

Received 18 July 2022

Accepted 20 July 2022

Edited by W. T. A. Harrison, University of  
Aberdeen, Scotland**Keywords:** piperazine; synthesis; crystal structure; molecular structure; hydrogen bonding; supramolecular assembly.**CCDC references:** 2191691; 2191690**Supporting information:** this article has supporting information at journals.iucr.org/e

# Syntheses and crystal structures of 4-(4-nitrophenyl)piperazin-1-ium benzoate monohydrate and 4-(4-nitrophenyl)piperazin-1-ium 2-carboxy-4,6-dinitrophenolate

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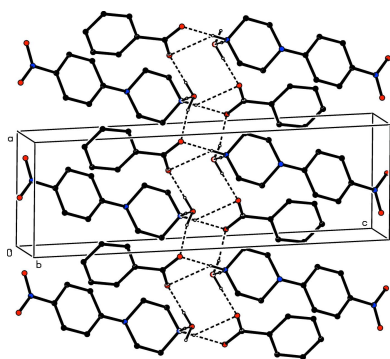
Crystal structures are reported for two molecular salts containing the 4-(4-nitrophenyl)piperazin-1-ium cation. Co-crystallization from methanol/ethyl acetate solution of *N*-(4-nitrophenyl)piperazine with benzoic acid gives the benzoate salt, which crystallizes as a monohydrate,  $C_{10}H_{14}N_3O_2 \cdot C_7H_5O_2 \cdot H_2O$ , (I), and similar co-crystallization with 3,5-dinitrosalicylic acid yields the 2-carboxy-4,6-dinitrophenolate salt,  $C_{10}H_{14}N_3O_2 \cdot C_7H_3N_2O_7$ , (II). In the structure of (I), a combination of  $O-H \cdots O$ ,  $N-H \cdots O$  and  $C-H \cdots O$  hydrogen bonds links the components into sheets, while in the structure of (II), the supramolecular assembly, generated by hydrogen bonds of the same types as in (I), is three dimensional. Comparisons are made with the structures of some related compounds.

## 1. Chemical context

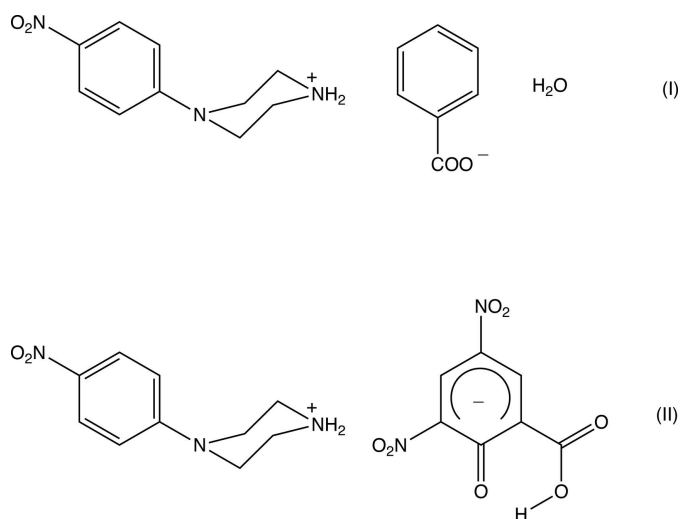
Piperazines and substituted piperazines are important pharmacophores, which can be found in many biologically active compounds (Berkheij, 2005) such as antifungal (Upadhayaya *et al.*, 2004), anti-bacterial, anti-malarial and anti-psychotic agents (Chaudhary *et al.*, 2006). Both the general pharmacological and specific antimicrobial activities of piperazine derivatives have been reviewed in recent years (Elliott, 2011; Kharb *et al.*, 2012). Among specific examples of piperazine derivatives, *N*-(4-nitrophenyl)piperazine has found use in the control of potassium channels (Lu, 2007). The crystal structures of a number of 4-(4-nitrophenyl)piperazin-1-ium salts have been reported (Lu, 2007; Mahesha *et al.*, 2022), and here we report the molecular and supramolecular structures of two further representatives of this family of salts, namely 4-(4-nitrophenyl)piperazin-1-ium benzoate monohydrate,  $C_{10}H_{14}N_3O_2 \cdot C_7H_5O_2 \cdot H_2O$ , (I), and 4-(4-nitrophenyl)piperazin-1-ium 2-carboxy-4,6-dinitrophenolate,  $C_{10}H_{14}N_3O_2 \cdot C_7H_3N_2O_7$ , (II).

## 2. Structural commentary

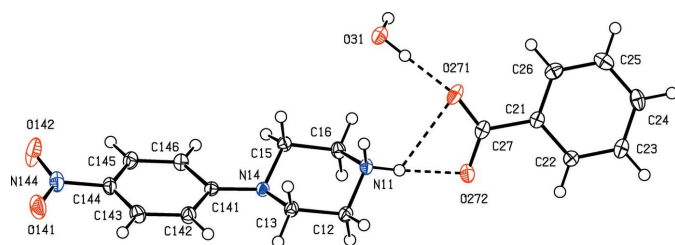
In each of compounds (I) and (II) (Figs. 1 and 2), the piperazine ring adopts a chair conformation, with the ring-puckering angle  $\theta$  (Cremer & Pople, 1975) calculated for the atom



sequence (N11/C12/C13/N14/C15/C16) close to the ideal value of zero (Boeyens, 1978):  $\theta = 6.42$  (11) for (I) and  $8.75$  (11) $^\circ$  for (II). However, in (I), the nitrophenyl substituent occupies an equatorial site, whereas in (II) this substituent occupies an axial site. In each compound, the *N*-nitrophenyl unit shows the pattern of distances typical of 4-nitroaniline derivatives, namely both C–N distances are short for their types (Allen *et al.*, 1987), while the nitro N–O distances are long for their type. In addition, the distances C141–C142 and C141–C146 lie in the range 1.4049 (16) to 1.4132 (15) Å whereas the remaining C–C distances for this ring are smaller, falling in the range 1.3764 (17) to 1.3881 (15) Å. These variations are most simply interpreted in terms of some 1,4-quinonoid type bond fixation, moderated by the high electronegativity of the nitro group, generally regarded as similar to that of a fluoro substituent (Huheey, 1966; Mullay, 1985).



In the anion of compound (II), the C21–O21 distance, 1.2788 (13) Å is more typical of those in ketones than those in phenols (Allen *et al.*, 1987); the distances C21–C22 and C21–C26, 1.4394 (15) and 1.4340 (15) Å are longer than the remaining C–C distances in the ring, which are in the range 1.3747 (15) to 1.3869 (15). These observations, taken together, indicate that the negative charge in this anion is delocalized over atoms C22–C26 rather than being localized on atom O21 (see Scheme).



**Figure 1**  
The molecular structure of (I), showing hydrogen bonds (drawn as dashed lines) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

**Table 1**  
Hydrogen-bond geometry (Å,  $^\circ$ ) for (I).

Cg1 is the centroid of the C21–C26 ring.

