)
C5—C4—C3—C2	0.0 (3)	C8—C9—C13—C12	-177.27 (16)
C6—C5—C4—C3	-0.9 (3)	C10—C9—C13—C12	0.6 (2)
C7—C5—C4—C3	179.50 (16)	C9—C10—C11—N3	-0.3 (3)
C4—C5—C6—C1	1.2 (2)	C9—C13—C12—N3	-0.6 (3)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots O2 ⁱ	0.96 (2)	1.79 (2)	2.742 (2)	170 (2)
N1—H1B \cdots O4 ⁱⁱⁱ	0.84 (2)	2.25 (2)	3.057 (2)	161 (2)
N1—H1B \cdots O5 ⁱⁱⁱ	0.84 (2)	2.47 (2)	3.174 (3)	141 (2)
N3—H3A \cdots O4	0.97 (2)	1.80 (2)	2.763 (2)	178 (2)
C1—H1 \cdots O2 ⁱ	0.93	2.58	3.258 (2)	130
C8—H8 \cdots O4 ⁱⁱⁱ	0.93	2.42	3.243 (2)	148
C10—H10 \cdots O1 ⁱⁱ	0.93	2.48	3.375 (2)	162
C11—H11 \cdots O5 ^{iv}	0.93	2.42	3.104 (3)	130
C12—H12 \cdots O3 ^v	0.93	2.34	3.191 (2)	152

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