The structures of eleven (4-phenyl)piperazinium salts containing organic anions

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Eleven (4-phenyl)piperazinium salts containing organic anions have been prepared and structurally characterized, namely, 4-phenylpiperazin-1-ium 4-fluorobenzoate monohydrate, C10H15N2+·C7H4FO2−·H2O, 1; 4-phenylpiperazin-1-ium 4-bromobenzoate monohydrate, C10H15N2+·C7H4BrO2−·H2O, 2; 4-phenylpiperazin-1-ium 4-iodobenzoate, C10H15N2+·C7H4IO2−·H2O, 3; 4-phenylpiperazin-1-ium 4-iodobenzoate, C10H15N2+·C7H4IO2−·H2O, 4; 4-phenylpiperazin-1-ium 4-nitrobenzoate, C10H15N2+·C7H4NO4−, 5; 4-phenylpiperazin-1-ium 3,5-dinitrosalicylate, C10H15N2+·C7H4O2N2–, 6; 4-phenylpiperazin-1-ium 3,5-dinitrobenzoate, C10H15N2+·C7H4N2O6−, 7; 4-phenylpiperazin-1-ium picrate, C10H15N2+·C6H3O3–, 8; 4-phenylpiperazin-1-ium benzoate monohydrate, C10H15N2+·C7H6O2−·H2O, 9; 4-phenylpiperazin-1-ium p-toluensulfonate, C10H15N2+·C7H7O3S, 10; and 4-phenylpiperazin-1-ium fumarate, C10H15N2+·C4H6O4–, 11. Compounds 1 and 3–11 are all 1:1 salts with the acid proton transferred to the phenylpiperazinium base N atom (the secondary amine) with the exception of 3 where there is disorder in the proton position with it being 68% attached to the base and 32% attached to the acid. Of the structures with similar stoichiometries only 3 and 9 are isomorphous. The 4-phenyl substituent in all cases occupies an equatorial position except for 12 where it is in an axial position. The crystal chosen for structure 7 was refined as a nonmerohedral twin. There is disorder in 5, 6, 10 and 11. For both 5 and 6, a nitro group is disordered and was modeled with two equivalent orientations with occupancies of 0.62 (3)/0.38 (3) and 0.690 (11)/0.310 (11), respectively. For 6, 10 and 11, this disorder is associated with the phenyl ring of the phenylpiperazinium cation with occupancies of 0.687 (10)/0.313 (10), 0.51 (7)/0.49 (7) and 0.611 (13)/0.389 (13), respectively. For all salts, the packing is dominated by the N—H···O hydrogen bonds formed by the cation and anion. In addition, several structures contain C—H···π (1, 3, 4, 8, 9, 10, and 12) and aromatic π···π stacking interactions (6 and 8) and one structure (5) contains a −NO2···π interaction. For all structures, the Hirshfeld surface fingerprint plots show the expected prominent spikes as a result of the N—H···O and O···H···O hydrogen bonds.

1. Chemical context

The pharmacological properties of phenylpiperazines and their derivatives have been described by various researchers (Cohen et al. 1982; Conrado et al. 2010; Neves et al. 2003; Hanano et al. 2000). The design and synthesis of phenylpiperazine derivatives as potent anticancer agents for prostate cancer have been reported (Demirci et al., 2019). Many pharmaceutical compounds are derived from 1-phenyl-
piperazine, including oxypertine (Archer et al., 1962), trazodone (Alhaider, 1992) and nefazodone. Derivatives of 1-phenylpiperazine have shown other interesting properties, such as \( \text{C}_{10}\text{H}_{15}\text{N}_{2}\text{Cl}_{2}\text{Pb}_{3}\text{Cl}_{10}^{4-} \) where dielectric relaxation spectroscopy has shown different molecular motions and measurements of AC conductivity as a function of frequency at different temperatures indicated a hopping conduction mechanism (Mathlouthi et al., 2017) and new organic-inorganic hybrid materials of formula \( \text{C}_{10}\text{H}_{15}\text{N}_{2}\text{Cl}_{7}\text{H}_{2}\text{O} \) (Lahbib et al., 2017).

As part of our ongoing studies of hydrogen-bonding patterns in molecular salts (Sagar et al., 2017; Kiran Kumar et al., 2019a,b, 2020, Harish Chinthal et al., 2020), the present paper reports the syntheses and crystal structures of eleven molecular salts of 1-phenylpiperazine, \( \text{C}_{10}\text{H}_{14}\text{N}_{2} \), viz.: 4-phenylpiperazin-1-ium 4-fluorobenzoate monohydrate, \( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{-}\cdot\text{C}_{7}\text{H}_{4}\text{FO}_{2}^{-}\cdot\text{H}_{2}\text{O} \); phenylpiperazin-1-ium 4-bromobenzoate monohydrate, \( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{-}\cdot\text{C}_{7}\text{H}_{4}\text{BrO}_{2}^{-}\cdot\text{H}_{2}\text{O} \); phenylpiperazin-1-ium 4-iodobenzoate, \( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{-}\cdot\text{C}_{7}\text{H}_{4}\text{IO}_{2}^{-} \); phenylpiperazin-1-ium 4-nitrobenzoate, \( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{-}\cdot\text{C}_{7}\text{H}_{4}\text{NO}_{4}^{-} \); phenylpiperazin-1-ium 3,5-dinitrosalicylate, \( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{-}\cdot\text{C}_{7}\text{H}_{3}\text{N}_{2}\text{O}_{7}^{-} \); phenylpiperazin-1-ium 3,5-dinitrobenzoate, \( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{-}\cdot\text{C}_{7}\text{H}_{3}\text{N}_{2}\text{O}_{6}^{-} \); phenylpiperazin-1-ium picrate, \( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{-}\cdot\text{C}_{6}\text{H}_{2}\text{N}_{3}\text{O}_{7}^{-} \); phenylpiperazin-1-ium benzoate monohydrate, \( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{+}\cdot\text{C}_{7}\text{H}_{4}\text{O}_{2}^{-}\cdot\text{H}_{2}\text{O} \); phenylpiperazin-1-ium p-toluenesulfonate, \( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{+}\cdot\text{C}_{7}\text{H}_{4}\text{O}_{3}\text{S}^{-} \); and phenylpiperazin-1-ium fumarate, \( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{+}\cdot\text{C}_{4}\text{H}_{3}\text{O}_{4}^{-} \).

2. Structural commentary

Compounds 1 and 3–12 (Figs. 1–11) are all 1:1 molecular salts with the acid proton transferred to the secondary N atom of...
the phenylpiperazine base with the exception of 3 where there is disorder in the proton position with it being 68% attached to the base and 32% attached to the acid. Compounds 1, 3 and 9 crystallize as mono-hydrates but the remaining crystals are solvent free. In compounds 1, 3, 4, 5 and 9, the anions are all benzoate ions or p-substituted benzoates but only 3 and 9 are isomorphous. Compounds 6, 7 and 8 contain picrate or nitrated benzoate anions while 10 contains a tosylate anion and 11 and 12 contain hydrogen tartarate and hydrogen fumarate mono-anions. Apart from the disorder in the acidic proton position mentioned above, there is disorder in 5, 6, 10 and 11. For 5 this disorder is confined to the nitro substituent on the benzoate anion, which is disordered over two orientations with occupancies of 0.62 (3)/0.38 (2). For 6, 10 and 11 the disorder is associated with the phenyl ring of the phenylpiperazinium cation, with occupancies of 0.687 (10)/0.313 (10), 0.51 (7)/0.49 (7) and 0.611 (13)/389 (13), respec-

Figure 5
The molecular structure of 6 with hydrogen bonds shown as dashed lines and disorder of the phenyl ring and one nitro group indicated. Atomic displacement parameters are at the 30% probability level.

Figure 6
The molecular structure of 7 with hydrogen bonds shown as dashed lines. Atomic displacement parameters are at the 30% probability level.

Figure 7
The molecular structure of 8 with hydrogen bonds shown as dashed lines. Atomic displacement parameters are at the 30% probability level.

Figure 8
The molecular structure of 9 with hydrogen bonds shown as dashed lines. Atomic displacement parameters are at the 30% probability level.

Figure 9
The molecular structure of 10 with hydrogen bonds shown as dashed lines and disorder of the phenyl rings indicated. Atomic displacement parameters are at the 30% probability level.

Figure 10
The molecular structure of 11 with hydrogen bonds shown as dashed lines and disorder of the phenyl ring indicated. Atomic displacement parameters are at the 30% probability level.

Figure 11
The molecular structure of 12 with hydrogen bonds shown as dashed lines. Atomic displacement parameters are at the 30% probability level. Note the axial conformation of the phenyl ring.
tively. This is a common feature of this moiety as shown in a recent study (Kiran Kumar et al., 2019a) of 12 salts of the 4-methoxyphenylpiperazinium cation, of which four were found to contain similar disorder of the phenyl ring.