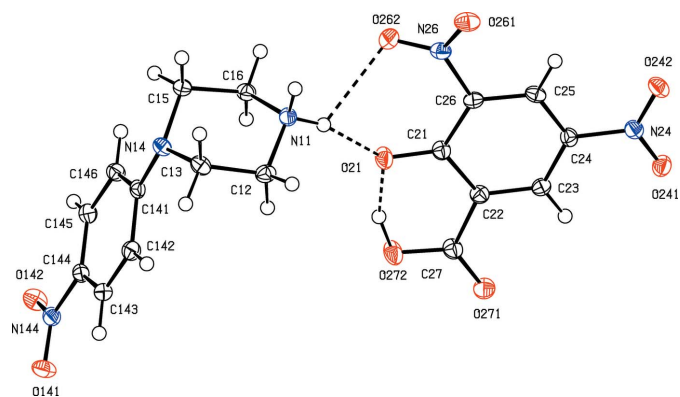
D–H...A	D–H	H...A	D...A	D–H...A
N11–H11...O271	0.926 (14)	2.564 (14)	3.1009 (13)	117.4 (10)
N11–H11...O272	0.926 (14)	1.857 (14)	2.7781 (12)	172.9 (13)
N11–H12...O31 <sup>i</sup>	0.920 (15)	1.884 (15)	2.7965 (14)	171.0 (12)
O31–H31...O271	0.892 (18)	1.757 (18)	2.6486 (13)	179 (3)
O31–H32...O272 <sup>ii</sup>	0.908 (17)	1.862 (17)	2.7581 (12)	168.8 (16)
C12–H12B...O272 <sup>iii</sup>	0.99	2.45	3.3751 (15)	156
C146–H146...Cg1 <sup>iv</sup>	0.95	2.67	3.4363 (13)	138

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

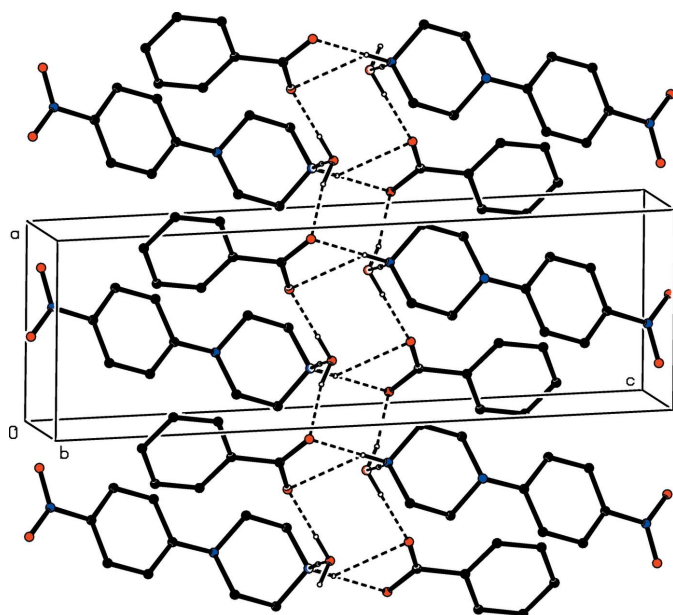
### 3. Supramolecular features

In each of compounds (I) and (II), the supramolecular assembly involves a combination of O–H...O, N–H...O and C–H...O hydrogen bonds, augmented in the case of (I) by a single C–H... $\pi$ (arene) hydrogen bond: however, aromatic  $\pi$ – $\pi$  stacking interactions are absent from both structures.

The supramolecular assembly in (I) is di-periodic and the formation of the sheet structure is readily analysed in terms of two mono-periodic sub-structures (Ferguson *et al.*, 1998*a,b*; Gregson *et al.*, 2000). Within the selected asymmetric unit for (I) (Fig. 1), the ionic components are linked by an asymmetric bifurcated (three-centre) N–H...O hydrogen bond (Table 1), while the water molecule is linked to the anion by an O–H...O hydrogen bond. In one of the two sub-structures, a combination of one two-centre N–H...O hydrogen bond and a second O–H...O hydrogen bond links these three-component aggregates (Fig. 1) into a chain of rings running parallel to the [100] direction (Fig. 3) in which there are two different types of  $R_6^4(12)$  ring (Bernstein *et al.*, 1995), centred at  $(n, 0.5, 0.5)$  and  $(n + 0.5, 0.5, 0.5)$ , respectively, where  $n$  represents an integer in each case. The second sub-structure, which includes the C–H...O hydrogen bond (Table 1, Fig. 4), takes the form of another chain of rings in which  $R_6^4(12)$  rings centred at  $(n + 0.5, n + 0.5, 0.5)$  alternate with  $R_4^2(10)$  rings

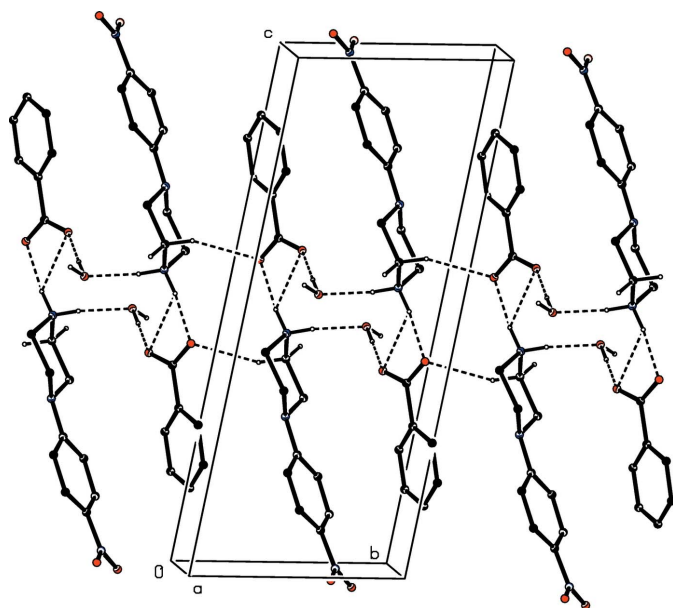


**Figure 2**  
The molecular structure of (II), showing hydrogen bonds (drawn as dashed lines) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 3**  
Part of the crystal structure of compound (I) showing the formation of a chain of hydrogen-bonded rings running parallel to the [100] direction. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have all been omitted.

centred at  $(n, n, 0.5)$ , where  $n$  again represents an integer, so forming a chain of rings running parallel to the [110] direction (Fig. 4). The combination of chains along [100] and [110] generates a sheet structure lying parallel to (001). The single  $C-H \cdots \pi(\text{arene})$  hydrogen bond (Table 1) lies within this sheet, and so has no influence on the dimensionality of the assembly.



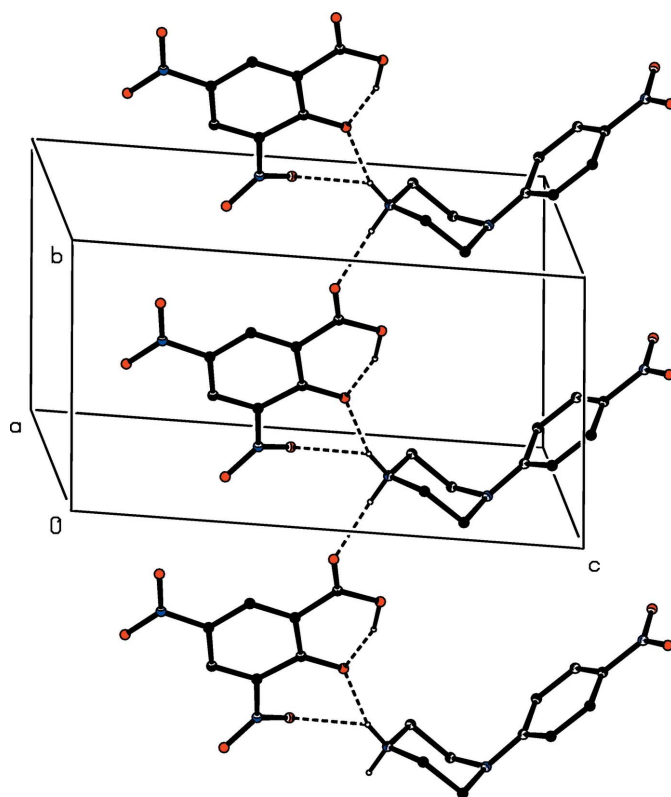
**Figure 4**  
Part of the crystal structure of compound (I) showing the formation of a chain of hydrogen-bonded rings running parallel to the [110] direction. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to those C atoms that are not involved in the motif shown have been omitted.

