

# Syntheses, crystal structures and Hirshfeld surface analysis of 4-(4-nitrophenyl)piperazin-1-ium trifluoroacetate and 4-(4-nitrophenyl)piperazin-1-ium trichloroacetate

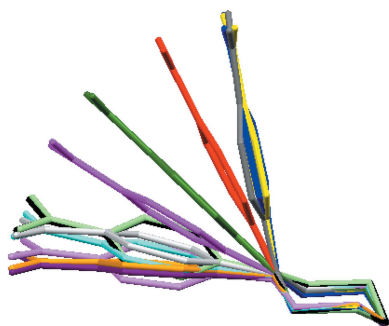
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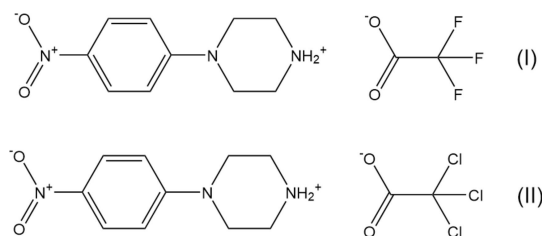
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The synthesis and crystal structures of the molecular salts of 4-(4-nitrophenyl)piperazine with trifluoroacetate, namely, 4-(4-nitrophenyl)piperazin-1-ium trifluoroacetate,  $C_{10}H_{14}N_3O_2^+ \cdot C_2F_3O_2^-$  (I), and with trichloroacetate, namely, 4-(4-nitrophenyl)piperazin-1-ium trichloroacetate,  $C_{10}H_{14}N_3O_2^+ \cdot C_2Cl_3O_2^-$  (II), are reported and compared. A partial positional disorder of the anions was found. In both structures, the piperazine rings adopt a chair conformation, whereas the positions of the nitrophenyl group on the piperazine ring differ from bisectonal in (I) to equatorial in (II). In both structures, the supra-molecular assemblies are mono-periodic on the basis of the chain-of-rings motifs supported by aromatic  $\pi$ - $\pi$  interactions. Hirshfeld surface analysis was used to explore the intermolecular close contacts in both crystals. The most dominant contacts of the Hirshfeld surface of the cation-anion pairs of the asymmetric units are  $O \cdots H/H \cdots O$ , and those with a contribution of halogen atoms:  $F \cdots H/H \cdots F$  in (I) and  $Cl \cdots H/H \cdots Cl$  in (II), respectively.

## 1. Chemical context

Piperazines and their derivatives have attracted growing attention for years (Berkheij *et al.*, 2005; Elliott, 2011; Asif, 2015; Brito *et al.*, 2019), mainly because of their multivalent biological profiles in a number of different therapeutic areas (Upadhayaya *et al.*, 2004; Chaudhary *et al.*, 2006; Kharb *et al.*, 2012). The pharmacological significance of piperazines is also manifested in the application of its framework in the assemblies of inclusion, hybrid and other functional materials (Brockunier *et al.*, 2004; Bogatcheva *et al.*, 2006; Jin *et al.*, 2020; Gharbi *et al.*, 2022). Among them, a potential application for 4-nitrophenylpiperazine (NPP) can be indicated (König *et al.*, 1997; Lu, 2007; Wang *et al.*, 2014). We have recently reported the crystal structures of eight salts of 4-nitrophenylpiperazine (Mahesha *et al.*, 2022; Shankara Prasad *et al.*, 2022). In view of the importance of piperazines in general and the use of 4-nitrophenylpiperazine in particular, the present article reports the synthesis, crystal structure and Hirshfeld surface analysis of two salts of 4-nitrophenylpiperazine with organic acids, namely, 4-(4-nitrophenyl)piperazin-1-ium trifluoroacetate,  $C_{12}H_{14}F_3N_3O_4$ , (I) and 4-(4-nitrophenyl)piperazin-1-ium trichloroacetate,  $C_{12}H_{14}Cl_3N_3O_4$ , (II).

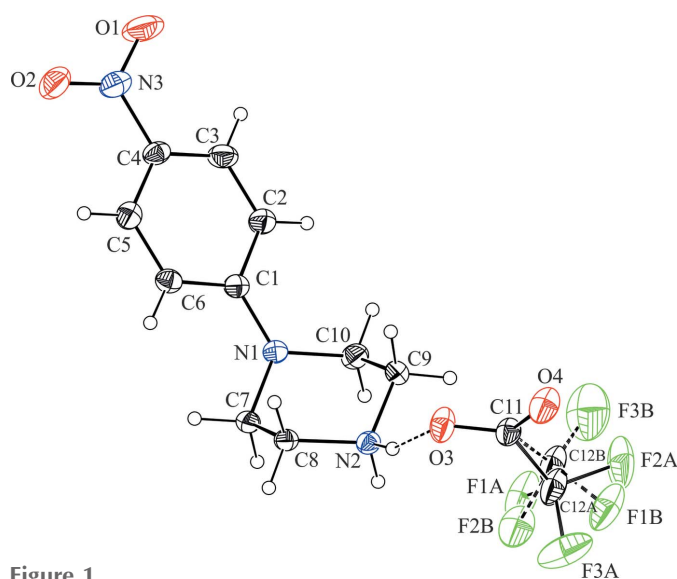




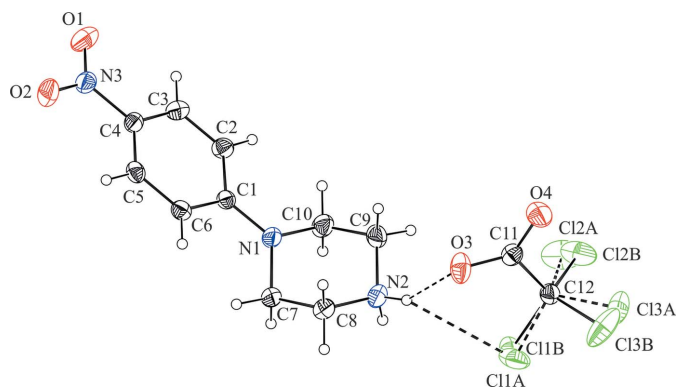
## 2. Structural commentary

The title compounds are shown in Figs. 1 and 2. The piperazine rings adopt a chair conformation with puckering parameters (Cremer & Pople, 1975) in (I) of  $Q = 0.576$  (2) Å,  $\theta = 177.8$  (2)°,  $\varphi = 182$  (4)°, and in (II) of  $Q = 0.571$  (2) Å,  $\theta = 177.1$  (2)°,  $\varphi = 189$  (4)°, respectively. The position of the nitrophenyl group on the piperazine ring differs in the two structures, from bisectonal in (I) to occupying an equatorial site in (II) (Fig. 3). The angle between the N1–C1 bond and the normal to the Cremer & Pople mean plane is 39.57 (11)° in (I) and 60.87 (14)° in (II) (Spek, 2020; see *Database survey section* for further comparisons). In addition, the delocalization effect within the benzene ring is slightly disturbed due to the presence of the electron-donating piperazinyl [ $-C_4H_8N_2$ ; for the structurally similar piperidino substituent the Hammett  $\sigma_p$  constant is  $-0.12$  (Perrin *et al.*, 1981)] and the electron-withdrawing nitro [ $-NO_2$ ,  $\sigma_p = 0.78$  (Hansch *et al.*, 1991)] groups located in the *para*- position: the lengthening of the C1–C2 and C1–C6 bonds is accompanied by the shortening of the remaining C–C bonds within the ring and C–N distances to the substituents.

In the anions, the C–O bond lengths in the carboxylate group are more similar in compound (II) than in compound



**Figure 1**  
Independent components of compound (I) showing the atom-labelling scheme and the hydrogen bond (drawn as dashed line) within the selected asymmetric unit. The major disorder component is drawn using unbroken lines (A) and the minor disorder component is drawn using dashed lines (B). Displacement ellipsoids are drawn at the 30% probability level.