For the structures containing benzoate or p-substituted benzoate anions, the C—O distances fall into two groups. In one group (3, 5), these distances are the same within experimental error at 2.246 (4) Å, while in the second group (1, 4, and 9) these are substantially different and average 2.235 (4) and 2.255 (4) Å.

For the structures containing the 3,5-dinitrosalicylic (6), 3,5-dinitrobenzoate (7) and 2,3,5-trinitrophenolate ions (8), some interesting patterns emerge. In the anion of compound 6, the carboxyl group is unionized, with C—O distances of 1.211 (4) and 1.309 (4) Å, and it is the phenolic H atom that has been lost (Fig. 5). The C12—O3 distance, 1.283 (4) Å, is closer to that normally found in ketones than to that of phenols or phenolates (Allen et al., 1987). In addition, the C11—C12 and C12—C13 distances, 1.428 (4) and 1.449 (5) Å, respectively, are significantly larger than the other C—C distances in this ring, which lie in the rather narrow range 1.370 (4)—1.398 (4) Å, but the C—N and N—O distances of the nitro substituents are all typical of their type. These observations indicate that the negative charge in this anion is delocalized over the five atoms C11, C13, C14, C15 and C16, but without any significant delocalization onto the nitro groups, as has been observed in trinitrophenolate (picrate) anions (Kavitha et al., 2006; Sagar et al., 2017; Shaibah et al., 2017a,b). The carboxylic anion in 7 contains similar C—O distances [C17—O1 = 1.251 (14); C17—O2 = 1.256 (14) Å]. Structure 8 contains a picrate anion. Here the situation is similar to that of 6 in that the C—O distance is even shorter at 1.244 (3) Å and in the phenyl ring the C—C bonds are not equal with C11—C12 and C11—C16 being 1.443 (3) and 1.445 (3) Å, respectively, while the remaining C—C bonds range from 1.360 (3) to 1.386 (3) Å. For the nitro groups the C—N distances range from 1.441 (3) to 1.456 (3) Å, indicating that the negative charge in this anion is also delocalized over the five atoms C11, C13, C14, C15 and C16, but without any significant delocalization onto the nitro groups.

Structure 10 contains the tosylate anion. There are two formula units in the asymmetric unit and in both anions the S—O distances are almost equal within experimental error ranging from 1.448 (12) to 1.462 (11) Å and 1.430 (13) to 1.473 (11) Å. Structures 11 and 12 contain the mono-anions of the di-carboxylic acids tartaric acid and fumaric acid. For both structures the metrical parameters of both cation and anion are in the normal range for such species. It notable that in 1 and 3—11, the phenyl substituent occupies an equatorial position in the piperazinium cation, but for 12 this substituent occupies an axial position.

3. Supramolecular features

In discussing the supramolecular features of these eleven molecular salts it is convenient to break these up into four groups based on the nature of the anion and the stoichiometry of the resulting salt. In the first group are structures 1, 3, 4, 5, and 9, which contain benzoate and substituted benzoate anions. In the second group are 6, 7, and 8 in which the anions contain nitrated phenyl rings. In the third group, 10 contains a tosylate anion, and in the fourth group, 11 and 12 contain the mono-deprotonated dicarboxylic anions hydrogen tartarate and hydrogen fumarate. The hydrogen bonds for 1 and 3–12 are listed in Tables 1–11.

Even though 1, 3, 4, 5, and 9 contain similar anions, only 3 and 9 are isomorphous. For 1 (Fig. 12), which contains a water molecule of crystallization, there are R21(12) rings (Etter et al., 1990) made up of N—H···O and O—H···O hydrogen bonds,

### Table 1

| D—H···A | D—H | H···A | D—A | D—H···A |
|---------|-----|------|-----|---------|
| N2—H21—O1 | 0.90 (2) | 2.65 (4) | 3.215 (6) | 122 (3) |
| N2—H21—O2 | 0.90 (2) | 1.89 (2) | 2.791 (5) | 175 (4) |
| N2—H22—O3 | 0.88 (2) | 1.96 (2) | 2.812 (5) | 163 (4) |
| C8—H8A—O4" | 0.97 | 2.53 | 3.481 (6) | 168 |
| C8—H8B—O3 | 0.97 | 2.60 | 3.341 (5) | 133 |
| O2—H2O—N2 | 0.82 | 2.00 | 2.780 (11) | 159 |
| O3—H3I—O2" | 0.81 (2) | 1.98 (2) | 2.782 (12) | 170 (7) |

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

### Table 2

| D—H···A | D—H | H···A | D—A | D—H···A |
|---------|-----|------|-----|---------|
| N2—H21—O2 | 0.89 | 1.90 | 2.780 (11) | 170 |
| N2—H22—O3 | 0.89 | 1.94 | 2.803 (12) | 164 (4) |
| C8—H8A—O3" | 0.97 | 2.64 | 3.377 (14) | 133 |
| C8—H8B—O2" | 0.97 | 2.53 | 3.475 (14) | 166 |
| O2—H2O—N2 | 0.82 | 2.00 | 2.780 (11) | 159 |
| O3—H3I—O2" | 0.81 (2) | 1.98 (2) | 2.782 (12) | 170 (7) |

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

### Table 3

| D—H···A | D—H | H···A | D—A | D—H···A |
|---------|-----|------|-----|---------|
| C9—H9A—O3 | 0.97 | 2.63 | 3.218 (4) | 119 |
| C9—H9A—O3" | 0.88 (2) | 1.94 (2) | 2.780 (4) | 160 (3) |
| N2—H22—O4 | 0.90 (2) | 1.74 (2) | 2.627 (4) | 173 (3) |
| C8—H8B—O2" | 0.87 (2) | 1.78 (2) | 2.643 (4) | 169 (3) |
| N4—H42—O3" | 0.85 (2) | 1.97 (2) | 2.809 (4) | 169 (4) |

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

### Table 4

| D—H···A | D—H | H···A | D—A | D—H···A |
|---------|-----|------|-----|---------|
| N2—H21—O2 | 0.90 (1) | 1.96 (2) | 2.846 (2) | 173 (2) |
| N2—H22—O1 | 0.93 (1) | 1.78 (2) | 2.7153 (19) | 179 (2) |
| N2—H22—O2 | 0.93 (1) | 2.49 (2) | 3.057 (2) | 120 (1) |
| C8—H8B—O1" | 0.97 | 2.50 | 3.468 (2) | 176 |
| C10—H10B—O44" | 0.97 | 2.61 | 3.276 (15) | 126 |

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

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Table 5
Hydrogen-bond geometry (Å, °) for 6.

| D—H—A   | D—H | H—A | D—A   | D—H—A |
|----------|------|------|-------|--------|
| O2···H20—O3 | 0.84(2) | 1.69(2) | 2.487(3) | 156(4)  |
| N2···H21—O3 | 0.88(2) | 2.03(2) | 2.873(4) | 159(3)  |
| N2···H21—O4 | 0.88(2) | 2.37(3) | 2.950(6) | 123(3)  |
| N2···H21—O4A | 0.88(2) | 2.40(4) | 2.966(10) | 122(3)  |
| N2···H22—O1i | 0.87(2) | 2.10(2) | 2.947(4) | 164(4)  |
| N2···H22—O2 | 0.87(2) | 2.62(3) | 3.270(4) | 132(3)  |
| C8···H8A—O7ii | 0.97 | 2.36 | 3.134(5) | 137 |
| C8···H8B—O4 | 0.97 | 2.44 | 3.000(6) | 116 |
| C9···H9A—O4A | 0.97 | 2.60 | 3.166(8) | 118 |
| C9···H9B—O5ii | 0.97 | 2.58 | 3.311(8) | 132 |
| C9···H9B—O5Aii | 0.97 | 2.29 | 3.040(13) | 133 |

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

Table 6
Hydrogen-bond geometry (Å, °) for 7.

| D—H—A   | D—H | H—A | D—A   | D—H—A |
|----------|------|------|-------|--------|
| C8···H8A—O3i | 0.97 | 2.43 | 3.250(14) | 142 |
| C10···H10B—O5ii | 0.97 | 2.58 | 3.366(16) | 138 |
| N2···H21—O2 | 0.87(3) | 1.81(4) | 2.672(13) | 172(13) |
| N2···H22—O1ii | 0.87(3) | 1.94(4) | 2.792(13) | 166(12) |

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

Table 7
Hydrogen-bond geometry (Å, °) for 8.

| D—H—A   | D—H | H—A | D—A   | D—H—A |
|----------|------|------|-------|--------|
| C8···H8B—O4ii | 0.97 | 2.42 | 3.265(4) | 145 |
| C9···H9A—O4ii | 0.97 | 2.60 | 3.353(4) | 134 |
| C9···H9A—O6ii | 0.97 | 2.61 | 3.455(4) | 146 |
| N2···H21—O2 | 0.83(5) | 2.06(3) | 2.871(3) | 166(3) |
| N2···H21—O7ii | 0.83(5) | 2.60(3) | 2.985(3) | 110(2) |
| N2···H22—O1ii | 0.98(3) | 1.74(3) | 2.705(3) | 168(3) |

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

which involve the water molecule, and R2(10) rings made up of N—H···O hydrogen bonds, which do not involve the water molecule. This combination of R2(10) and R2(10) rings form ribbons propagating in the a-axis direction. In addition, there is a C—H···π interaction involving C2—H2 and the C11—C16 phenyl ring (Cg1) [C2···Cg1 = 3.610 (6) Å; C2—H2···Cg1 = 133°; symmetry operation −x, −y, −z; (ii) x−1, y−1, z; (iii) x+1, y+1, z]. In the packing arrangement for 3 shown in Fig. 13, both R2(10) rings exhibit N—H···O and O—H···O hydrogen bonds involving the cation, anion and water molecule as well as R2(10) rings showing O—H···O hydrogen bonds just associated with the cations and anions. These link the cations, anions and water molecules into ribbons propagating in the [010] direction. In addition there is a C—H···π interaction involving C2—H2.