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

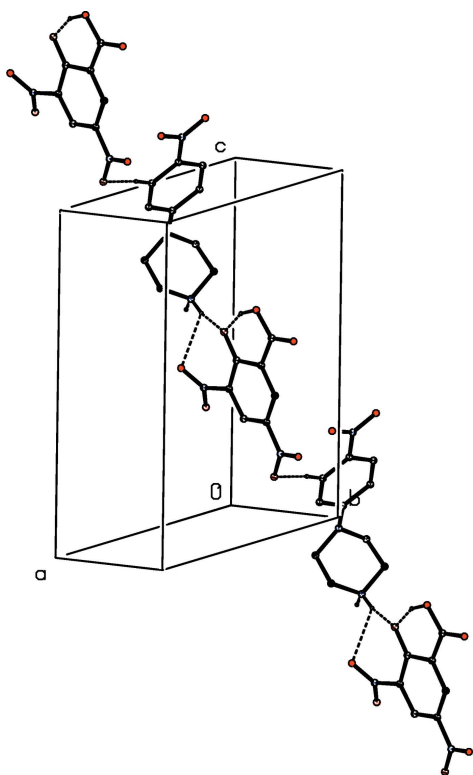
$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N11-H11 \cdots O21$	0.894 (14)	1.869 (14)	2.7356 (12)	162.8 (13)
$N11-H11 \cdots O262$	0.894 (14)	2.396 (14)	2.8937 (13)	115.4 (11)
$N11-H12 \cdots O271^i$	0.910 (14)	1.874 (14)	2.7668 (12)	166.2 (12)
$O272-H272 \cdots O21$	1.000 (17)	1.549 (17)	2.5020 (12)	157.4 (15)
$C12-H12B \cdots O142^{ii}$	0.99	2.41	3.3921 (14)	173
$C16-H16A \cdots O141^{ii}$	0.99	2.54	3.4906 (14)	161
$C145-H145 \cdots O242^{iii}$	0.95	2.46	3.3927 (15)	168
$C146-H146 \cdots O241^{iv}$	0.95	2.55	3.4227 (15)	153

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

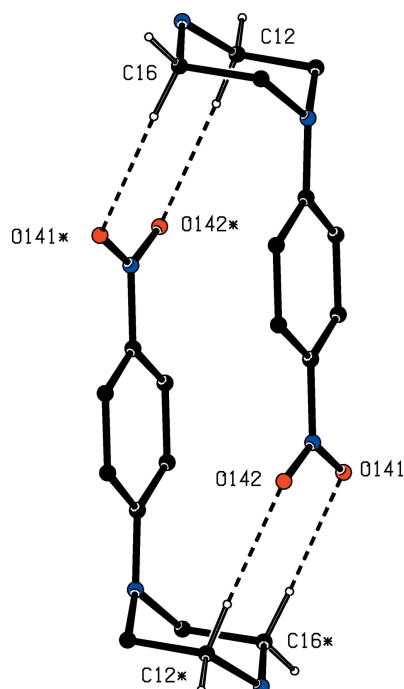
The supramolecular assembly for compound (II), by contrast, is tri-periodic (three dimensional) and, as for (I), the formation of the framework is readily analysed in terms of simple sub-structures. Within the selected asymmetric unit (Fig. 2), there is an intramolecular  $O-H \cdots O$  hydrogen bond in the anion, and the hydroxyl H atom plays no part in the supramolecular assembly. The two independent components are linked by a very asymmetric bifurcated  $N-H \cdots (O,O)$  hydrogen bond (Table 2), and a two-centre  $N-H \cdots O$  hydrogen bond links these ion pairs into a chain of rings running parallel to the [010] direction (Fig. 5). There are four  $C-H \cdots O$  hydrogen bonds in the structure of (II) and that involving atom C145 (Table 2) links the ion pairs into a second



**Figure 5**  
Part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded chain of rings running parallel to [010]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have all been omitted.

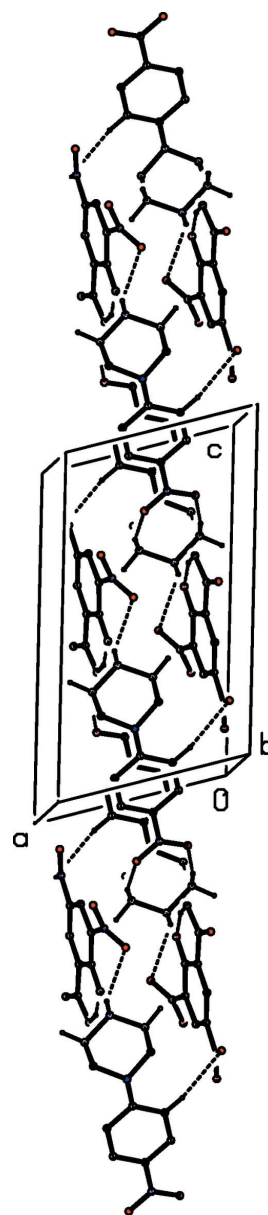


**Figure 6**  
Part of the crystal structure of compound (II) showing the formation of a chain of hydrogen-bonded rings running parallel to the [101] direction. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to those C atoms that are not involved in the motif shown have been omitted.



**Figure 7**  
Part of the crystal structure of compound (II) showing the linkage of an inversion-related pair of cations by two independent C—H...O hydrogen bonds, drawn as dashed lines. For the sake of clarity, the anions, the H atoms bonded to those C atoms that are not involved in the motif shown, and the unit-cell outline have been omitted. The atoms marked with an asterisk (\*) are at the symmetry position  $(1 - x, 1 - y, 2 - z)$ .

chain, this time running parallel to the [101] direction (Fig. 6). The two C—H...O hydrogen bonds involving atoms C12 and C16 link inversion-related pairs of cations into a centrosymmetric motif containing  $R_2^2(8)$  rings (Fig. 7), and the aggregates of this type are further linked by the final C—H...O hydrogen bond, that involves atom C146, to form a complex chain of rings running parallel to the [001] direction (Fig. 8). The combination of hydrogen-bonded chains parallel to [010], [001] and [101] generates a three-dimensional network. We also note a fairly short nitro–nitro contact, 2.823 (4) Å, between atom O142 at  $(x, y, z)$  and atom N24 at  $(1 + x, y, 1 + z)$ : this probably represents a dipolar attraction between negatively charged O and positively charged N atoms.



**Figure 8**  
Part of the crystal structure of compound (II) showing the formation of a chain of hydrogen-bonded rings running parallel to the [001] direction. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to those C atoms that are not involved in the motif shown have been omitted.

**Table 3**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{10}H_{14}N_3O_2^+ \cdot C_7H_5O_2^- \cdot H_2O$	$C_{10}H_{14}N_3O_2^+ \cdot C_7H_3N_2O_7^-$
$M_r$	347.37	435.35
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	90	90
$a, b, c$ (Å)	6.0768 (3), 7.4427 (4), 18.4737 (9)	7.9599 (4), 8.5391 (4), 14.2227 (5)
$\alpha, \beta, \gamma$ (°)	78.894 (2), 85.870 (3), 83.668 (2)	90.426 (2), 105.273 (1), 98.538 (2)
$V$ (Å <sup>3</sup> )	813.77 (7)	921.15 (7)
$Z$	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.11	0.13
Crystal size (mm)	0.24 × 0.22 × 0.17	0.22 × 0.18 × 0.12
Data collection		
Diffractometer	Bruker D8 Venture	Bruker D8 Venture
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\min}$ , $T_{\max}$	0.912, 0.971	0.919, 0.971
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	27142, 3737, 3164	38287, 4212, 3662
$R_{\text{int}}$	0.066	0.043
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.651	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.036, 0.091, 1.04	0.029, 0.077, 1.04
No. of reflections	3737	4212
No. of parameters	238	289
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.25, -0.20	0.28, -0.18

Computer programs: APEX3 (Bruker, 2016), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b) and PLATON (Spek, 2020).