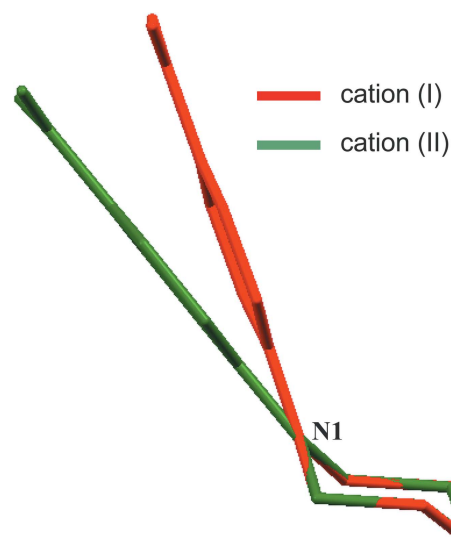


**Figure 2**  
Independent components of compound (II) showing the atom-labelling scheme and the hydrogen bonds (drawn as dashed lines) within the selected asymmetric unit. The disorder components A and B of chlorine atoms have equal site-occupancies (1/2) within s.u. Displacement ellipsoids are drawn at the 30% probability level.

(I), although in both cases these distances are shorter than the mean value for its type (Allen *et al.*, 1987). The geometries of the  $COO^-$  groups can be affected by the positional disorder of the  $CF_3$  group in (I) and the chlorine atoms in (II). In (I), the  $CF_3$  group is found to be disordered over two orientations, with a refined occupancy ratio of 0.779 (4):0.221 (4), while in (II), the disordered chlorine atoms in the  $CCl_3$  group show an almost equivalent contribution of components A and B [0.494 (15) and 0.506 (15)] (Figs. 1 and 2).

## 3. Supramolecular features

In (I), the 4-(4-nitrophenyl)piperazin-1-ium cation interacts with two trifluoroacetate anions, which are related by translation, by two N–H...O hydrogen bonds: N2–H21...O3 and N2–H21...O4( $x + 1, y, z$ ). Additionally, if one considers the C7–H7A...O3( $x + 1, y, z$ ) interaction the hydrogen-bonded



**Figure 3**  
Superposition of the 4-(4-nitrophenyl)piperazin-1-ium cations in (I) (red) and (II) (green).

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H21\cdots O3$	0.90 (2)	1.98 (2)	2.844 (2)	161 (2)
$N2-H22\cdots O4^i$	0.87 (2)	1.93 (2)	2.786 (2)	165 (2)
$C7-H7A\cdots O3^i$	0.97	2.53	3.492 (2)	169

 Symmetry code: (i)  $x + 1, y, z$ .

**Table 2**  
 Hydrogen-bond geometry (Å, °) for (II).

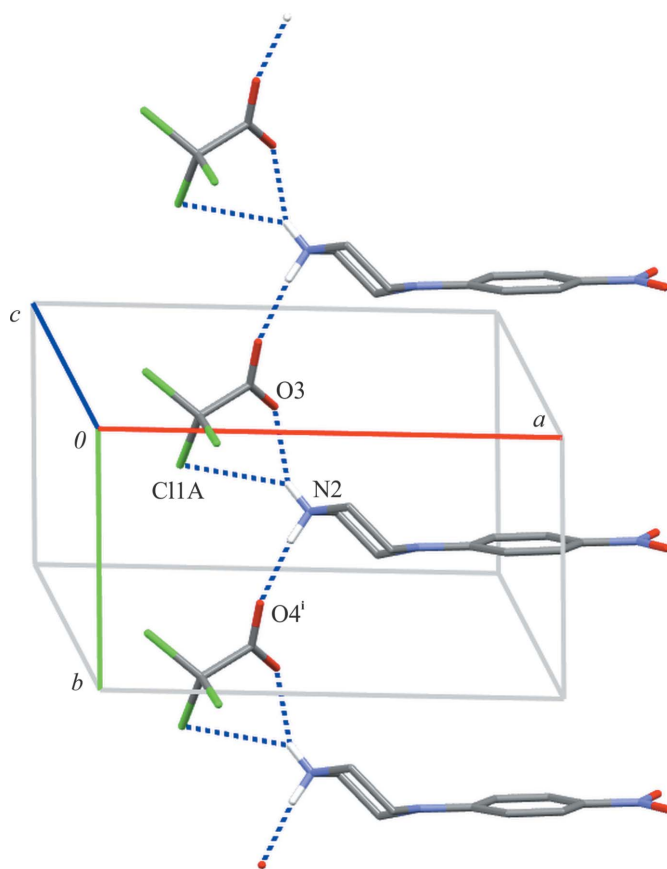
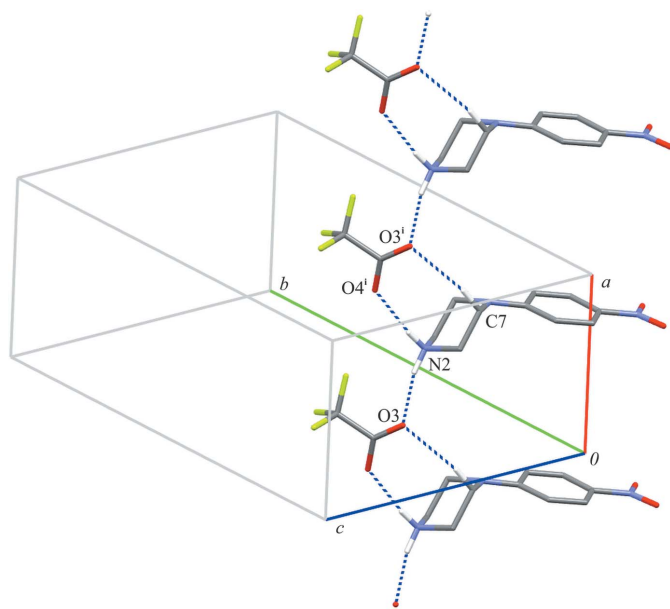
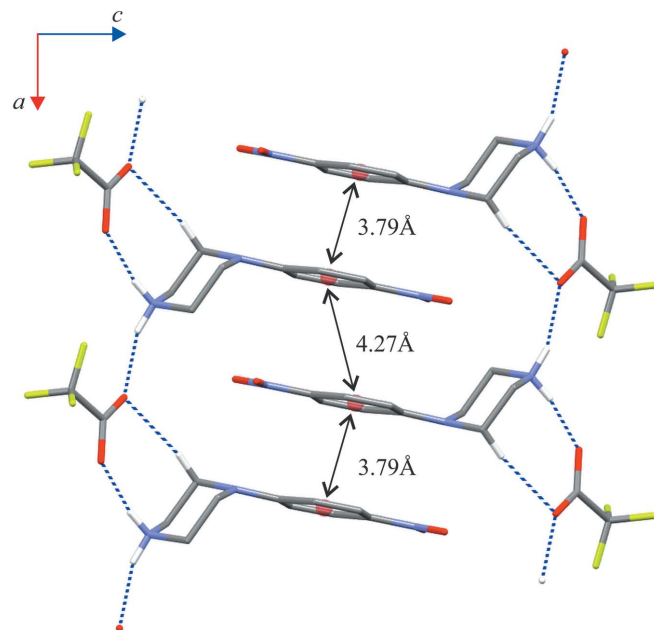
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H21\cdots O3$	0.87 (2)	2.01 (2)	2.795 (2)	151 (2)
$N2-H21\cdots C11A$	0.87 (2)	2.82 (2)	3.510 (5)	138 (2)
$N2-H22\cdots O4^i$	0.87 (2)	1.89 (2)	2.738 (2)	167 (2)

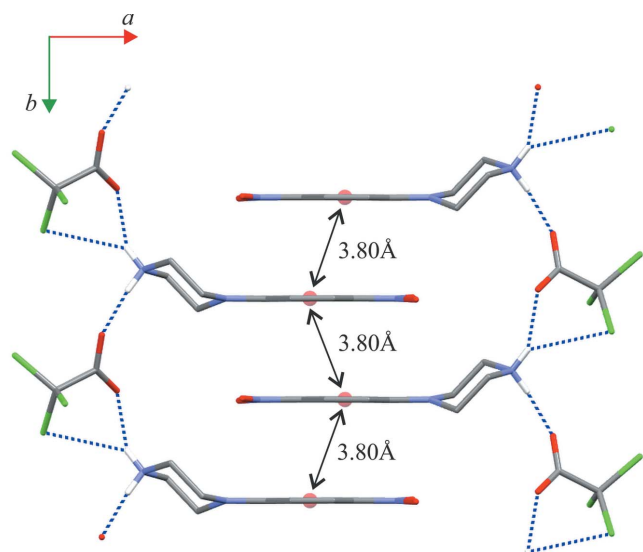
 Symmetry code: (i)  $x, y + 1, z$ .

motif can be described as a  $C(6)C(6)[R_2^2(8)]$  chain of rings (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995) running parallel to the [100] direction (Fig. 4, Table 1).