Figure 12
Packing diagram for 1 viewed along the a-axis showing the R2(12) rings made up of N—H···O and O—H···O hydrogen bonds, which involve the water molecule, and R2(10) rings made up of N—H···O hydrogen bonds, which do not involve the water molecule. This combination of R2(12) and R2(10) rings form ribbons propagating in the a-axis direction.

Figure 13
Packing diagram for 3 viewed along the [010] direction showing both R2(12) rings demonstrating N—H···O and O—H···O hydrogen bonds involving the cations, anions and water molecule as well as R2(10) rings showing O—H···O hydrogen bonds just associated with the cations and anions. These link the cations, anions and water molecules into ribbons propagating in the [010] direction.
and the C11–C16 phenyl ring (Cg1) [C2i···Cg1 = 3.6040 (14) Å; C2i—H2i···Cg1 = 133°; symmetry operation 1 – x, 1 – y, 1 – z].

In 4, there is no water molecule of crystallization. In this case there is an R̄̂ 2(4) ring with a topology analogous to the seam of a tennis ball (Fig. 14) involving N—H···O hydrogen bonds. These collections of cations and anions linked by R̄̂ 2(4) rings pack in the a-axis direction (Fig. 15). In addition there is a C—H···N interaction involving C19—H19 and the C21–C26 phenyl ring (Cg1) [C19···Cg1 = 3.750 (4) Å; C19—H19B···Cg1 = 154°; symmetry operation 1 – x, 1 – y, 1 – z].

In 5, R̄̂ 2(12) rings link the cations and anions via N–H···O hydrogen bonds and this collection forms ribbons in the b-axis direction (Fig. 16). In addition, the –NO2 group accepts an N—

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**Table 10**

Hydrogen-bond geometry (Å, °) for 11.

| D—H···A   | D—H   | H···A | D···A   | D—H···A |
|-----------|--------|-------|---------|---------|
| N2—H2i···O7ii | 0.88 (2) | 1.95 (2) | 2.808 (5) | 164 (4) |
| N2—H2ii···O1ii | 0.86 (2) | 2.52 (3) | 3.069 (4) | 122 (3) |
| N2—H2···O5 | 0.86 (2) | 2.22 (3) | 2.820 (3) | 127 (3) |
| N2—H2i···O6iii | 0.86 (2) | 2.41 (3) | 2.992 (3) | 125 (3) |
| C9—H9···O2ii | 0.97 | 2.61 | 3.276 (4) | 126 |
| O3—H3O···O2 | 0.83 (2) | 2.17 (3) | 2.614 (3) | 114 (3) |
| O3—H3O···O4i | 0.83 (2) | 2.04 (2) | 2.789 (3) | 150 (3) |
| O4—H4O···O1ii | 0.79 (2) | 2.06 (3) | 2.773 (3) | 151 (3) |
| O6—H6O···O2ii | 0.83 (2) | 1.67 (2) | 2.501 (3) | 174 (3) |
| O7—H7iO···O3 | 0.84 (2) | 1.95 (2) | 2.780 (3) | 171 (4) |
| O7—H7iiO···O1ii | 0.85 (2) | 1.97 (2) | 2.821 (3) | 178 (4) |

Symmetry codes: (i) x+y, y−z, −z+1; (ii) x, y−1, z+1; (iii) −x+y, z−1; (iv) x−y, z+1; (v) x, y−1, z; (vi) x−1, y, z.

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**Table 11**

Hydrogen-bond geometry (Å, °) for 12.

| D—H···A   | D—H   | H···A | D···A   | D—H···A |
|-----------|--------|-------|---------|---------|
| N2—H2i···O4 | 0.87 (2) | 1.88 (2) | 2.741 (2) | 168 (2) |
| N2—H2···O1ii | 0.89 (2) | 1.89 (2) | 2.775 (2) | 172 (2) |
| C7—H7A···O2ii | 0.97 | 2.51 | 3.317 (3) | 141 |
| C8—H8B···O3iii | 0.97 | 2.55 | 3.203 (3) | 124 |
| C9—H9A···O2iv | 0.97 | 2.66 | 3.318 (3) | 126 |
| O2—H2O···O3iv | 0.92 (2) | 1.54 (2) | 2.4610 (18) | 174 (2) |

Symmetry codes: (i) x+y, y−1, z+1; (ii) x, y−1, z+1; (iii) −x+y, z−1; (iv) x−y, z+1; (v) x, y−1, z; (vi) x−1, y, z.

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Figure 14

Partial packing diagram for 4 showing the R̄̂ 2(4) ring with a topology analogous to the seam of a tennis ball involving N—H···O hydrogen bonds.

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Figure 15

Packing diagram for 4 viewed along the c axis showing how the R̄̂ 2(24) rings pack in the a-axis direction.

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Figure 16

Packing diagram for 5 showing how the R̄̂ 2(12) rings link the cation and anion via N–H···O hydrogen bonds and this collection forms ribbons propagating in the b-axis direction.
In 6, there are $R_4^4(16)$ loops linking the phenylpiperazinium cations and the 3,5-dintosalicylate anions via $N—H—O$ and $O—H—O$ hydrogen bonds (Fig. 17). In addition, there are $\pi–\pi$ interactions involving the phenyl ring (C11–C16, $C_g1$) of the 3,5-dintosalicylate anions, which form offset stacks (slippages of 1.580 and 1.900 Å) in the [110] direction [$C_g1⋯C_g1 = 3.3600 (15)$ Å; symmetry operation $-x, 1 - y, 1 - z$; $C_g1⋯C_g1 = 3.3690 (15)$ Å; symmetry operation $-x, 2 - y, 1 - z$].

The packing of 7 is composed of $R_4^4(22)$ rings in the (101) plane made up of $N—H—O$ hydrogen bonds involving the phenylpiperazinium cation and carboxylate group of the 3,5-dinitrobenzoate anion (Fig. 18). These planes are linked in the [111] direction by $C_2^2(6)$ chains also involving $N—H—O$ hydrogen-bonding interactions involving the phenylpiperazinium cation and carboxylate group of the 3,5-dinitrobenzoate anion and weak $C—H—O$ interactions (Fig. 19). In this structure there are no $C—H—\pi$ or $\pi–\pi$ interactions.

In 8 there are $C_2^2(8)$ chains made up of $N—H—O$ hydrogen bonds involving the phenylpiperazinium cation and a nitro group of the picrate anion (Fig. 20). In addition, the picrate
anions form strong π–π interactions (C1–C6, Cg1) in the a-axis direction \([\text{Cg1} \cdots \text{Cg1} = 3.4395 (5) \AA; \text{symmetry operation} 2 - x, 1 - y, -z; \text{Cg1} \cdots \text{Cg1} = 3.4223 (5) \AA; \text{symmetry operation} 2 - x, -y, -z]\) (Fig. 21). Furthermore, there are C–H–π interactions involving the phenyl ring (C1–C6, Cg1) of the phenylpiperazinium cation \([\text{C3} \cdots \text{Cg1} = 3.683 (3) \AA, \text{C3} - \text{H3} \cdots \text{Cg1} = 134^\circ, \text{symmetry operation} 2 - x, \frac{1}{2} + y, \frac{1}{2} - z; \text{C8} \cdots \text{Cg1} = 3.512 (3) \AA, \text{C8} - \text{H8A} \cdots \text{Cg1} = 160^\circ, \text{symmetry operation} 1 - x, -\frac{1}{2} + y, \frac{1}{2} - z]\) (one example shown in Fig. 22).