#### 4. Database survey

The first structure report on a salt of *N*-(4-nitrophenyl)-piperazine concerned the chloride salt, which crystallizes as a monohydrate (Lu, 2007); despite the presence of hydrogen bonds of N—H···O, N—H···Cl and O—H···Cl types, the supramolecular assembly is only mono-periodic. The structures of six salts of *N*-(4-nitrophenyl)piperazine with aromatic carboxylic acids have recently been reported (Mahesha *et al.*, 2022): in all but one of these, the supramolecular assembly is mono-periodic, although it is di-periodic in the 4-ethoxybenzoate salt. This may be contrasted with the triperiodic assembly found here for compound (II).

In addition, we note that structures have been reported for a wide variety of salts derived from *N*-(4-fluorophenyl)-piperazine (Harish Chinthala, Yathirajan, Archana *et al.*, 2020; Harish Chinthala, Yathirajan, Kavitha *et al.*, 2020), and from *N*-(4-methoxyphenyl)piperazine (Kiran Kumar *et al.*, 2019, 2020). Finally, the structure of 4-(2-methoxyphenyl)piperazine-1-ium 3,5-dinitrosalicylate has been reported, but without any description of discussion of the geometry of the anion (Subha *et al.*, 2022).

#### 5. Synthesis and crystallization

For the preparation of compounds (I) and (II), a solution of *N*-(4-nitrophenyl)piperazine (100 mg, 0.483 mmol) in methanol (10 ml) was mixed with a solution of either benzoic acid (59 mg, 0.483 mmol) for (I) or 3,5-dinitrosalicylic acid

(110 mg, 0.483 mmol) for (II) in methanol/ethyl acetate (1:1 *v/v*, 20 ml). The solutions of the base and the corresponding acid were mixed, stirred at ambient temperature for 15 min, and then set aside to crystallize at ambient temperature and in the presence of air. After one week, crystals suitable for single-crystal X-ray diffraction were collected by filtration and dried in air: compound (I), pale yellow, m.p. 410–413 K; compound (II), orange, m.p. 446–448 K.

#### 6. Refinement

Crystal data, data collection and refinement details are summarized in Table 3. All H atoms were located in difference maps. The H atoms bonded to C atoms were then treated as riding atoms in geometrically idealized positions with C—H distances of 0.95 Å (aromatic) or 0.99 Å (CH<sub>2</sub>), and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . For the H atoms bonded to N or O atoms, the atomic coordinates were refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  or  $1.5U_{\text{eq}}(\text{O})$ , giving the N—H and O—H distances shown in Tables 1 and 2.

#### Acknowledgements

HJS is grateful to the University of Mysore for research facilities.

#### Funding information

HSY thanks the UGC for a BSR Faculty fellowship for three years.

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## supporting information

*Acta Cryst.* (2022). E78, 840-845 [https://doi.org/10.1107/S2056989022007472]

## Syntheses and crystal structures of 4-(4-nitrophenyl)piperazin-1-ium benzoate monohydrate and 4-(4-nitrophenyl)piperazin-1-ium 2-carboxy-4,6-dinitrophenolate

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### Computing details

For both structures, data collection: *APEX3* (Bruker, 2016); cell refinement: *APEX3* (Bruker, 2016); data reduction: *APEX3* (Bruker, 2016); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *PLATON* (Spek, 2020); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b) and *PLATON* (Spek, 2020).

### 4-(4-Nitrophenyl)piperazin-1-ium benzoate monohydrate (I)

#### Crystal data

$C_{10}H_{14}N_3O_2^+ \cdot C_7H_5O_2^- \cdot H_2O$

$M_r = 347.37$

Triclinic,  $P\bar{1}$

$a = 6.0768$  (3) Å

$b = 7.4427$  (4) Å

$c = 18.4737$  (9) Å

$\alpha = 78.894$  (2)°

$\beta = 85.870$  (3)°

$\gamma = 83.668$  (2)°

$V = 813.77$  (7) Å<sup>3</sup>

$Z = 2$

$F(000) = 368$

$D_x = 1.418$  Mg m<sup>-3</sup>

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

Cell parameters from 3737 reflections

$\theta = 2.3$ – $27.6$ °

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

$T = 90$  K

Block, pale yellow

$0.24 \times 0.22 \times 0.17$  mm

#### Data collection

Bruker D8 Venture  
diffractometer

Radiation source: microsource

Multilayer mirror monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.912$ ,  $T_{\max} = 0.971$

27142 measured reflections

3737 independent reflections

3164 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.066$

$\theta_{\max} = 27.6$ °,  $\theta_{\min} = 2.3$ °

$h = -7 \rightarrow 7$

$k = -9 \rightarrow 9$

$l = -23 \rightarrow 23$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.091$

$S = 1.04$

3737 reflections

238 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 0.2902P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

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

$$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$$

### 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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N11	0.22281 (16)	0.29238 (14)	0.44679 (5)	0.0163 (2)
H11	0.172 (2)	0.2234 (19)	0.4908 (8)	0.020*
H12	0.255 (2)	0.403 (2)	0.4565 (7)	0.020*
C12	0.04640 (18)	0.33021 (16)	0.39257 (6)	0.0175 (2)
H12A	-0.0854	0.3983	0.4129	0.021*
H12B	0.0020	0.2124	0.3839	0.021*
C13	0.12736 (18)	0.44242 (16)	0.32002 (6)	0.0172 (2)
H13A	0.0112	0.4575	0.2838	0.021*
H13B	0.1524	0.5664	0.3278	0.021*
N14	0.33332 (15)	0.35614 (13)	0.28973 (5)	0.0147 (2)
C15	0.50502 (18)	0.30670 (16)	0.34411 (6)	0.0163 (2)
H15A	0.5561	0.4205	0.3546	0.020*
H15B	0.6336	0.2365	0.3230	0.020*
C16	0.42143 (19)	0.19258 (16)	0.41561 (6)	0.0177 (2)
H16A	0.3830	0.0734	0.4063	0.021*
H16B	0.5394	0.1671	0.4515	0.021*
C141	0.40488 (18)	0.44038 (15)	0.21853 (6)	0.0149 (2)
C142	0.26572 (19)	0.57118 (16)	0.17307 (6)	0.0199 (2)
H142	0.1188	0.6040	0.1906	0.024*
C143	0.3394 (2)	0.65311 (16)	0.10304 (6)	0.0213 (3)
H143	0.2432	0.7399	0.0725	0.026*
C144	0.5535 (2)	0.60750 (16)	0.07820 (6)	0.0189 (2)
C145	0.6944 (2)	0.47632 (16)	0.12051 (6)	0.0199 (2)
H145	0.8406	0.4442	0.1021	0.024*
C146	0.61972 (19)	0.39295 (16)	0.18972 (6)	0.0178 (2)
H146	0.7152	0.3015	0.2186	0.021*
N144	0.63672 (18)	0.70469 (14)	0.00703 (6)	0.0242 (2)
O141	0.50758 (17)	0.81136 (14)	-0.03222 (5)	0.0352 (2)
O142	0.83458 (17)	0.67621 (15)	-0.01004 (6)	0.0421 (3)
C21	0.13555 (18)	0.09842 (14)	0.71032 (6)	0.0156 (2)
C22	-0.05414 (19)	0.01147 (15)	0.73666 (6)	0.0170 (2)
H22	-0.1565	-0.0072	0.7030	0.020*
C23	-0.0937 (2)	-0.04784 (16)	0.81206 (6)	0.0207 (2)
H23	-0.2239	-0.1058	0.8299	0.025*
C24	0.0564 (2)	-0.02246 (16)	0.86119 (6)	0.0229 (3)