In (II), the ionic components of the asymmetric unit are linked by two  $N2-H21\cdots O3$  and  $N2-H21\cdots C11A$  hydrogen bonds, forming an  $R_1^2(5)$  ring motif. This ring system is further propagated along the [010] direction through the  $N2-H22\cdots O3(x, y + 1, z)$  hydrogen bond; and a  $C(6)C(7)[R_1^2(5)]$  chain of rings is created (Fig. 5, Table 2).

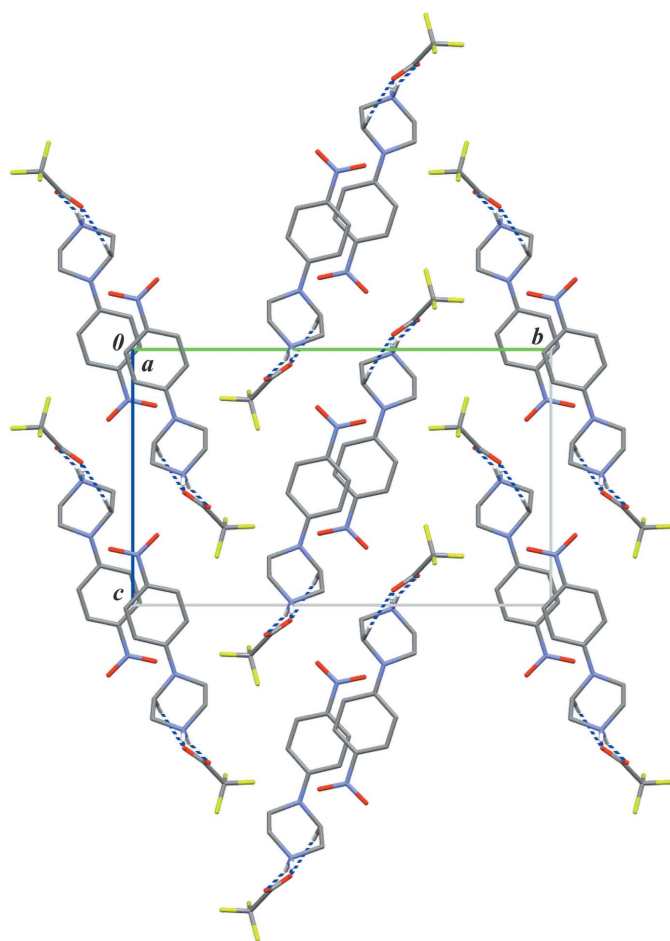
Close inspection of the crystal packings of both structures reveals the aromatic  $\pi-\pi$  interactions between adjacent chains of rings (Figs. 6 and 7). The centroid-centroid distances ( $Cg1\cdots Cg1$ ) between the phenyl rings are 3.788 (1) and 4.268 (1) Å in (I) and 3.800 (1) Å in (II); the perpendicular


**Figure 5**  
 Part of the crystal structure of compound (II) showing the formation of a chain of rings parallel to the [010] direction. Hydrogen bonds are drawn as dashed lines, and for the sake of clarity, the H atoms bonded to C atoms have been omitted. Symmetry code: (i)  $x, y + 1, z$ .

**Figure 4**  
 Part of the crystal structure of compound (I) showing the formation of a chain of rings 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 been omitted. Symmetry code: (i)  $x + 1, y, z$ .

**Figure 6**  
 A part of the crystal structure of compound (I) showing the aromatic  $\pi-\pi$  interactions between adjacent chains of rings. Red balls represent the centroids of the phenyl rings ( $Cg1$ ).



**Figure 7**  
A part of the crystal structure of compound (II) showing the aromatic  $\pi$ - $\pi$  interactions between adjacent chains of rings. Red balls represent the centroids of the phenyl rings (Cg1).

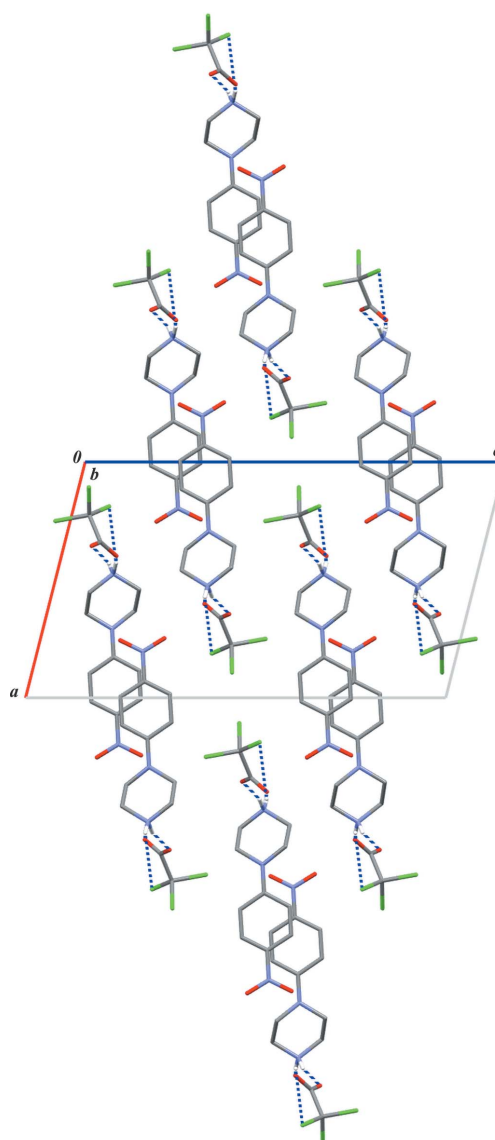
distances from the centroid to the plane of the opposite ring are 3.333 (1) and 3.253 (1) Å in (I) and 3.303 (1) Å in (II).



**Figure 8**  
Crystal packing of (I) in a view along the crystallographic *a* axis (herringbone type).

Although in (I) the slippage distance (2.764 Å) between the centroids spaced by 4.27 Å is markedly far from a value of 1.8 Å (suggesting an overlap of rings), one can still consider molecular stacks along the [100] direction to be comparable to those undoubtedly observed in structure (II) in the [010] direction.

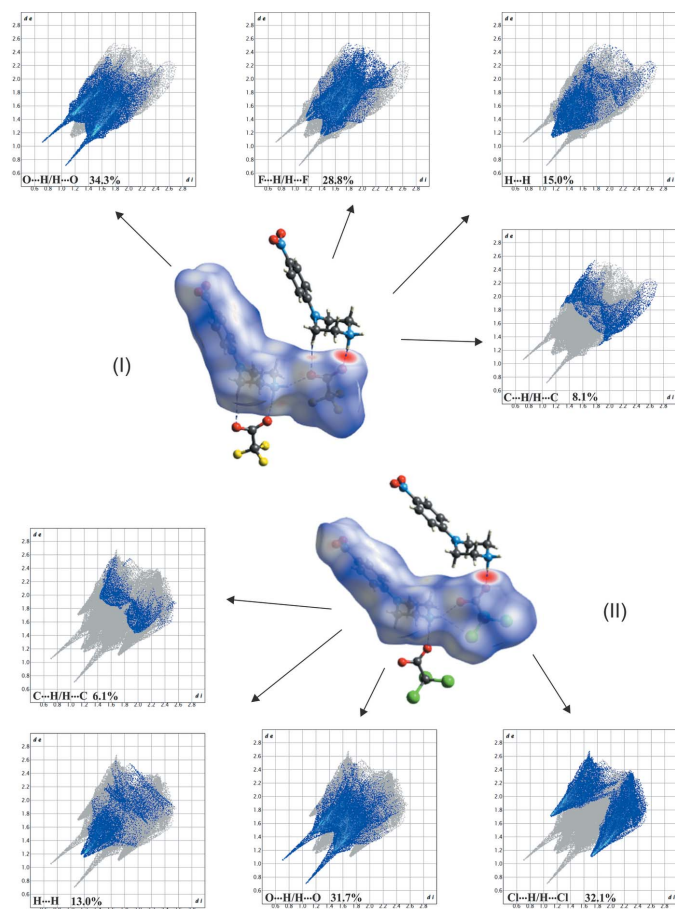
Finally, both supramolecular structures can be described as mono-periodic; no other specific close contacts or interactions can be found in addition to those mentioned above. Despite the similarities in the formation of 1D-chains of rings and their stacking assemblies, the packing of these motifs in the analysed crystals is fundamentally different. In (I), the packing fashion can be described as herringbone-type (Fig. 8), whereas in (II) a linear mode is seen (Fig. 9). It seems that the halogen atoms [F in (I) and Cl in (II)] in the anions influence the crystal-packing modes because of the difference in their van der Waals radii.