In the case of 9 there are two anti-parallel \(C_2(6)\) chains linked by N–H–O hydrogen bonds as well as C–H–O interactions involving the water oxygen atom, which combine to form ribbons propagating in the a-axis direction (Fig. 23). In addition, there are C–H–π interactions (C11–C16, Cg1) involving the benzoate phenyl ring \([\text{C2} \cdots \text{Cg1} = 3.710 (4) \AA, \text{C2} - \text{H2} \cdots \text{Cg1} = 141^\circ, \text{symmetry operation} -x, 1 - y, 1 - z; \text{C6} \cdots \text{Cg1} = 3.656 (4) \AA, \text{C6} - \text{H6} \cdots \text{Cg1} = 142^\circ, \text{symmetry operation} 1 - x, 1 - y, 2 - z]\). The overall packing is shown in Fig. 24.

The structure of 10 contains the tosylate anion, which contains the non-planar –SO3− group. This results in a packing arrangement in which N–H–O hydrogen bonds involving the phenylpiperazinium cations and tosylate anions are arranged such that there are hydrophilic and hydrophobic (110) planes (Fig. 25). This structure also contains C–H–π interactions involving one of the phenylpiperazinium cations (C18–C23, Cg1) and tosylate anions \([\text{C30} \cdots \text{Cg1} = 3.74 (3) \AA, \text{C30} - \text{H30A} \cdots \text{Cg1} = 144^\circ, \text{symmetry operation} 1 - x, -\frac{1}{2} + y, \frac{1}{2} - z]\).

Structure 11 has a complicated packing arrangement as in addition to the phenylpiperazinium NH2 group, the flexible tartarate anion contains four OH groups and there is a water
molecule of crystallization. Multiple N—H⋯O and O−H⋯O hydrogen-bonding interactions combine to form a three-dimensional array (Fig. 26).

Structure 12 contains a phenylpiperazinium cation and the monoanion of fumaric acid. In the packing of this structure, there are two $C_1(7)$ chains in the $b$-axis direction involving the fumarate anions and composed of O—H⋯O hydrogen bonds. These chains are in turn cross-linked by both N—H⋯O hydrogen bonds and C—H⋯O interactions (Fig. 27). There are also C—H⋯π interactions involving the phenyl ring (C1–C6, Cg1) of the phenylpiperazinium cation [C5⋯Cg1 = 3.723 (3) Å, C5—H5⋯Cg1 = 144°, symmetry operation $-x, -y, -\frac{1}{2} + z$; C10⋯Cg1 = 3.608 (3) Å, C10−H10A⋯Cg1 = 145°, symmetry operation $-x, -y, -\frac{1}{2} + z$].

The Hirshfeld surface fingerprint plots for 1 and 3–12 generated using CrystalExplorer are available in the supporting information. All of them show the distinctive ‘pincer spikes’ associated with the N—H⋯O and/or O—H⋯O hydrogen bonds (Spackman et al., 2021).

4. Database survey

The structural versatility of the 1-phenylpiperazine moiety itself is shown by its involvement in many structural forms, including as neutral co-crystals [Cambridge Structural Database (Groom et al., 2016) refcodes HINOUR and HINRAY, Müller-Buschbaum & Zurawski, 2007], as neutral ligands (HIWJAY, Stocker et al., 1999; HIWJAY01, VIYPIE, VIYPOK, VIYPUQ; Pike et al., 2014), as simultaneously both neutral ligands and co-crystals (FITTEI and FITTIM, Quitmann & Müller-Buschbaum, 2005; HOCEBE, HOCEBIL, PIYXEB, Zurawski & Müller-Buschbaum, 2008). In addition, there have been many structural investigations of 1-phenylpiperazine as a cation, combined with simple anions (DMPIPZ, Chothia & Pauling, 1978; JEHXIE, Batsanov et al., 2006; KUZWUY, Marouani et al., 2010; LOHOIL, Oueslati et al., 2019; QORVEB, Marouani et al., 2012; SUYXEQ, Essid et al., 2019), with simple anionic metal salts (BEBKAX, Lahbib et al., 2017; CEBHIB, Garbia et al., 2005; PENWAJ, Mathlouthi et al., 2017; PHPIPZ, Battaglia et al., 1979; QIZPIA, Dhibe et al., 2014; SUKXAM, Dhibe et al., 2015; ZAMHUX, Zouari et al., 1995), combined with anionic carboxylates (IGOGUI, Pang et al., 2015; VAKCIW, Zong et al., 2016; Mahessa et al., 2022), combined with anionic pyrimidines (DUPMUY, DUPNAF, Al-Alshaikh et al., 2015), combined with anionic ligands (WOKKAW, Lo et al., 2019), combined with a clathrate (GUBHOB, Wu et al., 2009), and combined with anionic metal complexes (DUJPIK, Shin et al., 2020; SICGUJ, Nast et al., 2018; SICGUJ01, Khedhiri et al., 2018).
### Table 12: Experimental details.

|        | 1                  | 3                  | 4                  | 5                  |
|--------|--------------------|--------------------|--------------------|--------------------|
| **Crystal data** |                    |                    |                    |                   |
| Chemical formula | C₆H₅N₂⁺·C₂H₅FO₂⁻·H₂O | C₆H₅N₂⁺·C₂H₅BrO₂⁻·H₂O | C₆H₅N₂⁺·C₂H₅IO⁻ | C₆H₅N₂⁺·C₆H₅NO₄⁻ |
| M₁     | 320.36             | 381.27             | 410.24             | 329.35             |
| Crystal system, space group | Triclinic, P̅₁ | Monoclinic, P2₁/c | Monoclinic, P2₁/c | Monoclinic, P2₁/c |
| Temperature (K) | 26.239 (1), 7.496 (1), 17.817 (3) | 6.183 (2), 37.748 (7), 7.506 (2) | 10.8507 (4), 23.4045 (7), 13.3019 (4) | 13.0683 (9), 15.7868 (9), 7.9255 (5) |
| a, b, c (Å) | 93.55 (2), 92.94 (2), 94.87 (2) | 90, 93.69 (4), 90 | 90, 102.491 (4), 90 | 90, 95.137 (6), 90 |
| V (Å³) | 827.3 (2) | 1748.2 (8) | 3298.13 (19) | 1628.52 (18) |
| Z      | 4                 | 8                 | 8                 | 4                 |
| Radiation type | Mo Kα            | Mo Kα             | Mo Kα             | Mo Kα             |
| μ (mm⁻¹) | 0.10              | 2.37              | 1.95              | 0.10              |
| Crystal size (mm) | 0.44 × 0.32 × 0.16 | 0.46 × 0.20 × 0.12 | 0.48 × 0.48 × 0.40 | 0.48 × 0.44 × 0.16 |

| **Data collection** |                    |                    |                    |                   |
| Diffractometer     | Oxford Diffraction Xcalibur with Sapphire CCD | Oxford Diffraction Xcalibur with Sapphire CCD | Oxford Diffraction Xcalibur with Sapphire CCD | Oxford Diffraction Xcalibur with Sapphire CCD |
| Absorption correction | Multi-scan (CrysAlis RED; Oxford Diffraction, 2007) | Multi-scan (CrysAlis RED; Oxford Diffraction, 2007) | Multi-scan (CrysAlis RED; Oxford Diffraction, 2007) | Multi-scan (CrysAlis RED; Oxford Diffraction, 2007) |
| Tmax, Tmin         | 0.613, 1.000       | 0.613, 1.000       | 0.575, 1.000       | 0.790, 1.000       |
| No. of measured, independent and observed | | | | |
| reflections | 4669, 3013, 1611 | 6103, 3170, 1374 | 14154, 7079, 4641 | 11699, 3587, 2088 |
| R(int), (sin θ/λ)max (Å⁻¹) | 0.033, 0.602 | 0.061, 0.602 | 0.024, 0.657 | 0.035, 0.660 |

| **Refinement** |                    |                    |                    |                   |
| R[F² > 2σ(F²)], wR(F²), S | | | | |
| No. of reflections | 3013 | 3170 | 7079 | 3587 |
| No. of parameters | 220 | 215 | 409 | 251 |
| No. of restraints | 4 | 7 | 4 | 83 |
| 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 | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |
| Δρmax, Δρmin (e Å⁻³) | 0.27, −0.20 | 0.49, −0.61 | 0.77, −1.25 | 0.15, −0.13 |
| Absolute structure parameter | | | | |
| Absolute structure parameter | | | | |