H24	0.0297	-0.0636	0.9127	0.027*
C25	0.2458 (2)	0.06303 (16)	0.83528 (7)	0.0236 (3)
H25	0.3494	0.0793	0.8691	0.028*
C26	0.2842 (2)	0.12465 (16)	0.76032 (7)	0.0203 (2)
H26	0.4127	0.1852	0.7429	0.024*
C27	0.18134 (19)	0.16532 (15)	0.62878 (6)	0.0179 (2)
O271	0.32916 (15)	0.27141 (13)	0.61005 (5)	0.0293 (2)
O272	0.06693 (14)	0.11185 (11)	0.58360 (4)	0.02171 (19)
O31	0.70609 (15)	0.35347 (12)	0.53628 (5)	0.02152 (19)
H31	0.579 (3)	0.325 (2)	0.5608 (9)	0.032*
H32	0.813 (3)	0.268 (2)	0.5570 (9)	0.032*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N11	0.0197 (5)	0.0150 (5)	0.0136 (5)	-0.0029 (4)	0.0017 (4)	-0.0017 (4)
C12	0.0152 (5)	0.0199 (6)	0.0168 (5)	-0.0021 (4)	0.0012 (4)	-0.0027 (4)
C13	0.0147 (5)	0.0189 (5)	0.0165 (5)	0.0002 (4)	0.0009 (4)	-0.0011 (4)
N14	0.0129 (4)	0.0170 (5)	0.0133 (4)	-0.0004 (4)	0.0003 (3)	-0.0016 (3)
C15	0.0142 (5)	0.0186 (5)	0.0153 (5)	0.0005 (4)	-0.0002 (4)	-0.0023 (4)
C16	0.0189 (6)	0.0174 (5)	0.0154 (5)	0.0014 (4)	-0.0004 (4)	-0.0015 (4)
C141	0.0166 (5)	0.0138 (5)	0.0149 (5)	-0.0035 (4)	0.0003 (4)	-0.0038 (4)
C142	0.0173 (6)	0.0229 (6)	0.0178 (6)	0.0004 (5)	0.0000 (4)	-0.0011 (4)
C143	0.0238 (6)	0.0203 (6)	0.0181 (6)	0.0008 (5)	-0.0032 (5)	-0.0002 (4)
C144	0.0267 (6)	0.0166 (5)	0.0138 (5)	-0.0061 (5)	0.0018 (4)	-0.0023 (4)
C145	0.0203 (6)	0.0205 (6)	0.0186 (6)	-0.0023 (5)	0.0036 (4)	-0.0048 (4)
C146	0.0181 (6)	0.0167 (5)	0.0174 (5)	0.0009 (4)	0.0003 (4)	-0.0020 (4)
N144	0.0324 (6)	0.0222 (5)	0.0170 (5)	-0.0051 (4)	0.0035 (4)	-0.0018 (4)
O141	0.0423 (6)	0.0372 (6)	0.0203 (5)	-0.0024 (5)	-0.0027 (4)	0.0089 (4)
O142	0.0364 (6)	0.0463 (6)	0.0329 (5)	0.0013 (5)	0.0165 (4)	0.0092 (5)
C21	0.0167 (5)	0.0110 (5)	0.0180 (5)	0.0009 (4)	0.0008 (4)	-0.0019 (4)
C22	0.0169 (5)	0.0158 (5)	0.0186 (5)	-0.0011 (4)	0.0002 (4)	-0.0043 (4)
C23	0.0226 (6)	0.0172 (6)	0.0209 (6)	-0.0024 (5)	0.0060 (5)	-0.0026 (4)
C24	0.0348 (7)	0.0164 (6)	0.0158 (5)	0.0018 (5)	0.0008 (5)	-0.0021 (4)
C25	0.0302 (7)	0.0180 (6)	0.0236 (6)	0.0003 (5)	-0.0100 (5)	-0.0047 (5)
C26	0.0190 (6)	0.0142 (5)	0.0271 (6)	-0.0019 (4)	-0.0013 (5)	-0.0024 (4)
C27	0.0171 (5)	0.0130 (5)	0.0211 (6)	0.0017 (4)	0.0036 (4)	-0.0004 (4)
O271	0.0260 (5)	0.0318 (5)	0.0282 (5)	-0.0127 (4)	0.0070 (4)	0.0012 (4)
O272	0.0275 (5)	0.0213 (4)	0.0157 (4)	-0.0036 (3)	0.0013 (3)	-0.0020 (3)
O31	0.0203 (4)	0.0214 (4)	0.0228 (4)	-0.0045 (4)	0.0042 (3)	-0.0044 (3)

*Geometric parameters (Å, °)*

N11—C16	1.4857 (14)	C144—C145	1.3841 (17)
N11—C12	1.4870 (14)	C144—N144	1.4581 (14)
N11—H11	0.925 (14)	C145—C146	1.3780 (16)
N11—H12	0.921 (15)	C145—H145	0.9500
C12—C13	1.5167 (15)	C146—H146	0.9500

C12—H12A	0.9900	N144—O141	1.2226 (14)
C12—H12B	0.9900	N144—O142	1.2268 (14)
C13—N14	1.4671 (14)	C21—C26	1.3911 (16)
C13—H13A	0.9900	C21—C22	1.3953 (16)
C13—H13B	0.9900	C21—C27	1.5084 (15)
N14—C141	1.4044 (14)	C22—C23	1.3896 (16)
N14—C15	1.4688 (14)	C22—H22	0.9500
C15—C16	1.5134 (15)	C23—C24	1.3840 (18)
C15—H15A	0.9900	C23—H23	0.9500
C15—H15B	0.9900	C24—C25	1.3869 (18)
C16—H16A	0.9900	C24—H24	0.9500
C16—H16B	0.9900	C25—C26	1.3838 (17)
C141—C142	1.4049 (16)	C25—H25	0.9500
C141—C146	1.4081 (16)	C26—H26	0.9500
C142—C143	1.3853 (16)	C27—O271	1.2476 (14)
C142—H142	0.9500	C27—O272	1.2692 (14)
C143—C144	1.3764 (17)	O31—H31	0.893 (17)
C143—H143	0.9500	O31—H32	0.909 (17)
C16—N11—C12	109.33 (9)	C141—C142—H142	119.5
C16—N11—H11	110.2 (8)	C144—C143—C142	119.36 (11)
C12—N11—H11	110.3 (8)	C144—C143—H143	120.3
C16—N11—H12	111.3 (8)	C142—C143—H143	120.3
C12—N11—H12	108.0 (8)	C143—C144—C145	121.48 (11)
H11—N11—H12	107.6 (12)	C143—C144—N144	119.32 (11)
N11—C12—C13	110.80 (9)	C145—C144—N144	119.16 (11)
N11—C12—H12A	109.5	C146—C145—C144	119.05 (11)
C13—C12—H12A	109.5	C146—C145—H145	120.5
N11—C12—H12B	109.5	C144—C145—H145	120.5
C13—C12—H12B	109.5	C145—C146—C141	121.42 (10)
H12A—C12—H12B	108.1	C145—C146—H146	119.3
N14—C13—C12	112.32 (9)	C141—C146—H146	119.3
N14—C13—H13A	109.1	O141—N144—O142	123.28 (11)
C12—C13—H13A	109.1	O141—N144—C144	118.78 (11)
N14—C13—H13B	109.1	O142—N144—C144	117.94 (10)
C12—C13—H13B	109.1	C26—C21—C22	119.26 (10)
H13A—C13—H13B	107.9	C26—C21—C27	119.54 (10)
C141—N14—C13	115.67 (9)	C22—C21—C27	121.19 (10)
C141—N14—C15	115.77 (9)	C23—C22—C21	120.20 (11)
C13—N14—C15	112.34 (9)	C23—C22—H22	119.9
N14—C15—C16	112.12 (9)	C21—C22—H22	119.9
N14—C15—H15A	109.2	C24—C23—C22	119.98 (11)
C16—C15—H15A	109.2	C24—C23—H23	120.0
N14—C15—H15B	109.2	C22—C23—H23	120.0
C16—C15—H15B	109.2	C23—C24—C25	120.06 (11)
H15A—C15—H15B	107.9	C23—C24—H24	120.0
N11—C16—C15	110.12 (9)	C25—C24—H24	120.0
N11—C16—H16A	109.6	C26—C25—C24	120.10 (11)