**Figure 9**  
Crystal packing of (II) in a view along the crystallographic *b* axis (linear type).

#### 4. Hirshfeld surface analysis

The Hirshfeld surface analysis is a valuable tool for understanding crystal packing. It offers both identification and visualization of intermolecular interactions, as well as reflecting the interplay between atoms in the structure. The Hirshfeld surfaces of ionic pairs in the asymmetric units of (I) and (II), are shown in Fig. 10. In addition, in Fig. 10, the corresponding 2D fingerprint plots of the most dominant contacts are also presented and combined with the information about their percentage contributions to the Hirshfeld surface. For both structures, the most significant contacts percentages are attributed to O··H/H··O interactions, 34.3% in (I) and 31.7% in (II). The closest contacts of this type appear as two sharp symmetric spikes in the 2D maps, and the intermolecular contacts as representatives are visualized between the Hirshfeld surface of the ionic components and neighbouring molecules. Competing close contacts are those with halogen atom, Cl··H/H··Cl type in (I) (32.1%) and F··H/H··F in (II) (28.8%). The former contacts in the fingerprint plot of (II) can be seen as wings, whereas the latter contacts dominate in the structure of (I) are spread over the



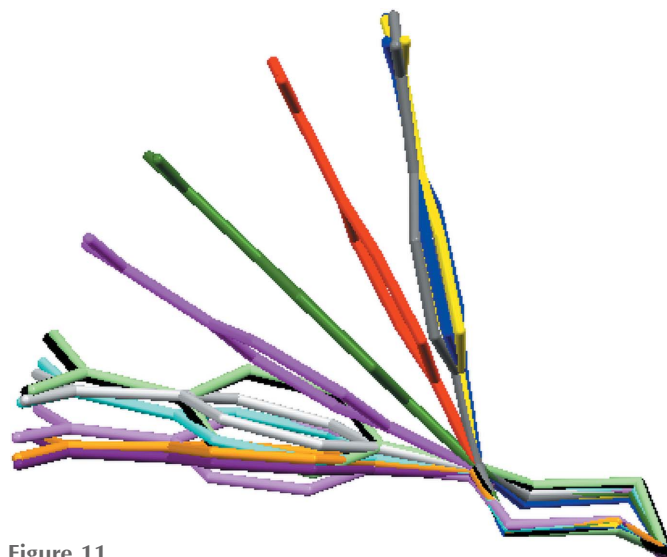
**Figure 10**

Views of the Hirshfeld surfaces of the ionic components of (I) (upper) and (II) (lower) mapped over  $d_{\text{norm}}$  showing intermolecular hydrogen bonds as dashed lines. Hirshfeld surface analysis were carried out using *CrystalExplorer* (Spackman & Jayatilaka, 2009; Turner *et al.*, 2017).

central part of plot; their distances are essentially comparable or longer than the sum of the van der Waals radii of the atoms involved. The much lower contributions of the H··H contacts are consistent with the moderate number of H atoms per two molecules in the asymmetric units. The contributions of the remaining contact types constitute about 20%, among which 6–8% of the Hirshfeld surface area of (I) and (II) is covered by C··H/H··C contacts.

#### 5. Database survey

A search of the Cambridge Structural Database (CSD version 5.43, September 2022; Groom *et al.* 2016) for 4-nitrophenylpiperazines in organic compounds revealed 45 structures, most of which contain a substituent at the N2 atom. Only a few compounds are directly comparable to title compounds (I) and (II): eight structures of 4-nitrophenylpiperazin-1-ium salts with different benzoate anions (NEBVOJ; NEBVUP; NEBWAW; NEBWEA; NEBWIE; NEBWOK; Mahesha *et al.*, 2022; BEFGIG; BEFGOM, Shankara Prasad *et al.*, 2022) and one with chloride (LIJNAU; Lu, 2007). In addition, two neutral NPP molecules have been reported in an inclusion material (König *et al.*, 1997) or co-crystal (Wang *et al.*, 2014). We have compared the molecular conformation of thirteen independent 4-(4-nitrophenyl)piperazin-1-ium cations: nine published structures (2 with  $Z' > 1$ ) and the two reported in this article. As shown in Fig. 11, the molecular structures of the NPP cations differ from each other with respect to the position of the nitrophenyl group on the piperazine ring: the equatorial site is preferred (9/13), whereas the axial position (3/13) is rare, and bisectonal is uncommon (1/13). All compared piperazine rings adopt a chair conformation.



**Figure 11**

An overlay of thirteen 4-(4-nitrophenyl)piperazin-1-ium cations, showing the best fit for the piperazine ring: the colour code is red = (I), green = (II), orange = BEFGIG, blue = BEFGOM, black = NEBVOJ, light green = NEBVUP, purple = NEBWAW, cyan = NEBWEA, light grey = NEBWIE (molecule 1), grey = NEBWIE (molecule 2), violet = NEBWOK (molecule 1), magenta = NEBWOK (molecule 2) and yellow = LIJNAU.

**Table 3**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{10}H_{14}N_3O_2^+ \cdot C_2F_3O_2^-$	$C_{10}H_{14}N_3O_2^+ \cdot C_2Cl_3O_2^-$
$M_r$	321.26	370.61
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	293	293
$a, b, c$ (Å)	6.6889 (4), 18.376 (1), 11.2600 (7)	11.7825 (5), 6.6142 (3), 20.3271 (9)
$\beta$ (°)	91.131 (6)	104.173 (4)
$V$ (Å <sup>3</sup> )	1383.76 (14)	1535.91 (12)
$Z$	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.14	0.62
Crystal size (mm)	0.50 × 0.44 × 0.44	0.48 × 0.44 × 0.40
Data collection		
Diffractometer	Oxford Diffraction Xcalibur with Sapphire CCD	Oxford Diffraction Xcalibu with Sapphire CCD
Absorption correction	Multi-scan ( <i>CrysAlis RED</i> ; Oxford Diffraction (2009))	Multi-scan ( <i>CrysAlis RED</i> ; Oxford Diffraction (2009))
$T_{min}, T_{max}$	0.784, 1.000	0.840, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	4855, 2515, 1908	5078, 2802, 2068
$R_{int}$	0.020	0.013
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.041, 0.106, 1.02	0.036, 0.104, 1.09
No. of reflections	2515	2802
No. of parameters	239	236
No. of restraints	84	35
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
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.28, -0.28	0.25, -0.28

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXT* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

## 6. Synthesis and crystallization

A solution of commercially available (from Sigma-Aldrich) 4-nitrophenylpiperazine (100 mg, 0.483 mol) in methanol (10 ml) was mixed with equimolar solutions of the appropriate acids in methanol (10 ml) *viz.*, trifluoroacetic acid (55 mg, 0.483 mol) for (I) and trichloroacetic acid (79 mg, 0.483 mol) for (II). The corresponding solutions were stirred for 30 minutes at 323 K and allowed to stand at room temperature. X-ray quality crystals were formed on slow evaporation for a week for both of the compounds, where ethanol ethyl acetate (1:1) was used for crystallization. The corresponding melting points were 425–427 K (I) and 388–390 K (II).

## 7. Refinement

Crystal data, data collection and structure refinement details for both compounds are summarized in Table 3. In both structures, an extinction parameter was refined.