|        | 6                  | 7                  | 8                  | 9                  |
|--------|--------------------|--------------------|--------------------|--------------------|
| **Crystal data** |                    |                    |                    |                   |
| Chemical formula | C₆H₅N₂⁺·C₂H₅FO₂⁻·H₂O | C₆H₅N₂⁺·C₂H₅BrO₂⁻·H₂O | C₆H₅N₂⁺·C₂H₅IO⁻ | C₆H₅N₂⁺·C₆H₅NO₄⁻ |
| M₁     | 390.35             | 374.35             | 391.34             | 302.36             |
| Crystal system, space group | Monoclinic, P2₁/c | Monoclinic, P2₁/c | Monoclinic, P2₁/c | Monoclinic, P2₁/c |
| Temperature (K) | 293 | 293 | 293 | 293 |
| a, b, c (Å) | 7.779 (3), 7.411 (3), 31.357 (9) | 5.707 (2), 12.505 (3), 13.116 (3) | 8.517 (1), 13.3019 (4) | 6.202 (2), 15.7868 (9), 7.9255 (5) |
| V (Å³) | 1794.9 (11) | 97.41 (2), 93.28 (2), 102.82 (2) | 90, 95.33 (1), 90 | 90, 95.137 (6), 90 |
| Z      | 4                 | 4                 | 4                 | 4                 |
| Radiation type | Mo Kα            | Mo Kα             | Mo Kα             | Mo Kα             |
| μ (mm⁻¹) | 0.11              | 0.11              | 0.12              | 0.09              |
| Crystal size (mm) | 0.20 × 0.18 × 0.12 | 0.48 × 0.08 × 0.04 | 0.50 × 0.36 × 0.20 | 0.32 × 0.20 × 0.16 |

| **Data collection** |                    |                    |                    |                   |
| Diffractometer     | Oxford Diffraction Xcalibur with Sapphire CCD | Oxford Diffraction Xcalibur with Sapphire CCD | Oxford Diffraction Xcalibur with Sapphire CCD | Oxford Diffraction Xcalibur with Sapphire CCD |
| Absorption correction | Multi-scan (CrysAlis RED; Oxford Diffraction, 2007) | Multi-scan (CrysAlis RED; Oxford Diffraction, 2007) | Multi-scan (CrysAlis RED; Oxford Diffraction, 2007) | Multi-scan (CrysAlis RED; Oxford Diffraction, 2007) |
| Tmax, Tmin         | 0.959, 1.000       | 0.647, 1.000       | 0.835, 1.000       | 0.985, 1.000       |
| No. of measured, independent and observed | | | | |
| reflections | 7737, 3882, 1590 | 7800, 7800, 2647 | 12427, 3893, 2389 | 6075, 3492, 1387 |
| R(int), (sin θ/λ)max (Å⁻¹) | 0.055, 0.087 | 0.076, 0.060 | 0.039, 0.065 | |
5. Synthesis and crystallization

For the synthesis of salts 1–12, a solution of commercially available 1-phenylpiperazine (100 mg, 0.62 mol) (from Sigma-Aldrich) in methanol (10 ml) was mixed with an equimolar solution of (1) 4-fluorobenzoic acid (87 mg, 0.62 mol), (2) 4-chlorobenzoic acid (97 mg, 0.62 mol), (3) 4-bromobenzoic acid (125 mg, 0.62 mol), (4) 4-iodobenzoic acid (154 mg, 0.62 mol), (5) 4-nitrobenzoic acid (104 mg, 0.62 mol), (6) 3,5-dinitrosalicylic acid (104 mg, 0.62 mol), (7) 3,5-dinitrobenzoic acid (132 mg, 0.62 mol), (8) picric acid (142 mg, 0.62 mol), (9) benzoic acid (76 mg, 0.62 mol), (10) p-toluene sulfonic acid (107 mg, 0.62 mol), (11) tartaric acid (93 mg, 0.62 mol) and (12) fumaric acid (72 mg, 0.62 mol). The resulting mixture was stirred for 30 min at 323 K and allowed to stand at room temperature. X-ray quality crystals of 1 and 3–12 were formed on slow evaporation after one week (m.p. 381–384 K (1), 328–387 K (3), 413–418 K (4), 423–428 K (5), 431–436 K (6), 427–429 K (7), 430–433 K (8), 455–457 K (9), 377–380 K (10), 416–420 K (11) and 438–440 K (12). No crystals of (2) (m.p. 488–490 K) suitable for X-ray diffraction were obtained.

6. Refinement

Crystal data, data collection and structure refinement details for structures 1 and 3–12 are summarized in Table 12. All hydrogen atoms were positioned geometrically with their $U_{iso}$ values 1.2 times that of their attached atoms. For some structures (6, 10, and 11), the phenyl ring of the piperazinium cation was disordered over two orientations in ratios of 0.687 (10)/0.313 (10); 0.51 (7)/0.49 (7), and 0.611 (13)/
The nitro group was disordered and modeled with two orientations with occupancies of 0.62 (3)/0.38 (3) and 0.690 (11)/0.310 (11), respectively.

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The structures of eleven (4-phenyl)piperazinium salts containing organic anions

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Computing details
For all structures, data collection: CrysAlis CCD (Oxford Diffraction, 2007); cell refinement: CrysAlis RED (Oxford Diffraction, 2007); data reduction: CrysAlis RED (Oxford Diffraction, 2007). Program(s) used to solve structure: SHELXT (Sheldrick, 2015a) for (1), (3), (4), (5), (6), (7), (8), (9), (10), (11); SHELXT2014 (Sheldrick, 2015a) for (12). Program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b) for (1), (3), (4), (5), (6), (7), (8), (9), (10); SHELXL2014/6 (Sheldrick, 2015b) for (11), (12). For all structures, molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

4-Phenylpiperazin-1-ium 4-fluorobenzoate monohydrate (1)

Crystal data

| Parameter | Value |
|-----------|-------|
| Formula   | C<sub>10</sub>H<sub>15</sub>N<sub>2</sub>+:C<sub>7</sub>H<sub>4</sub>FO<sub>2</sub>−·H<sub>2</sub>O |
| M<sub>r</sub> | 320.36 |
| Space group | P<sup>T</sup> |
| a          | 6.239 (1) Å |
| b          | 7.496 (1) Å |
| c          | 17.817 (3) Å |
| α         | 93.55 (2)° |
| β         | 92.94 (2)° |
| γ         | 94.87 (2)° |
| V         | 827.3 (2) Å<sup>3</sup> |
| Z         | 2 |
| F(000)    | 340 |
| D<sub>x</sub> | 1.286 Mg m<sup>−3</sup> |
| Mo Kα radiation, λ = 0.71073 Å |
| Cell parameters from 1437 reflections |

Data collection

| Parameter | Value |
|-----------|-------|
| Radiation source: Enhance (Mo) X-ray Source |
| ω and φ scans |
| Radiation source: Enhance (Mo) X-ray Source |
| Absorption correction: multi-scan (CrisalisRED; Oxford Diffraction, 2007) |
| Tmin = 0.613, Tmax = 1.000 |

Refinement

| Parameter | Value |
|-----------|-------|
| Refinement on F<sup>2</sup> | 4669 measured reflections |
| Least-squares matrix: full | 3013 independent reflections |
| R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.090 | 1611 reflections with I > 2σ(I) |
| wR(F<sup>2</sup>) = 0.226 | R<sub>int</sub> = 0.033 |
| S = 1.10 | θ<sub>max</sub> = 25.3°, θ<sub>min</sub> = 2.9° |
| 3013 reflections | h = −7→7 |
| 220 parameters | k = −9→8 |
|  | l = −21→20 |
|  | 4 restraints |
|  | Primary atom site location: dual |
|  | Secondary atom site location: difference Fourier map |
|  | Hydrogen site location: mixed |
|  | H atoms treated by a mixture of independent and constrained refinement |
$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.6694P]$