C15—C16—H16A	109.6	C26—C25—H25	119.9
N11—C16—H16B	109.6	C24—C25—H25	119.9
C15—C16—H16B	109.6	C25—C26—C21	120.38 (11)
H16A—C16—H16B	108.2	C25—C26—H26	119.8
N14—C141—C142	121.85 (10)	C21—C26—H26	119.8
N14—C141—C146	120.53 (10)	O271—C27—O272	124.07 (11)
C142—C141—C146	117.62 (10)	O271—C27—C21	117.57 (11)
C143—C142—C141	121.01 (11)	O272—C27—C21	118.35 (10)
C143—C142—H142	119.5	H31—O31—H32	106.4 (14)
C16—N11—C12—C13	-58.34 (12)	C144—C145—C146—C141	-0.95 (17)
N11—C12—C13—N14	54.53 (12)	N14—C141—C146—C145	-178.85 (10)
C12—C13—N14—C141	172.83 (9)	C142—C141—C146—C145	2.33 (17)
C12—C13—N14—C15	-51.20 (12)	C143—C144—N144—O141	-7.29 (17)
C141—N14—C15—C16	-171.67 (9)	C145—C144—N144—O141	175.18 (11)
C13—N14—C15—C16	52.40 (12)	C143—C144—N144—O142	171.98 (12)
C12—N11—C16—C15	59.27 (12)	C145—C144—N144—O142	-5.55 (17)
N14—C15—C16—N11	-56.67 (12)	C26—C21—C22—C23	0.09 (16)
C13—N14—C141—C142	-13.70 (15)	C27—C21—C22—C23	-179.53 (10)
C15—N14—C141—C142	-148.15 (11)	C21—C22—C23—C24	-0.69 (17)
C13—N14—C141—C146	167.53 (10)	C22—C23—C24—C25	0.35 (18)
C15—N14—C141—C146	33.07 (14)	C23—C24—C25—C26	0.59 (18)
N14—C141—C142—C143	179.86 (11)	C24—C25—C26—C21	-1.19 (17)
C146—C141—C142—C143	-1.33 (17)	C22—C21—C26—C25	0.85 (17)
C141—C142—C143—C144	-1.02 (18)	C27—C21—C26—C25	-179.52 (10)
C142—C143—C144—C145	2.49 (18)	C26—C21—C27—O271	-12.91 (16)
C142—C143—C144—N144	-174.99 (11)	C22—C21—C27—O271	166.71 (11)
C143—C144—C145—C146	-1.51 (18)	C26—C21—C27—O272	167.61 (10)
N144—C144—C145—C146	175.97 (10)	C22—C21—C27—O272	-12.77 (16)

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C21—C26 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N11—H11...O271	0.926 (14)	2.564 (14)	3.1009 (13)	117.4 (10)
N11—H11...O272	0.926 (14)	1.857 (14)	2.7781 (12)	172.9 (13)
N11—H12...O31 <sup>i</sup>	0.920 (15)	1.884 (15)	2.7965 (14)	171.0 (12)
O31—H31...O271	0.892 (18)	1.757 (18)	2.6486 (13)	179 (3)
O31—H32...O272 <sup>ii</sup>	0.908 (17)	1.862 (17)	2.7581 (12)	168.8 (16)
C12—H12 <i>B</i> ...O272 <sup>iii</sup>	0.99	2.45	3.3751 (15)	156
C146—H146...Cg1 <sup>iv</sup>	0.95	2.67	3.4363 (13)	138

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

## 4-(4-Nitrophenyl)piperazin-1-ium 2-carboxy-4,6-dinitrophenolate (II)

## Crystal data

 $C_{10}H_{14}N_3O_2^+ \cdot C_7H_3N_2O_7^-$  $M_r = 435.35$ Triclinic,  $P\bar{1}$  $a = 7.9599$  (4) Å $b = 8.5391$  (4) Å $c = 14.2227$  (5) Å $\alpha = 90.426$  (2)° $\beta = 105.273$  (1)° $\gamma = 98.538$  (2)° $V = 921.15$  (7) Å<sup>3</sup> $Z = 2$  $F(000) = 452$  $D_x = 1.570$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4212 reflections

 $\theta = 2.4$ – $27.5$ ° $\mu = 0.13$  mm<sup>-1</sup> $T = 90$  K

Block, orange

 $0.22 \times 0.18 \times 0.12$  mm

## Data collection

Bruker D8 Venture  
diffractometer

Radiation source: microsource

Multilayer mirror monochromator

 $\varphi$  and  $\omega$  scansAbsorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015) $T_{\min} = 0.919$ ,  $T_{\max} = 0.971$ 

38287 measured reflections

4212 independent reflections

3662 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.043$  $\theta_{\max} = 27.5$ °,  $\theta_{\min} = 2.4$ ° $h = -10 \rightarrow 10$  $k = -11 \rightarrow 11$  $l = -18 \rightarrow 17$ 

## Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.029$  $wR(F^2) = 0.077$  $S = 1.04$ 

4212 reflections

289 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 0.3527P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.28$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.18$  e Å<sup>-3</sup>

## 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N11	0.30883 (12)	0.10386 (11)	0.64405 (7)	0.01693 (19)
H11	0.2967 (17)	0.1840 (17)	0.6040 (10)	0.020*
H12	0.2796 (17)	0.0129 (17)	0.6057 (10)	0.020*
C12	0.17915 (14)	0.10314 (13)	0.70340 (8)	0.0188 (2)
H12A	0.0579	0.0733	0.6608	0.023*
H12B	0.1890	0.2107	0.7328	0.023*
C13	0.21403 (14)	-0.01389 (13)	0.78350 (8)	0.0187 (2)
H13A	0.1321	-0.0092	0.8248	0.022*
H13B	0.1931	-0.1229	0.7541	0.022*