The CF<sub>3</sub> group of (I) was found to be disordered over two orientations, with a refined occupancy ratio of 0.779 (4):0.221 (4). The disorder was restrained using SIMU, ISOR and DELU commands in *SHELXL* for the six resulting fluorine atoms. Anisotropic displacement parameters for pairs of the disordered carbon atom (C12A and C12B) were constrained to be the same. The three C–F bonds of the minor disorder component (B) and two C11–C12 bonds were restrained to be similar in length.

In (II), the refined occupancies of disordered chlorine atoms in the CCl<sub>3</sub> group of 0.494 (15) and 0.506 (15), show the equivalent contribution of the components A and B. The ellipsoids of three chlorine atoms of the B disorder component were modelled using SIMU, ISOR and DELU commands in *SHELXL*. All six C–Cl distances were restrained to be similar in length.

In both structures, the H atoms bound to C atoms were positioned geometrically with C–H distances of 0.93 Å (aromatic) and 0.97 Å (CH<sub>2</sub>), and with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The positions of the NH<sub>2</sub> hydrogen atoms were refined. N–H distances within the NH<sub>2</sub> group were restrained to 0.87 (2) Å.

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## supporting information

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## Syntheses, crystal structures and Hirshfeld surface analysis of 4-(4-nitrophenyl)-piperazin-1-ium trifluoroacetate and 4-(4-nitrophenyl)piperazin-1-ium tri-chloroacetate

Holehundi J. Shankara Prasad, Devaraju, Subbaiah M. Murthy, Hanna Kaspiaruk, Hemmige S. Yathirajan, Sabine Foro and Lilianna Chęcińska

### Computing details

For both structures, data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2019/2* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### 4-(4-Nitrophenyl)piperazin-1-ium trifluoroacetate (I)

#### Crystal data

$C_{10}H_{14}N_3O_2^+ \cdot C_2F_3O_2^-$   
 $M_r = 321.26$   
 Monoclinic,  $P2_1/c$   
 $a = 6.6889$  (4) Å  
 $b = 18.376$  (1) Å  
 $c = 11.2600$  (7) Å  
 $\beta = 91.131$  (6)°  
 $V = 1383.76$  (14) Å<sup>3</sup>  
 $Z = 4$

$F(000) = 664$   
 $D_x = 1.542$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 2766 reflections  
 $\theta = 2.9\text{--}27.8^\circ$   
 $\mu = 0.14$  mm<sup>-1</sup>  
 $T = 293$  K  
 Prism, yellow  
 $0.50 \times 0.44 \times 0.44$  mm

#### Data collection

Oxford Diffraction Xcalibur with Sapphire  
 CCD  
 diffractometer  
 Radiation source: Enhance (Mo) X-ray Source  
 Rotation method data acquisition using  $\omega$  scans.  
 Absorption correction: multi-scan  
 (CrysAlis RED; Oxford Diffraction (2009))  
 $T_{\min} = 0.784$ ,  $T_{\max} = 1.000$

4855 measured reflections  
 2515 independent reflections  
 1908 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$   
 $\theta_{\max} = 25.3^\circ$ ,  $\theta_{\min} = 2.9^\circ$   
 $h = -8 \rightarrow 7$   
 $k = -17 \rightarrow 22$   
 $l = -11 \rightarrow 13$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.106$   
 $S = 1.02$   
 2515 reflections  
 239 parameters

84 restraints  
 Primary atom site location: structure-invariant  
 direct methods  
 Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement



$$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.5034P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.28 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$$

Extinction correction: *SHELXL2019/2*

(Sheldrick, 2015b),

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.053 (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 ( $\text{Å}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.6694 (3)	0.05792 (11)	-0.27331 (14)	0.0805 (6)	
O2	0.6790 (2)	-0.05336 (10)	-0.21928 (14)	0.0636 (5)	
N1	0.8545 (2)	0.10090 (8)	0.26900 (12)	0.0356 (4)	
N2	0.6570 (2)	0.12077 (8)	0.48752 (13)	0.0312 (4)	
N3	0.6925 (2)	0.01145 (11)	-0.19696 (15)	0.0476 (5)	
C1	0.8114 (2)	0.07873 (10)	0.15542 (15)	0.0312 (4)	
C2	0.8000 (3)	0.12928 (11)	0.06160 (16)	0.0419 (5)	
H2	0.818859	0.178501	0.077433	0.050*	
C3	0.7615 (3)	0.10711 (12)	-0.05228 (17)	0.0447 (5)	
H3	0.753987	0.141171	-0.113294	0.054*	
C4	0.7339 (3)	0.03448 (11)	-0.07686 (15)	0.0365 (4)	
C5	0.7466 (2)	-0.01673 (11)	0.01221 (16)	0.0377 (4)	
H5	0.729993	-0.065848	-0.005234	0.045*	
C6	0.7840 (3)	0.00528 (10)	0.12678 (16)	0.0355 (4)	
H6	0.791371	-0.029400	0.186860	0.043*	
C7	0.8875 (3)	0.05084 (10)	0.36718 (15)	0.0341 (4)	
H7A	1.001562	0.066979	0.414794	0.041*	
H7B	0.917467	0.002845	0.336392	0.041*	
C8	0.7060 (3)	0.04672 (9)	0.44371 (15)	0.0320 (4)	
H8A	0.593779	0.027324	0.397946	0.038*	
H8B	0.732201	0.014504	0.510461	0.038*	
C9	0.6318 (3)	0.17363 (10)	0.38863 (16)	0.0373 (4)	
H9A	0.610217	0.221963	0.420550	0.045*	
H9B	0.515721	0.160535	0.340249	0.045*	
C10	0.8162 (3)	0.17372 (10)	0.31302 (16)	0.0401 (5)	
H10A	0.796762	0.206785	0.246641	0.048*	
H10B	0.930352	0.190504	0.359862	0.048*	
C11	0.1577 (3)	0.17011 (10)	0.61221 (17)	0.0386 (5)	
C12A	0.2811 (6)	0.2193 (2)	0.6965 (3)	0.0574 (11)	0.779 (4)
C12B	0.295 (2)	0.2305 (8)	0.6565 (13)	0.0574 (11)	0.221 (4)
O3	0.2518 (2)	0.12351 (8)	0.55930 (14)	0.0522 (4)	
O4	-0.0240 (2)	0.18168 (9)	0.61548 (14)	0.0593 (5)	
F1A	0.4768 (4)	0.22180 (19)	0.6652 (3)	0.0873 (11)	0.779 (4)
F2A	0.2265 (4)	0.28753 (13)	0.6917 (4)	0.0974 (13)	0.779 (4)