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

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

$\Delta \rho_{\text{max}} = 0.27 \text{ e Å}^{-3}$

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

**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 (Å²)**

|     | x       | y       | z       | $U_{eq}$  |
|-----|---------|---------|---------|-----------|
| N1  | 0.1673 (5) | 0.6916 (4) | 0.28754 (18) | 0.0488 (8) |
| N2  | 0.2637 (6) | 0.7578 (5) | 0.4474 (2) | 0.0582 (10) |
| H21 | 0.321 (6) | 0.736 (6) | 0.4932 (14) | 0.070* |
| H22 | 0.222 (6) | 0.867 (3) | 0.453 (2) | 0.070* |
| C1  | 0.1054 (6) | 0.7113 (5) | 0.2116 (2) | 0.0517 (10) |
| C2  | -0.0937 (8) | 0.6442 (7) | 0.1796 (3) | 0.0795 (15) |
| H2  | -0.193159 | 0.589826 | 0.210092 | 0.095* |
| C3  | -0.1510 (9) | 0.6546 (8) | 0.1045 (3) | 0.1007 (19) |
| H3  | -0.285388 | 0.604546 | 0.084997 | 0.121* |
| C4  | -0.0122 (11) | 0.7376 (9) | 0.0585 (3) | 0.1030 (19) |
| H4  | -0.049909 | 0.745192 | 0.007649 | 0.124* |
| C5  | 0.1822 (10) | 0.8090 (10) | 0.0887 (3) | 0.122 (3) |
| H5  | 0.278723 | 0.865814 | 0.057892 | 0.147* |
| C6  | 0.2409 (9) | 0.7997 (8) | 0.1637 (3) | 0.0979 (19) |
| H6  | 0.373978 | 0.853592 | 0.182809 | 0.117* |
| C7  | 0.3620 (6) | 0.8019 (6) | 0.3177 (2) | 0.0608 (11) |
| H7A | 0.332558 | 0.927034 | 0.320838 | 0.073* |
| H7B | 0.476070 | 0.788623 | 0.283301 | 0.073* |
| C8  | 0.4378 (7) | 0.7509 (6) | 0.3946 (2) | 0.0616 (12) |
| H8A | 0.484338 | 0.630572 | 0.390672 | 0.074* |
| H8B | 0.560050 | 0.832523 | 0.413731 | 0.074* |
| C9  | 0.0695 (7) | 0.6398 (6) | 0.4170 (2) | 0.0599 (11) |
| H9A | -0.045974 | 0.649597 | 0.451027 | 0.072* |
| H9B | 0.103679 | 0.515781 | 0.413417 | 0.072* |
| C10 | -0.0033 (6) | 0.6933 (6) | 0.3403 (2) | 0.0558 (11) |
| H10A | -0.124568 | 0.611513 | 0.320378 | 0.067* |
| H10B | -0.051786 | 0.812879 | 0.345074 | 0.067* |
| F1  | 0.5316 (7) | 0.7684 (6) | 0.94599 (18) | 0.1434 (15) |
| O1  | 0.1448 (6) | 0.8383 (6) | 0.6190 (2) | 0.1136 (14) |
| O2  | 0.4185 (6) | 0.6849 (4) | 0.59104 (18) | 0.0761 (10) |
| C11 | 0.3677 (6) | 0.7628 (5) | 0.7197 (2) | 0.0519 (10) |
| C12 | 0.5515 (7) | 0.6900 (6) | 0.7457 (2) | 0.0605 (11) |
| H12 | 0.639144 | 0.638731 | 0.711219 | 0.073* |
| C13 | 0.6074 (8) | 0.6918 (7) | 0.8214 (3) | 0.0777 (14) |
| H13 | 0.731513 | 0.642435 | 0.838182 | 0.093* |
| C14 | 0.4782 (10) | 0.7668 (8) | 0.8711 (3) | 0.0885 (16) |
sup-3

Atomic displacement parameters ($\AA^2$)

|   | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|---|--------------|--------------|--------------|--------------|--------------|--------------|
| N1 | 0.0464 (19)  | 0.0462 (19)  | 0.053 (2)    | −0.0029 (14) | 0.0061 (15)  | 0.0075 (14)  |
| N2 | 0.072 (2)    | 0.048 (2)    | 0.055 (2)    | 0.0064 (18)  | −0.0066 (19) | 0.0061 (17)  |
| C1 | 0.058 (3)    | 0.048 (2)    | 0.048 (3)    | 0.0003 (19)  | 0.005 (2)    | 0.0056 (18)  |
| C2 | 0.079 (3)    | 0.094 (4)    | 0.060 (3)    | −0.022 (3)   | −0.005 (3)   | 0.017 (3)    |
| C3 | 0.104 (4)    | 0.118 (5)    | 0.070 (4)    | −0.036 (4)   | −0.021 (3)   | 0.017 (3)    |
| C4 | 0.129 (5)    | 0.120 (5)    | 0.056 (3)    | −0.015 (4)   | −0.006 (3)   | 0.014 (3)    |
| C5 | 0.116 (5)    | 0.185 (7)    | 0.059 (4)    | −0.045 (5)   | 0.008 (3)    | 0.029 (4)    |
| C6 | 0.088 (4)    | 0.141 (5)    | 0.058 (3)    | −0.039 (4)   | 0.003 (3)    | 0.020 (3)    |
| C7 | 0.049 (2)    | 0.072 (3)    | 0.059 (3)    | −0.009 (2)   | 0.004 (2)    | 0.009 (2)    |
| C8 | 0.053 (3)    | 0.065 (3)    | 0.065 (3)    | 0.000 (2)    | −0.002 (2)   | 0.003 (2)    |
| C9 | 0.064 (3)    | 0.056 (3)    | 0.058 (3)    | −0.008 (2)   | 0.005 (2)    | 0.007 (2)    |
| C10| 0.049 (2)    | 0.058 (3)    | 0.060 (3)    | −0.0019 (19) | 0.006 (2)    | 0.006 (2)    |
| F1 | 0.180 (4)    | 0.187 (4)    | 0.060 (2)    | 0.003 (3)    | −0.002 (2)   | 0.004 (2)    |
| O1 | 0.090 (3)    | 0.140 (4)    | 0.114 (3)    | 0.037 (3)    | −0.027 (2)   | 0.029 (3)    |
| O2 | 0.097 (2)    | 0.069 (2)    | 0.061 (2)    | 0.0018 (18)  | −0.0046 (18) | 0.0101 (16)  |
| C11| 0.049 (2)    | 0.041 (2)    | 0.066 (3)    | −0.0054 (18) | 0.007 (2)    | 0.0126 (19)  |
| C12| 0.062 (3)    | 0.056 (3)    | 0.062 (3)    | 0.004 (2)    | −0.001 (2)   | 0.006 (2)    |
| C13| 0.082 (3)    | 0.083 (4)    | 0.067 (3)    | 0.009 (3)    | −0.009 (3)   | 0.010 (3)    |
| C14| 0.105 (4)    | 0.098 (4)    | 0.059 (3)    | −0.005 (3)   | −0.002 (3)   | 0.004 (3)    |
| C15| 0.097 (4)    | 0.093 (4)    | 0.079 (4)    | 0.004 (3)    | 0.031 (3)    | 0.001 (3)    |
| C16| 0.057 (3)    | 0.066 (3)    | 0.096 (4)    | 0.002 (2)    | 0.012 (3)    | 0.018 (3)    |
| C17| 0.056 (3)    | 0.049 (3)    | 0.076 (3)    | −0.012 (2)   | −0.009 (2)   | 0.020 (2)    |
| O3 | 0.071 (2)    | 0.065 (2)    | 0.088 (3)    | 0.0124 (18)  | −0.0088 (18) | 0.0039 (17)  |

Geometric parameters ($\AA$, $^\circ$)

| Bond          | Length     | Angle       |
|---------------|------------|-------------|
| N1—C1         | 1.408 (5)  |             |
| N1—C10        | 1.456 (5)  |             |
| N1—C7         | 1.468 (5)  |             |
| N2—C8         | 1.475 (5)  |             |
| N2—C9         | 1.495 (5)  |             |
| N2—H21        | 0.904 (19) |             |
| N2—H22        | 0.881 (19) |             |
| C1—C2         | 1.381 (6)  |             |
| C1—C6         | 1.389 (6)  |             |
| C2—C3         | 1.377 (6)  |             |

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### C2—H2 0.9300  C11—C16 1.386 (6)
### C3—C4 1.361 (8)  C11—C17 1.496 (6)
### C3—H3 0.9300  C12—C13 1.375 (6)
### C4—C5 1.355 (8)  C12—H12 0.9300
### C4—H4 0.9300  C13—C14 1.356 (7)
### C5—C6 1.375 (7)  C13—H13 0.9300
### C5—H5 0.9300  C14—C15 1.366 (7)
### C6—H6 0.9300  C15—C16 1.377 (7)
### C7—C8 1.509 (5)  C15—H15 0.9300
### C7—H7A 0.9700  C16—H16 0.9300
### C7—H7B 0.9700  O3—H31 0.83 (2)
### C8—H8A 0.9700  O3—H32 0.83 (2)