N14	0.39625 (12)	0.02405 (11)	0.84356 (6)	0.01699 (19)
C15	0.51561 (14)	0.00483 (13)	0.78325 (8)	0.0170 (2)
H15A	0.4884	-0.1043	0.7536	0.020*
H15B	0.6388	0.0215	0.8245	0.020*
C16	0.49616 (14)	0.12299 (13)	0.70345 (8)	0.0172 (2)
H16A	0.5334	0.2322	0.7330	0.021*
H16B	0.5729	0.1055	0.6610	0.021*
C141	0.44287 (14)	0.13710 (12)	0.91966 (7)	0.0156 (2)
C142	0.31639 (14)	0.18318 (13)	0.96323 (8)	0.0185 (2)
H142	0.1955	0.1406	0.9370	0.022*
C143	0.36498 (14)	0.28859 (13)	1.04300 (8)	0.0182 (2)
H143	0.2783	0.3179	1.0717	0.022*
C144	0.54137 (14)	0.35176 (12)	1.08126 (7)	0.0161 (2)
C145	0.66886 (14)	0.31362 (13)	1.03852 (8)	0.0173 (2)
H145	0.7887	0.3601	1.0640	0.021*
C146	0.62025 (14)	0.20794 (13)	0.95897 (8)	0.0174 (2)
H146	0.7078	0.1821	0.9299	0.021*
N144	0.59245 (12)	0.46290 (11)	1.16455 (6)	0.01728 (19)
O141	0.47859 (11)	0.49209 (10)	1.20379 (6)	0.02406 (19)
O142	0.74805 (11)	0.52457 (10)	1.19410 (6)	0.02329 (18)
C21	0.24532 (14)	0.43648 (13)	0.46951 (8)	0.0171 (2)
C22	0.20094 (14)	0.59329 (12)	0.45355 (8)	0.0168 (2)
C23	0.15472 (14)	0.65011 (13)	0.36161 (8)	0.0163 (2)
H23	0.1308	0.7557	0.3537	0.020*
C24	0.14290 (14)	0.55395 (13)	0.28038 (8)	0.0164 (2)
C25	0.17807 (14)	0.40041 (13)	0.28998 (8)	0.0165 (2)
H25	0.1656	0.3340	0.2339	0.020*
C26	0.23134 (14)	0.34521 (12)	0.38199 (8)	0.0162 (2)
O21	0.28898 (12)	0.38660 (9)	0.55580 (6)	0.02378 (19)
C27	0.20933 (15)	0.70160 (13)	0.53734 (8)	0.0199 (2)
O271	0.16416 (12)	0.83252 (9)	0.52573 (6)	0.02424 (19)
O272	0.26860 (13)	0.65093 (10)	0.62536 (6)	0.0294 (2)
H272	0.288 (2)	0.540 (2)	0.6144 (12)	0.044*
N24	0.09824 (12)	0.61730 (11)	0.18421 (7)	0.01767 (19)
O241	0.08439 (11)	0.75980 (9)	0.17920 (6)	0.02152 (18)
O242	0.07873 (11)	0.52884 (10)	0.11242 (6)	0.02219 (18)
N26	0.27842 (12)	0.18676 (11)	0.38689 (7)	0.01824 (19)
O261	0.20718 (11)	0.09218 (9)	0.31673 (6)	0.02451 (19)
O262	0.38998 (12)	0.15381 (10)	0.45879 (6)	0.02596 (19)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N11	0.0230 (5)	0.0128 (4)	0.0146 (4)	0.0040 (4)	0.0037 (4)	-0.0003 (4)
C12	0.0177 (5)	0.0181 (5)	0.0198 (5)	0.0037 (4)	0.0032 (4)	-0.0033 (4)
C13	0.0188 (5)	0.0191 (5)	0.0171 (5)	-0.0008 (4)	0.0051 (4)	-0.0030 (4)
N14	0.0184 (4)	0.0179 (4)	0.0142 (4)	0.0015 (4)	0.0045 (3)	-0.0018 (3)
C15	0.0195 (5)	0.0162 (5)	0.0159 (5)	0.0045 (4)	0.0048 (4)	-0.0012 (4)

C16	0.0194 (5)	0.0157 (5)	0.0175 (5)	0.0030 (4)	0.0066 (4)	-0.0006 (4)
C141	0.0210 (5)	0.0132 (5)	0.0128 (5)	0.0032 (4)	0.0044 (4)	0.0028 (4)
C142	0.0163 (5)	0.0207 (5)	0.0176 (5)	0.0029 (4)	0.0030 (4)	0.0004 (4)
C143	0.0192 (5)	0.0199 (5)	0.0173 (5)	0.0064 (4)	0.0063 (4)	0.0020 (4)
C144	0.0218 (5)	0.0130 (5)	0.0133 (5)	0.0031 (4)	0.0039 (4)	0.0005 (4)
C145	0.0175 (5)	0.0168 (5)	0.0170 (5)	0.0012 (4)	0.0045 (4)	0.0015 (4)
C146	0.0190 (5)	0.0176 (5)	0.0169 (5)	0.0031 (4)	0.0071 (4)	0.0011 (4)
N144	0.0211 (5)	0.0150 (4)	0.0161 (4)	0.0033 (4)	0.0054 (4)	0.0013 (3)
O141	0.0240 (4)	0.0273 (4)	0.0229 (4)	0.0058 (3)	0.0092 (3)	-0.0061 (3)
O142	0.0213 (4)	0.0234 (4)	0.0230 (4)	-0.0029 (3)	0.0058 (3)	-0.0057 (3)
C21	0.0188 (5)	0.0154 (5)	0.0162 (5)	0.0013 (4)	0.0039 (4)	-0.0003 (4)
C22	0.0183 (5)	0.0142 (5)	0.0172 (5)	0.0014 (4)	0.0042 (4)	-0.0017 (4)
C23	0.0156 (5)	0.0146 (5)	0.0187 (5)	0.0024 (4)	0.0043 (4)	-0.0001 (4)
C24	0.0151 (5)	0.0189 (5)	0.0146 (5)	0.0018 (4)	0.0034 (4)	0.0011 (4)
C25	0.0143 (5)	0.0176 (5)	0.0174 (5)	-0.0001 (4)	0.0054 (4)	-0.0042 (4)
C26	0.0164 (5)	0.0131 (5)	0.0196 (5)	0.0024 (4)	0.0059 (4)	-0.0013 (4)
O21	0.0394 (5)	0.0160 (4)	0.0151 (4)	0.0071 (3)	0.0044 (3)	0.0009 (3)
C27	0.0252 (6)	0.0158 (5)	0.0178 (5)	0.0013 (4)	0.0051 (4)	-0.0015 (4)
O271	0.0347 (5)	0.0153 (4)	0.0218 (4)	0.0066 (3)	0.0046 (3)	-0.0032 (3)
O272	0.0541 (6)	0.0178 (4)	0.0151 (4)	0.0096 (4)	0.0051 (4)	-0.0019 (3)
N24	0.0141 (4)	0.0220 (5)	0.0168 (4)	0.0022 (4)	0.0043 (3)	0.0004 (4)
O241	0.0228 (4)	0.0206 (4)	0.0216 (4)	0.0054 (3)	0.0056 (3)	0.0050 (3)
O242	0.0224 (4)	0.0284 (4)	0.0151 (4)	0.0022 (3)	0.0049 (3)	-0.0038 (3)
N26	0.0207 (5)	0.0153 (4)	0.0209 (5)	0.0031 (4)	0.0093 (4)	-0.0007 (4)
O261	0.0267 (4)	0.0178 (4)	0.0285 (4)	0.0023 (3)	0.0074 (3)	-0.0087 (3)
O262	0.0329 (5)	0.0245 (4)	0.0226 (4)	0.0132 (4)	0.0061 (3)	0.0031 (3)

*Geometric parameters (Å, °)*

N11—C16	1.4919 (14)	C145—C146	1.3765 (15)
N11—C12	1.4951 (14)	C145—H145	0.9500
N11—H11	0.894 (14)	C146—H146	0.9500
N11—H12	0.910 (14)	N144—O142	1.2315 (12)
C12—C13	1.5187 (15)	N144—O141	1.2355 (12)
C12—H12A	0.9900	C21—O21	1.2788 (13)
C12—H12B	0.9900	C21—C26	1.4340 (15)
C13—N14	1.4635 (14)	C21—C22	1.4394 (15)
C13—H13A	0.9900	C22—C23	1.3747 (15)
C13—H13B	0.9900	C22—C27	1.4844 (15)
N14—C141	1.3812 (13)	C23—C24	1.3869 (15)
N14—C15	1.4625 (14)	C23—H23	0.9500
C15—C16	1.5169 (15)	C24—C25	1.3811 (15)
C15—H15A	0.9900	C24—N24	1.4498 (13)
C15—H15B	0.9900	C25—C26	1.3750 (15)
C16—H16A	0.9900	C25—H25	0.9500
C16—H16B	0.9900	C26—N26	1.4540 (14)
C141—C142	1.4125 (15)	C27—O271	1.2236 (14)
C141—C146	1.4133 (15)	C27—O272	1.3171 (14)