F3A	0.2611 (5)	0.2012 (2)	0.8079 (2)	0.1261 (13)	0.779 (4)
F1B	0.2251 (14)	0.2549 (8)	0.7591 (12)	0.089 (3)	0.221 (4)
F2B	0.4517 (17)	0.1991 (8)	0.7164 (11)	0.090 (3)	0.221 (4)
F3B	0.2926 (17)	0.2875 (5)	0.5852 (13)	0.129 (3)	0.221 (4)
H21	0.541 (3)	0.1200 (11)	0.5272 (17)	0.047 (6)*	
H22	0.752 (2)	0.1340 (10)	0.5372 (15)	0.038 (5)*	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.1184 (16)	0.0917 (14)	0.0310 (8)	-0.0055 (11)	-0.0098 (9)	0.0050 (9)
O2	0.0640 (10)	0.0726 (12)	0.0539 (10)	0.0033 (8)	-0.0089 (8)	-0.0253 (8)
N1	0.0441 (9)	0.0359 (8)	0.0268 (8)	0.0041 (7)	0.0012 (6)	0.0023 (7)
N2	0.0272 (8)	0.0362 (8)	0.0301 (8)	0.0006 (7)	-0.0020 (6)	-0.0032 (7)
N3	0.0359 (9)	0.0719 (13)	0.0349 (9)	0.0018 (9)	-0.0004 (7)	-0.0080 (9)
C1	0.0234 (8)	0.0406 (10)	0.0298 (9)	0.0020 (7)	0.0030 (7)	0.0014 (8)
C2	0.0518 (12)	0.0397 (11)	0.0341 (10)	0.0012 (9)	0.0002 (8)	0.0025 (9)
C3	0.0508 (12)	0.0527 (13)	0.0306 (10)	0.0033 (10)	-0.0012 (8)	0.0079 (9)
C4	0.0277 (9)	0.0528 (12)	0.0289 (9)	0.0020 (8)	-0.0003 (7)	-0.0037 (9)
C5	0.0269 (9)	0.0433 (11)	0.0429 (11)	-0.0001 (8)	0.0005 (8)	-0.0064 (9)
C6	0.0317 (9)	0.0404 (11)	0.0344 (10)	0.0005 (8)	0.0001 (7)	0.0038 (8)
C7	0.0342 (9)	0.0388 (10)	0.0291 (9)	0.0075 (8)	-0.0028 (7)	0.0002 (8)
C8	0.0358 (9)	0.0312 (9)	0.0288 (9)	0.0000 (8)	-0.0048 (7)	0.0006 (7)
C9	0.0438 (11)	0.0314 (10)	0.0363 (10)	0.0062 (8)	-0.0056 (8)	0.0005 (8)
C10	0.0523 (11)	0.0346 (10)	0.0335 (10)	-0.0058 (9)	-0.0005 (8)	0.0011 (8)
C11	0.0313 (10)	0.0398 (11)	0.0446 (11)	-0.0015 (8)	-0.0029 (8)	-0.0100 (9)
C12A	0.0369 (14)	0.068 (2)	0.067 (3)	0.0037 (13)	0.0025 (19)	-0.036 (2)
C12B	0.0369 (14)	0.068 (2)	0.067 (3)	0.0037 (13)	0.0025 (19)	-0.036 (2)
O3	0.0386 (8)	0.0484 (8)	0.0695 (10)	0.0011 (7)	-0.0020 (7)	-0.0248 (8)
O4	0.0308 (8)	0.0745 (11)	0.0724 (11)	-0.0014 (7)	-0.0055 (7)	-0.0315 (8)
F1A	0.0316 (11)	0.103 (2)	0.128 (3)	-0.0196 (12)	0.0112 (14)	-0.0703 (18)
F2A	0.0739 (15)	0.0495 (14)	0.168 (4)	0.0015 (12)	-0.012 (2)	-0.0513 (17)
F3A	0.146 (3)	0.168 (3)	0.0625 (16)	-0.035 (2)	-0.0317 (15)	-0.0260 (18)
F1B	0.055 (4)	0.112 (6)	0.100 (5)	-0.010 (5)	0.006 (4)	-0.068 (4)
F2B	0.036 (4)	0.120 (5)	0.111 (5)	0.015 (4)	-0.032 (4)	-0.057 (4)
F3B	0.126 (5)	0.083 (5)	0.178 (6)	-0.035 (4)	0.003 (5)	-0.029 (5)

*Geometric parameters (Å, °)*

O1—N3	1.219 (2)	C7—C8	1.505 (2)
O2—N3	1.220 (2)	C7—H7A	0.9700
N1—C1	1.368 (2)	C7—H7B	0.9700
N1—C10	1.452 (2)	C8—H8A	0.9700
N1—C7	1.452 (2)	C8—H8B	0.9700
N2—C9	1.485 (2)	C9—C10	1.512 (3)
N2—C8	1.486 (2)	C9—H9A	0.9700
N2—H21	0.901 (15)	C9—H9B	0.9700
N2—H22	0.873 (15)	C10—H10A	0.9700

N3—C4	1.439 (2)	C10—H10B	0.9700
C1—C6	1.399 (3)	C11—O3	1.224 (2)
C1—C2	1.408 (2)	C11—O4	1.235 (2)
C2—C3	1.365 (3)	C11—C12B	1.518 (15)
C2—H2	0.9300	C11—C12A	1.539 (4)
C3—C4	1.375 (3)	C12A—F2A	1.306 (5)
C3—H3	0.9300	C12A—F3A	1.307 (5)
C4—C5	1.377 (3)	C12A—F1A	1.364 (5)
C5—C6	1.370 (3)	C12B—F3B	1.319 (13)
C5—H5	0.9300	C12B—F1B	1.332 (14)
C6—H6	0.9300	C12B—F2B	1.365 (14)
C1—N1—C10	123.95 (15)	N2—C8—C7	109.25 (14)
C1—N1—C7	123.34 (15)	N2—C8—H8A	109.8
C10—N1—C7	110.45 (13)	C7—C8—H8A	109.8
C9—N2—C8	111.88 (13)	N2—C8—H8B	109.8
C9—N2—H21	107.2 (13)	C7—C8—H8B	109.8
C8—N2—H21	110.4 (13)	H8A—C8—H8B	108.3
C9—N2—H22	111.7 (13)	N2—C9—C10	109.95 (15)
C8—N2—H22	107.8 (12)	N2—C9—H9A	109.7
H21—N2—H22	107.9 (18)	C10—C9—H9A	109.7
O1—N3—O2	122.05 (18)	N2—C9—H9B	109.7
O1—N3—C4	118.42 (19)	C10—C9—H9B	109.7
O2—N3—C4	119.53 (19)	H9A—C9—H9B	108.2
N1—C1—C6	121.82 (16)	N1—C10—C9	110.05 (15)
N1—C1—C2	120.84 (17)	N1—C10—H10A	109.7
C6—C1—C2	117.31 (16)	C9—C10—H10A	109.7
C3—C2—C1	120.96 (18)	N1—C10—H10B	109.7
C3—C2—H2	119.5	C9—C10—H10B	109.7
C1—C2—H2	119.5	H10A—C10—H10B	108.2
C2—C3—C4	120.06 (18)	O3—C11—O4	130.58 (17)
C2—C3—H3	120.0	O3—C11—C12B	111.0 (6)
C4—C3—H3	120.0	O4—C11—C12B	116.9 (6)
C3—C4—C5	120.72 (17)	O3—C11—C12A	115.9 (2)
C3—C4—N3	119.83 (18)	O4—C11—C12A	113.3 (2)
C5—C4—N3	119.45 (18)	F2A—C12A—F3A	104.5 (4)
C6—C5—C4	119.45 (18)	F2A—C12A—F1A	103.1 (4)
C6—C5—H5	120.3	F3A—C12A—F1A	112.0 (4)
C4—C5—H5	120.3	F2A—C12A—C11	113.1 (3)
C5—C6—C1	121.49 (17)	F3A—C12A—C11	112.2 (3)
C5—C6—H6	119.3	F1A—C12A—C11	111.5 (3)
C1—C6—H6	119.3	F3B—C12B—F1B	105.1 (13)
N1—C7—C8	110.83 (14)	F3B—C12B—F2B	129.5 (15)
N1—C7—H7A	109.5	F1B—C12B—F2B	89.6 (11)
C8—C7—H7A	109.5	F3B—C12B—C11	112.5 (10)
N1—C7—H7B	109.5	F1B—C12B—C11	108.2 (11)
C8—C7—H7B	109.5	F2B—C12B—C11	107.8 (11)
H7A—C7—H7B	108.1		

C10—N1—C1—C6	-157.34 (17)	C10—N1—C7—C8	61.08 (19)
C7—N1—C1—C6	3.9 (3)	C9—N2—C8—C7	54.85 (18)
C10—N1—C1—C2	24.9 (2)	N1—C7—C8—N2	-57.36 (18)
C7—N1—C1—C2	-173.79 (16)	C8—N2—C9—C10	-54.97 (19)
N1—C1—C2—C3	178.48 (17)	C1—N1—C10—C9	103.02 (19)
C6—C1—C2—C3	0.7 (3)	C7—N1—C10—C9	-60.34 (19)
C1—C2—C3—C4	-0.2 (3)	N2—C9—C10—N1	56.90 (19)
C2—C3—C4—C5	-0.7 (3)	O3—C11—C12A—F2A	139.1 (3)
C2—C3—C4—N3	179.71 (17)	O4—C11—C12A—F2A	-45.3 (4)
O1—N3—C4—C3	-4.9 (3)	O3—C11—C12A—F3A	-103.0 (3)
O2—N3—C4—C3	175.97 (18)	O4—C11—C12A—F3A	72.6 (4)
O1—N3—C4—C5	175.49 (18)	O3—C11—C12A—F1A	23.5 (5)
O2—N3—C4—C5	-3.6 (3)	O4—C11—C12A—F1A	-160.9 (3)
C3—C4—C5—C6	1.1 (3)	O3—C11—C12B—F3B	98.1 (11)
N3—C4—C5—C6	-179.33 (15)	O4—C11—C12B—F3B	-69.4 (12)
C4—C5—C6—C1	-0.6 (3)	O3—C11—C12B—F1B	-146.3 (10)
N1—C1—C6—C5	-178.08 (16)	O4—C11—C12B—F1B	46.2 (12)
C2—C1—C6—C5	-0.3 (3)	O3—C11—C12B—F2B	-50.7 (12)
C1—N1—C7—C8	-102.40 (18)	O4—C11—C12B—F2B	141.8 (10)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H21 $\cdots$ O3	0.90 (2)	1.98 (2)	2.844 (2)	161 (2)
N2—H22 $\cdots$ O4 <sup>i</sup>	0.87 (2)	1.93 (2)	2.786 (2)	165 (2)
C7—H7A $\cdots$ O3 <sup>i</sup>	0.97	2.53	3.492 (2)	169

Symmetry code: (i)  $x+1, y, z$ .