| Angle | Value  | Comment         | Value  |
|-------|--------|-----------------|--------|
| C1—N1—C7 | 116.2 (3) | C7—C8—H8B | 109.5 |
| C1—N1—C10 | 115.9 (3) | H8A—C8—H8B | 108.1 |
| C10—N1—C7 | 111.5 (3) | N2—C9—C10 | 110.4 (3) |
| C8—N2—C9 | 110.3 (3) | N2—C9—H9A | 109.6 |
| C8—N2—H21 | 107 (3) | C10—C9—H9A | 109.6 |
| C9—N2—H21 | 117 (3) | N2—C9—H9B | 109.6 |
| C8—N2—H22 | 111 (3) | C10—C9—H9B | 109.6 |
| C9—N2—H22 | 106 (3) | H9A—C9—H9B | 108.1 |
| H21—N2—H22 | 105 (4) | N1—C10—C9 | 112.3 (3) |
| C2—C1—C6 | 115.5 (4) | N1—C10—H10A | 109.1 |
| C2—C1—N1 | 122.4 (4) | C9—C10—H10A | 109.1 |
| C6—C1—N1 | 122.2 (4) | N1—C10—H10B | 109.1 |
| C3—C2—C1 | 122.7 (5) | C9—C10—H10B | 109.1 |
| C3—C2—H2 | 118.7 | H10A—C10—H10B | 107.9 |
| C1—C2—H2 | 118.7 | C12—C11—C16 | 117.8 (4) |
| C4—C3—C2 | 120.5 (5) | C12—C11—C17 | 121.9 (4) |
| C4—C3—H3 | 119.8 | C16—C11—C17 | 120.2 (4) |
| C2—C3—H3 | 119.8 | C13—C12—C11 | 121.4 (4) |
| C5—C4—C3 | 118.2 (5) | C13—C12—H12 | 119.3 |
| C5—C4—H4 | 120.9 | C11—C12—H12 | 119.3 |
| C3—C4—H4 | 120.9 | C14—C13—C12 | 118.8 (5) |
| C4—C5—C6 | 121.8 (5) | C14—C13—H13 | 120.6 |
| C4—C5—H5 | 119.1 | C12—C13—H13 | 120.6 |
| C6—C5—H5 | 119.1 | C13—C14—F1 | 119.2 (6) |
| C5—C6—C1 | 121.3 (5) | C13—C14—C15 | 122.3 (5) |
| C5—C6—H6 | 119.4 | F1—C14—C15 | 118.5 (6) |
| C1—C6—H6 | 119.4 | C14—C15—C16 | 118.3 (5) |
| N1—C7—C8 | 112.4 (3) | C14—C15—H15 | 120.9 |
| N1—C7—H7A | 109.1 | C16—C15—H15 | 120.9 |
| C8—C7—H7A | 109.1 | C15—C16—C11 | 121.4 (5) |
| N1—C7—H7B | 109.1 | C15—C16—H16 | 119.3 |
| C8—C7—H7B | 109.1 | C11—C16—H16 | 119.3 |
| H7A—C7—H7B | 107.9 | O1—C17—O2 | 123.6 (5) |
| N2—C8—C7 | 110.8 (3) | O1—C17—C11 | 117.7 (5) |
| N2—C8—H8A | 109.5 | O2—C17—C11 | 118.7 (4) |
Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H | H···A | D···A | D—H···A |
|-----------|------|-------|-------|----------|
| N2—H21···O1 | 0.90 (2) | 2.65 (4) | 3.215 (6) | 122 (3) |
| N2—H21···O2 | 0.90 (2) | 1.89 (2) | 2.791 (5) | 175 (4) |
| N2—H22···O3i | 0.88 (2) | 1.96 (2) | 2.812 (5) | 163 (4) |
| C8—H8A···O2i | 0.97 | 2.53 | 3.481 (6) | 168 |
| C8—H8B···O3 | 0.97 | 2.60 | 3.341 (5) | 133 |
| C9—H9A···O3iii | 0.97 | 2.59 | 3.416 (6) | 143 |
| O3—H31···O1iv | 0.83 (2) | 1.79 (2) | 2.619 (5) | 176 (6) |
| O3—H32···O2 | 0.83 (2) | 1.96 (2) | 2.773 (5) | 167 (6) |

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

4-Phenylpiperazin-1-ium 4-bromobenzoate monohydrate (3)

Crystal data

\[
\begin{align*}
C_{10}H_{15}N_{2}^+ \cdot C_{7}H_{4}BrO_{2}^- \cdot H_{2}O & \quad F(000) = 784 \\
M_r &= 381.27 \\
\text{Monoclinic, } P2_1/c & \quad \lambda = 0.71073 \AA \\
a &= 6.183 (2) \AA & \quad \text{Mo } K\alpha \text{ radiation, } \theta = 2.8 - 27.7^\circ \\
b &= 37.748 (7) \AA & \quad \text{Cell parameters from 1437 reflections} \\
c &= 7.506 (2) \AA & \quad \mu = 2.37 \text{ mm}^{-1} \\
\beta &= 93.69 (4)^\circ & \quad T = 293 \text{ K} \\
V &= 1748.2 (8) \text{ Å}^3 & \quad \text{Rod, colourless} \\
Z &= 4 & \quad 0.46 \times 0.20 \times 0.12 \text{ mm}
\end{align*}
\]
Data collection

Oxford Diffraction Xcalibur with Sapphire CCD
diffractometer
Radiation source: Enhance (Mo) X-ray Source
ω and φ scans
Absorption correction: multi-scan (CrysalisRED; Oxford Diffraction, 2007)

6103 measured reflections
3170 independent reflections
1374 reflections with I > 2σ(I)

θmax = 25.4°, θmin = 2.8°

h = −4→7
k = −45→24
l = −8→9

Refinement

Refinement on F²
Least-squares matrix: full
wR(F²) = 0.138
S = 1.03
3170 reflections
215 parameters
7 restraints

Secondary atom site location: difference Fourier map

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 (Å²)

| X    | Y    | Z    | Uiso* | Occ. (<1) |
|------|------|------|-------|-----------|
| N1   | 0.7034 (12) | 0.4002 (2) | 0.2295 (10) | 0.047 (2) |
| N2   | 0.7744 (14) | 0.4754 (2) | 0.2661 (11) | 0.057 (2) |
| H2N1 | 0.816948 | 0.495983 | 0.221941 | 0.068* |
| H2N2 | 0.734325 | 0.479226 | 0.376244 | 0.068* |
| C1   | 0.6526 (17) | 0.3649 (3) | 0.2644 (14) | 0.052 (3) |
| C2   | 0.4510 (19) | 0.3499 (3) | 0.2008 (17) | 0.077 (4) |
| H2   | 0.347995 | 0.364177 | 0.140653 | 0.092* |
| C3   | 0.406 (2) | 0.3151 (4) | 0.226 (2) | 0.095 (4) |
| H3   | 0.275365 | 0.305737 | 0.179024 | 0.114* |
| C4   | 0.552 (3) | 0.2938 (4) | 0.320 (2) | 0.101 (5) |
| H4   | 0.518855 | 0.270118 | 0.340272 | 0.122* |
| C5   | 0.745 (3) | 0.3071 (4) | 0.385 (2) | 0.109 (5) |
| H5   | 0.846262 | 0.292510 | 0.444957 | 0.131* |
| C6   | 0.790 (2) | 0.3418 (3) | 0.361 (2) | 0.091 (4) |
| H6   | 0.919874 | 0.350644 | 0.411615 | 0.109* |
| C7   | 0.8936 (15) | 0.4148 (3) | 0.3321 (15) | 0.056 (3) |
| H7A  | 0.863266 | 0.416060 | 0.457161 | 0.067* |
| H7B  | 1.015626 | 0.398972 | 0.321899 | 0.067* |
| C8   | 0.9530 (18) | 0.4502 (3) | 0.2711 (16) | 0.066 (3) |
| H8A  | 1.070611 | 0.459306 | 0.349995 | 0.080* |
### Atomic displacement parameters (Å²)

| Atom | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{12}$  | $U_{13}$  | $U_{23}$  |
|------|-----------|-----------|-----------|-----------|-----------|-----------|
| N1   | 0.044 (5) | 0.050 (5) | 0.046 (5) | 0.003 (4) | 0.002 (4) | −0.005 (4) |
| N2   | 0.063 (6) | 0.056 (5) | 0.052 (5) | −0.003 (5) | 0.011 (4) | 0.000 (4)  |
| C1   | 0.054 (6) | 0.053 (6) | 0.048 (6) | 0.007 (5) | −0.001 (5) | −0.010 (5) |
| C2   | 0.066 (8) | 0.085 (9) | 0.076 (8) | −0.005 (7) | −0.021 (7) | 0.021 (7)  |
| C3   | 0.092 (10) | 0.077 (9) | 0.113 (12) | −0.021 (8) | −0.018 (9) | 0.004 (9)  |
| C4   | 0.119 (13) | 0.067 (9) | 0.116 (12) | −0.010 (9) | −0.015 (10) | 0.016 (9)  |
| C5   | 0.127 (13) | 0.062 (9) | 0.134 (14) | 0.012 (9) | −0.021 (11) | 0.010 (9)  |
| C6   | 0.085 (9) | 0.068 (8) | 0.117 (12) | −0.004 (7) | −0.015 (8) | 0.000 (8)  |
| C7   | 0.039 (6) | 0.060 (7) | 0.068 (7) | 0.003 (5) | 0.000 (5) | −0.003 (6) |
| C8   | 0.056 (7) | 0.084 (9) | 0.061 (7) | −0.004 (6) | 0.010 (6) | 0.004 (6)  |
| C9   | 0.054 (7) | 0.068 (7) | 0.066 (7) | 0.003 (6) | 0.005 (6) | 0.006 (6)  |
| C10  | 0.065 (7) | 0.060 (7) | 0.045 (6) | 0.004 (6) | −0.012 (5) | −0.003 (5) |
| Br1  | 0.266 (3) | 0.0626 (11) | 0.169 (2) | −0.0154 (13) | −0.020 (2) | −0.006 (12) |
| O1   | 0.091 (7) | 0.131 (9) | 0.123 (8) | −0.028 (6) | 0.036 (7) | 0.037 (7)  |
| O2   | 0.098 (6) | 0.063 (5) | 0.072 (6) | −0.005 (5) | 0.015 (5) | 0.005 (4)  |
| C11  | 0.052 (6) | 0.074 (7) | 0.033 (5) | 0.004 (6) | 0.006 (5) | −0.005 (5) |
| C12  | 0.069 (7) | 0.074 (8) | 0.047 (6) | 0.004 (6) | 0.008 (6) | −0.003 (6) |
| C13  | 0.085 (9) | 0.069 (8) | 0.060 (8) | −0.015 (7) | −0.003 (6) | 0.000 (7)  |
| C14  | 0.128 (13) | 0.067 (8) | 0.071 (9) | 0.011 (9) | 0.012 (9) | 0.006 (7)  |