C142—C143	1.3774 (15)	O272—H272	1.003 (18)
C142—H142	0.9500	N24—O242	1.2277 (12)
C143—C144	1.3881 (15)	N24—O241	1.2389 (12)
C143—H143	0.9500	N26—O262	1.2303 (12)
C144—C145	1.3875 (15)	N26—O261	1.2343 (12)
C144—N144	1.4437 (13)		
C16—N11—C12	113.90 (8)	C144—C143—H143	120.2
C16—N11—H11	108.4 (9)	C145—C144—C143	120.87 (10)
C12—N11—H11	108.3 (9)	C145—C144—N144	119.43 (10)
C16—N11—H12	111.0 (8)	C143—C144—N144	119.67 (10)
C12—N11—H12	108.3 (9)	C146—C145—C144	119.48 (10)
H11—N11—H12	106.8 (12)	C146—C145—H145	120.3
N11—C12—C13	110.16 (9)	C144—C145—H145	120.3
N11—C12—H12A	109.6	C145—C146—C141	121.42 (10)
C13—C12—H12A	109.6	C145—C146—H146	119.3
N11—C12—H12B	109.6	C141—C146—H146	119.3
C13—C12—H12B	109.6	O142—N144—O141	122.45 (9)
H12A—C12—H12B	108.1	O142—N144—C144	118.77 (9)
N14—C13—C12	109.99 (9)	O141—N144—C144	118.78 (9)
N14—C13—H13A	109.7	O21—C21—C26	124.86 (10)
C12—C13—H13A	109.7	O21—C21—C22	120.75 (9)
N14—C13—H13B	109.7	C26—C21—C22	114.38 (9)
C12—C13—H13B	109.7	C23—C22—C21	121.89 (10)
H13A—C13—H13B	108.2	C23—C22—C27	117.59 (10)
C141—N14—C15	121.02 (9)	C21—C22—C27	120.49 (10)
C141—N14—C13	121.10 (9)	C22—C23—C24	120.26 (10)
C15—N14—C13	109.06 (8)	C22—C23—H23	119.9
N14—C15—C16	110.28 (9)	C24—C23—H23	119.9
N14—C15—H15A	109.6	C25—C24—C23	120.99 (10)
C16—C15—H15A	109.6	C25—C24—N24	119.55 (9)
N14—C15—H15B	109.6	C23—C24—N24	119.43 (10)
C16—C15—H15B	109.6	C26—C25—C24	118.95 (10)
H15A—C15—H15B	108.1	C26—C25—H25	120.5
N11—C16—C15	109.87 (9)	C24—C25—H25	120.5
N11—C16—H16A	109.7	C25—C26—C21	123.45 (10)
C15—C16—H16A	109.7	C25—C26—N26	115.98 (9)
N11—C16—H16B	109.7	C21—C26—N26	120.55 (9)
C15—C16—H16B	109.7	O271—C27—O272	121.14 (10)
H16A—C16—H16B	108.2	O271—C27—C22	121.85 (10)
N14—C141—C142	121.47 (10)	O272—C27—C22	117.01 (10)
N14—C141—C146	121.20 (10)	C27—O272—H272	105.0 (10)
C142—C141—C146	117.30 (10)	O242—N24—O241	123.40 (9)
C143—C142—C141	121.27 (10)	O242—N24—C24	118.92 (9)
C143—C142—H142	119.4	O241—N24—C24	117.67 (9)
C141—C142—H142	119.4	O262—N26—O261	122.85 (9)
C142—C143—C144	119.59 (10)	O262—N26—C26	119.17 (9)
C142—C143—H143	120.2	O261—N26—C26	117.95 (9)

C16—N11—C12—C13	-50.40 (12)	C26—C21—C22—C23	-1.93 (15)
N11—C12—C13—N14	56.08 (11)	O21—C21—C22—C27	1.51 (16)
C12—C13—N14—C141	84.07 (12)	C26—C21—C22—C27	-179.98 (10)
C12—C13—N14—C15	-63.61 (11)	C21—C22—C23—C24	2.55 (16)
C141—N14—C15—C16	-83.73 (12)	C27—C22—C23—C24	-179.35 (10)
C13—N14—C15—C16	63.98 (11)	C22—C23—C24—C25	-0.39 (16)
C12—N11—C16—C15	50.41 (11)	C22—C23—C24—N24	-178.48 (9)
N14—C15—C16—N11	-56.47 (11)	C23—C24—C25—C26	-2.25 (16)
C15—N14—C141—C142	164.67 (10)	N24—C24—C25—C26	175.84 (9)
C13—N14—C141—C142	20.80 (15)	C24—C25—C26—C21	2.85 (16)
C15—N14—C141—C146	-17.23 (15)	C24—C25—C26—N26	-175.67 (9)
C13—N14—C141—C146	-161.10 (10)	O21—C21—C26—C25	177.64 (10)
N14—C141—C142—C143	175.90 (10)	C22—C21—C26—C25	-0.79 (16)
C146—C141—C142—C143	-2.27 (16)	O21—C21—C26—N26	-3.90 (17)
C141—C142—C143—C144	0.36 (16)	C22—C21—C26—N26	177.67 (9)
C142—C143—C144—C145	1.84 (16)	C23—C22—C27—O271	5.49 (17)
C142—C143—C144—N144	179.67 (10)	C21—C22—C27—O271	-176.38 (10)
C143—C144—C145—C146	-2.02 (16)	C23—C22—C27—O272	-174.21 (10)
N144—C144—C145—C146	-179.86 (10)	C21—C22—C27—O272	3.93 (16)
C144—C145—C146—C141	0.00 (16)	C25—C24—N24—O242	5.79 (14)
N14—C141—C146—C145	-176.08 (10)	C23—C24—N24—O242	-176.09 (9)
C142—C141—C146—C145	2.09 (16)	C25—C24—N24—O241	-173.14 (9)
C145—C144—N144—O142	1.91 (15)	C23—C24—N24—O241	4.98 (14)
C143—C144—N144—O142	-175.95 (10)	C25—C26—N26—O262	150.18 (10)
C145—C144—N144—O141	-177.77 (10)	C21—C26—N26—O262	-28.38 (15)
C143—C144—N144—O141	4.37 (15)	C25—C26—N26—O261	-27.86 (14)
O21—C21—C22—C23	179.56 (10)	C21—C26—N26—O261	153.57 (10)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N11—H11 $\cdots$ O21	0.894 (14)	1.869 (14)	2.7356 (12)	162.8 (13)
N11—H11 $\cdots$ O262	0.894 (14)	2.396 (14)	2.8937 (13)	115.4 (11)
N11—H12 $\cdots$ O271 <sup>i</sup>	0.910 (14)	1.874 (14)	2.7668 (12)	166.2 (12)
O272—H272 $\cdots$ O21	1.000 (17)	1.549 (17)	2.5020 (12)	157.4 (15)
C12—H12B $\cdots$ O142 <sup>ii</sup>	0.99	2.41	3.3921 (14)	173
C16—H16A $\cdots$ O141 <sup>ii</sup>	0.99	2.54	3.4906 (14)	161
C145—H145 $\cdots$ O242 <sup>iii</sup>	0.95	2.46	3.3927 (15)	168
C146—H146 $\cdots$ O241 <sup>iv</sup>	0.95	2.55	3.4227 (15)	153

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