## 4-(4-Nitrophenyl)piperazin-1-ium trichloroacetate (II)

## Crystal data

 $C_{10}H_{14}N_3O_2^+ \cdot C_2Cl_3O_2^-$  $M_r = 370.61$ Monoclinic,  $P2_1/c$  $a = 11.7825$  (5)  $\text{\AA}$  $b = 6.6142$  (3)  $\text{\AA}$  $c = 20.3271$  (9)  $\text{\AA}$  $\beta = 104.173$  (4) $^\circ$  $V = 1535.91$  (12)  $\text{\AA}^3$  $Z = 4$  $F(000) = 760$  $D_x = 1.603$   $\text{Mg m}^{-3}$ Mo  $K\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$ 

Cell parameters from 2813 reflections

 $\theta = 3.0\text{--}27.8^\circ$  $\mu = 0.62$   $\text{mm}^{-1}$  $T = 293$  K

Prism, brown

 $0.48 \times 0.44 \times 0.40$  mm

## Data collection

Oxford Diffraction Xcalibu with Sapphire CCD diffractometer

Radiation source: Enhance (Mo) X-ray Source

Rotation method data acquisition using  $\omega$  scans.

Absorption correction: multi-scan

(CrysAlis RED; Oxford Diffraction (2009))

 $T_{\min} = 0.840$ ,  $T_{\max} = 1.000$ 

5078 measured reflections

2802 independent reflections

2068 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.013$  $\theta_{\max} = 25.4^\circ$ ,  $\theta_{\min} = 3.0^\circ$

$h = -14 \rightarrow 13$   
 $k = -7 \rightarrow 6$

$l = -24 \rightarrow 14$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

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

$wR(F^2) = 0.104$

$S = 1.09$

2802 reflections

236 parameters

35 restraints

Primary atom site location: structure-invariant  
 direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
 and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.1937P]$

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

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

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

$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL2019/2*

(Sheldrick, 2015b),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0084 (12)

### 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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	1.25261 (14)	0.5140 (3)	0.20561 (10)	0.0741 (5)	
O2	1.24364 (14)	0.5039 (2)	0.30936 (10)	0.0669 (5)	
N1	0.70718 (14)	0.5089 (3)	0.16441 (8)	0.0449 (4)	
N2	0.47368 (15)	0.3654 (3)	0.13414 (9)	0.0428 (4)	
N3	1.19635 (15)	0.5092 (2)	0.24883 (10)	0.0477 (5)	
C1	0.82694 (16)	0.5103 (2)	0.18508 (9)	0.0332 (4)	
C2	0.89695 (17)	0.5088 (3)	0.13812 (10)	0.0410 (5)	
H2	0.861345	0.508580	0.091922	0.049*	
C3	1.01632 (18)	0.5077 (3)	0.15913 (11)	0.0432 (5)	
H3	1.061159	0.506564	0.127313	0.052*	
C4	1.07033 (16)	0.5084 (3)	0.22736 (10)	0.0369 (4)	
C5	1.00483 (17)	0.5083 (3)	0.27476 (10)	0.0379 (5)	
H5	1.041717	0.507704	0.320778	0.046*	
C6	0.88472 (17)	0.5091 (3)	0.25404 (9)	0.0370 (4)	
H6	0.840985	0.508872	0.286420	0.044*	
C7	0.63004 (17)	0.5611 (3)	0.20782 (11)	0.0452 (5)	
H7A	0.590860	0.688009	0.192889	0.054*	
H7B	0.675741	0.578246	0.254138	0.054*	
C8	0.54056 (16)	0.3977 (3)	0.20527 (10)	0.0425 (5)	
H8A	0.579293	0.273110	0.223440	0.051*	
H8B	0.487520	0.436125	0.232840	0.051*	
C9	0.55236 (18)	0.3230 (3)	0.08906 (10)	0.0466 (5)	
H9A	0.506515	0.312758	0.042528	0.056*	
H9B	0.591456	0.194556	0.101561	0.056*	
C10	0.64214 (18)	0.4869 (3)	0.09421 (10)	0.0489 (5)	
H10A	0.695324	0.453110	0.066221	0.059*	

H10B	0.603791	0.613458	0.077935	0.059*	
O3	0.39831 (14)	-0.0360 (2)	0.13071 (8)	0.0613 (5)	
O4	0.35547 (15)	-0.3109 (2)	0.06595 (8)	0.0619 (5)	
C11	0.33900 (17)	-0.1382 (3)	0.08446 (10)	0.0412 (5)	
C12	0.22438 (17)	-0.0367 (3)	0.04153 (9)	0.0394 (5)	
Cl1A	0.1882 (4)	0.1717 (9)	0.0837 (2)	0.0708 (9)	0.494 (15)
Cl2A	0.2502 (7)	0.0289 (11)	-0.0355 (3)	0.0911 (17)	0.494 (15)
Cl3A	0.1076 (4)	-0.2089 (7)	0.0240 (3)	0.0746 (11)	0.494 (15)
Cl1B	0.2023 (4)	0.2189 (9)	0.0640 (4)	0.0790 (16)	0.506 (15)
Cl2B	0.2284 (6)	-0.0136 (10)	-0.0438 (2)	0.0839 (13)	0.506 (15)
Cl3B	0.1049 (4)	-0.1756 (13)	0.0517 (5)	0.100 (2)	0.506 (15)
H21	0.4277 (18)	0.263 (3)	0.1340 (11)	0.047 (6)*	
H22	0.4300 (19)	0.468 (3)	0.1176 (11)	0.061 (7)*	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0405 (9)	0.0979 (15)	0.0875 (13)	0.0003 (9)	0.0227 (9)	-0.0052 (10)
O2	0.0443 (9)	0.0759 (12)	0.0697 (11)	-0.0015 (8)	-0.0068 (8)	-0.0106 (9)
N1	0.0330 (9)	0.0664 (12)	0.0364 (9)	-0.0058 (8)	0.0106 (7)	-0.0123 (8)
N2	0.0334 (9)	0.0375 (10)	0.0536 (11)	-0.0019 (8)	0.0033 (8)	0.0032 (8)
N3	0.0357 (9)	0.0363 (10)	0.0689 (13)	0.0012 (7)	0.0087 (9)	-0.0069 (8)
C1	0.0344 (10)	0.0273 (9)	0.0388 (10)	-0.0020 (8)	0.0106 (8)	-0.0025 (8)
C2	0.0406 (11)	0.0483 (12)	0.0350 (10)	0.0030 (9)	0.0108 (8)	0.0016 (9)
C3	0.0405 (11)	0.0439 (12)	0.0491 (12)	0.0042 (9)	0.0181 (9)	0.0022 (9)
C4	0.0333 (10)	0.0252 (9)	0.0506 (12)	-0.0004 (8)	0.0076 (8)	-0.0017 (8)
C5	0.0429 (11)	0.0286 (10)	0.0395 (10)	-0.0014 (8)	0.0046 (9)	-0.0032 (8)
C6	0.0423 (11)	0.0349 (10)	0.0359 (10)	-0.0026 (8)	0.0136 (8)	-0.0024 (8)
C7	0.0348 (10)	0.0567 (12)	0.0464 (12)	-0.0050 (9)	0.0144 (9)	-0.0130 (10)
C8	0.0368 (10)	0.0466 (12)	0.0442 (11)	0.0020 (9)	0.0104 (8)	0.0017 (9)
C9	0.0449 (12)	0.0509 (12)	0.0388 (11)	0.0026 (10)	0.0001 (9)	-0.0060 (9)
C10	0.0391 (11)	0.0675 (15)	0.0386 (11)	-0.0004 (10)	0.0066 (8)	-0.0006 (10)
O3	0.0579 (10)	0.0507 (9)	0.0598 (10)	-0.0039 (8)	-0.0152 (8)	0.0023 (7)
O4	0.0640 (10)	0.0505 (9)	0.0616 (10)	0.0210 (8)	-0.0030 (8)	-0.0044 (8)
C11	0.0383 (11)	0.0456 (12)	0.0375 (11)	0.0031 (9)	0.0054 (8)	0.0057 (9)
C12	0.0386 (11)	0.0401 (10)	0.0378 (11)	0.0010 (9)	0.0062 (8)	-0.0024 (8)
Cl1A	0.0801 (15)	0.0735 (19)	0.0577 (13)	0.0376 (13)	0.0150 (12)	-0.0120 (11)
Cl2A	0.121 (3)	0.099 (3)	0.067 (3)	0.040 (2)	0.050 (2)	0.053 (2)
Cl3A	0.0501 (11)	0.0651 (12)	0.095 (2)	-0.0146 (8)	-0.0082 (13)	0.0026 (15)
Cl1B	0.0603 (14)	0.0597 (17)	0.095 (3)	0.0272 (12)	-0.0224 (15)	-0.0358 (18)
Cl2B	0.100 (2)	0.107 (3)	0.0388 (11)	0.060 (2)	0.0071 (13)	0.0062 (15)
Cl3B	0.0427 (9)	0.115 (3)	0.137 (4)	-0.0141 (15)	0.0102 (19)	0.063 (3)

*Geometric parameters (Å, °)*

O1—N3	1.224 (3)	C7—C8	1.502 (3)
O2—N3	1.221 (2)	C7—H7A	0.9700
N1—C1	1.370 (2)	C7—H7B	0.9700

N1—C10	1.452 (2)	C8—H8A	0.9700
N1—C7	1.455 (2)	C8—H8B	0.9700
N2—C9	1.481 (3)	C9—C10	1.501 (3)
N2—C8	1.483 (2)	C9—H9A	0.9700
N2—H21	0.867 (16)	C9—H9B	0.9700
N2—H22	0.870 (16)	C10—H10A	0.9700
N3—C4	1.442 (2)	C10—H10B	0.9700
C1—C6	1.400 (3)	O3—C11	1.228 (2)
C1—C2	1.406 (3)	O4—C11	1.233 (2)
C2—C3	1.366 (3)	C11—C12	1.568 (3)
C2—H2	0.9300	C12—C12A	1.722 (4)
C3—C4	1.377 (3)	C12—C11A	1.730 (5)
C3—H3	0.9300	C12—C13B	1.736 (4)
C4—C5	1.374 (3)	C12—C12B	1.753 (5)
C5—C6	1.374 (3)	C12—C13A	1.754 (5)
C5—H5	0.9300	C12—C11B	1.787 (4)
C6—H6	0.9300		
C1—N1—C10	123.91 (16)	H7A—C7—H7B	108.1
C1—N1—C7	124.18 (17)	N2—C8—C7	109.76 (16)
C10—N1—C7	111.23 (17)	N2—C8—H8A	109.7
C9—N2—C8	111.52 (15)	C7—C8—H8A	109.7
C9—N2—H21	109.6 (14)	N2—C8—H8B	109.7
C8—N2—H21	107.4 (14)	C7—C8—H8B	109.7
C9—N2—H22	108.0 (16)	H8A—C8—H8B	108.2
C8—N2—H22	112.8 (16)	N2—C9—C10	110.93 (16)
H21—N2—H22	107 (2)	N2—C9—H9A	109.5
O2—N3—O1	122.05 (19)	C10—C9—H9A	109.5
O2—N3—C4	119.16 (19)	N2—C9—H9B	109.5
O1—N3—C4	118.79 (19)	C10—C9—H9B	109.5
N1—C1—C6	121.24 (17)	H9A—C9—H9B	108.0
N1—C1—C2	121.54 (17)	N1—C10—C9	109.53 (17)
C6—C1—C2	117.21 (18)	N1—C10—H10A	109.8
C3—C2—C1	121.20 (18)	C9—C10—H10A	109.8
C3—C2—H2	119.4	N1—C10—H10B	109.8
C1—C2—H2	119.4	C9—C10—H10B	109.8
C2—C3—C4	120.09 (19)	H10A—C10—H10B	108.2
C2—C3—H3	120.0	O3—C11—O4	129.89 (19)
C4—C3—H3	120.0	O3—C11—C12	116.20 (18)
C5—C4—C3	120.39 (18)	O4—C11—C12	113.91 (17)
C5—C4—N3	120.10 (18)	C11—C12—C12A	107.1 (3)
C3—C4—N3	119.52 (18)	C11—C12—C11A	110.38 (19)
C4—C5—C6	119.88 (18)	C12A—C12—C11A	111.7 (2)
C4—C5—H5	120.1	C11—C12—C13B	108.7 (2)
C6—C5—H5	120.1	C11—C12—C12B	111.1 (2)
C5—C6—C1	121.24 (18)	C13B—C12—C12B	112.5 (3)
C5—C6—H6	119.4	C11—C12—C13A	111.2 (2)
C1—C6—H6	119.4	C12A—C12—C13A	106.4 (3)

N1—C7—C8	110.22 (17)	C11A—C12—C13A	110.0 (2)
N1—C7—H7A	109.6	C11—C12—C11B	114.97 (18)
C8—C7—H7A	109.6	C13B—C12—C11B	107.3 (2)
N1—C7—H7B	109.6	C12B—C12—C11B	102.2 (3)
C8—C7—H7B	109.6		
C10—N1—C1—C6	-172.70 (18)	C10—N1—C7—C8	60.7 (2)
C7—N1—C1—C6	17.6 (3)	C9—N2—C8—C7	54.7 (2)
C10—N1—C1—C2	6.0 (3)	N1—C7—C8—N2	-57.0 (2)
C7—N1—C1—C2	-163.77 (18)	C8—N2—C9—C10	-54.9 (2)
N1—C1—C2—C3	-179.19 (18)	C1—N1—C10—C9	129.3 (2)
C6—C1—C2—C3	-0.5 (3)	C7—N1—C10—C9	-59.8 (2)
C1—C2—C3—C4	-0.1 (3)	N2—C9—C10—N1	56.4 (2)
C2—C3—C4—C5	0.6 (3)	O3—C11—C12—C12A	105.8 (4)
C2—C3—C4—N3	-179.41 (18)	O4—C11—C12—C12A	-74.1 (4)
O2—N3—C4—C5	2.1 (3)	O3—C11—C12—C11A	-16.0 (3)
O1—N3—C4—C5	-178.32 (17)	O4—C11—C12—C11A	164.1 (3)
O2—N3—C4—C3	-177.92 (18)	O3—C11—C12—C13B	-117.0 (5)
O1—N3—C4—C3	1.7 (3)	O4—C11—C12—C13B	63.2 (5)
C3—C4—C5—C6	-0.5 (3)	O3—C11—C12—C12B	118.7 (3)
N3—C4—C5—C6	179.50 (16)	O4—C11—C12—C12B	-61.1 (3)
C4—C5—C6—C1	-0.1 (3)	O3—C11—C12—C13A	-138.3 (3)
N1—C1—C6—C5	179.29 (17)	O4—C11—C12—C13A	41.8 (3)
C2—C1—C6—C5	0.6 (3)	O3—C11—C12—C11B	3.3 (5)
C1—N1—C7—C8	-128.4 (2)	O4—C11—C12—C11B	-176.6 (4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H21 $\cdots$ O3	0.87 (2)	2.01 (2)	2.795 (2)	151 (2)
N2—H21 $\cdots$ C11A	0.87 (2)	2.82 (2)	3.510 (5)	138 (2)
N2—H22 $\cdots$ O4 <sup>i</sup>	0.87 (2)	1.89 (2)	2.738 (2)	167 (2)

Symmetry code: (i)  $x, y+1, z$ .