**H8B** 1.005544 0.448322 0.152505 0.080*

**C9** 0.5886 (17) 0.4613 (3) 0.1532 (15) 0.063 (3)

**H9A** 0.628083 0.459435 0.030616 0.075*

**H9B** 0.466823 0.477483 0.156218 0.057 (3)

**C10** 0.5255 (17) 0.4260 (3) 0.2189 (14) 0.057 (3)

**H10A** 0.471137 0.428689 0.336512 0.069*

**H10B** 0.408395 0.416774 0.140070 0.069*

**Br1** 0.9708 (5) 0.72340 (4) 0.1736 (4) 0.1674 (14)

**O1** 0.6289 (16) 0.5558 (3) 0.3222 (15) 0.114 (4)

**O2** 0.9081 (15) 0.5426 (2) 0.1687 (11) 0.077 (2)

**H2O** 0.853628 0.522821 0.170738 0.093* 0.32 (16)

**C11** 0.8325 (17) 0.6031 (3) 0.2219 (13) 0.053 (3)

**C12** 1.0163 (19) 0.6155 (3) 0.1465 (14) 0.063 (3)

**H12** 1.115409 0.599557 0.104078 0.076*

**C13** 1.053 (2) 0.6508 (3) 0.1343 (16) 0.072 (3)

**H13** 1.177707 0.658367 0.083258 0.086*

**C14** 0.919 (3) 0.6747 (4) 0.1911 (19) 0.088 (4)

**C15** 0.741 (3) 0.6638 (4) 0.277 (2) 0.097 (5)

**H15** 0.650657 0.680550 0.324796 0.116*

**C16** 0.694 (2) 0.6281 (4) 0.2929 (17) 0.080 (4)

**H16** 0.572770 0.620785 0.349992 0.096*

**C17** 0.787 (2) 0.5643 (4) 0.2376 (14) 0.062 (3)

**O3** 0.7207 (13) 0.4756 (4) 0.696 (17) 0.109*

**H31** 0.830 (15) 0.4755 (18) 0.696 (17) 0.109*
Supporting information

C15 0.110 (12) 0.090 (11) 0.089 (10) 0.036 (9) 0.006 (10) −0.016 (9)
C16 0.079 (9) 0.102 (11) 0.060 (7) 0.006 (8) 0.010 (6) 0.009 (8)
C17 0.058 (7) 0.089 (9) 0.037 (6) −0.009 (7) −0.013 (5) 0.008 (6)
O3 0.081 (6) 0.073 (5) 0.064 (5) −0.015 (4) 0.010 (4) −0.006 (4)

**Geometric parameters (Å, °)**

| Bond/Angle | Value |
|------------|-------|
| N1—C1     | 1.398 (12) |
| N1—C10    | 1.467 (12) |
| N1—C7     | 1.471 (12) |
| N2—C8     | 1.456 (13) |
| N2—C9     | 1.481 (13) |
| N2—H2N1   | 0.8900 |
| N2—H2N2   | 0.8900 |
| C1—C6     | 1.387 (16) |
| C1—C2     | 1.424 (15) |
| C2—C3     | 1.356 (17) |
| C2—H2     | 0.9300 |
| C3—C4     | 1.38 (2) |
| C3—H3     | 0.9300 |
| C4—C5     | 1.35 (2) |
| C4—H4     | 0.9300 |
| C5—C6     | 1.352 (17) |
| C5—H5     | 0.9300 |
| C6—H6     | 0.9300 |
| C7—C8     | 1.467 (14) |
| C7—H7A    | 0.9700 |
| C7—H7B    | 0.9700 |
| C8—H8A    | 0.9700 |
| C8—H8B    | 0.9700 |

| Bond/Angle | Value |
|------------|-------|
| C1—N1—C10 | 117.8 (8) |
| C1—N1—C7  | 116.2 (8) |
| C10—N1—C7 | 110.5 (7) |
| C8—N2—C9  | 109.8 (8) |
| C8—N2—H2N1| 109.7    |
| C9—N2—H2N1| 109.7    |
| C8—N2—H2N2| 109.7    |
| C9—N2—H2N2| 109.7    |
| H2N1—N2—H2N2| 108.2 |
| C6—C1—N1  | 124.0 (10) |
| C6—C1—C2  | 114.6 (10) |
| N1—C1—C2  | 121.3 (9)  |
| C3—C2—C1  | 121.5 (11) |
| C3—C2—H2  | 119.3      |
| C1—C2—H2  | 119.3      |
| C2—C3—C4  | 120.3 (13) |
| C2—C3—H3  | 119.8      |
C4—C3—H3 119.8  C16—C11—C17 120.4 (11)
C5—C4—C3 120.0 (14)  C13—C12—C11 120.4 (11)
C5—C4—H4 120.0  C13—C12—H12 119.8
C3—C4—H4 120.0  C11—C12—H12 119.8
C6—C5—C4 119.8 (15)  C14—C13—C12 123.0 (13)
C5—C6—C1 123.7 (13)  C13—C14—Br1 122.7 (13)
C5—C6—H6 118.2  C13—C14—Br1 118.1 (12)
C1—C6—H6 118.2  C15—C14—Br1 120.5 (13)
C8—C7—N1 112.7 (9)  C14—C15—C16 119.1 (13)
C8—C7—H7A 109.0  C14—C15—H15 119.7
N1—C7—H7A 109.0  C16—C15—H15 119.7
C8—C7—H7B 109.0  C15—C16—C11 119.2 (12)
N1—C7—H7B 109.0  C15—C16—H16 120.4
H7A—C7—H7B 107.8  C11—C16—H16 120.4
N2—C8—C7 113.5 (9)  O1—C17—O2 123.8 (12)
N2—C8—H8A 108.9  O1—C17—C11 116.9 (12)
C7—C8—H8A 108.9  O2—C17—C11 119.3 (10)
N2—C8—H8B 108.9  H31—O3—H32 109 (4)
C10—N1—C7—C8 172.4 (9)  C17—C11—C16—C15 179.7 (11)
C7—N1—C1—C6 −147.2 (11)  C16—C11—C17—O1 173.4 (10)
C7—N1—C1—C2 33.1 (14)  N2—C9—C10—N1 −55.9 (12)
C7—N1—C1—C6 167.6 (10)  C16—C11—C17—O2 −5.8 (15)
C6—C1—C2—C3 −3.4 (18)  C9—N2—C8—C7 −55.9 (12)
C6—C1—C2—C3 176.3 (12)  N2—C8—H8A···O3ii 0.97 2.53 3.475 (14) 166
N1—C1—C2—C3 3 (2)  C9—N2—C8—N2 53.6 (12)
C1—C2—C3—C4 3 (2)  C12—C11—C17—O2 −5.8 (15)
C2—C3—C4—C5 −2 (3)  C16—C11—C17—O2 177.8 (10)
C3—C4—C5—C6 −2 (3)  C15—C11—C17—O2 177.8 (10)
C4—C5—C6—C1 −3 (3)  C14—C11—C17—O2 −5.8 (15)
N1—C1—C6—C5 −175.8 (14)  C12—C11—C17—O2 177.8 (10)
C2—C1—C6—C5 4 (2)  C14—C15—C16—C11 1 (2)
C1—N1—C7—C8 172.4 (9)  C12—C11—C16—C15 3.2 (17)
C10—N1—C7—C8 −50.0 (11)  C17—C11—C16—C15 179.7 (11)
C9—N2—C8—C7 −55.9 (12)  C12—C11—C16—C15 179.7 (11)
N1—C7—C8—N2 53.6 (12)  C16—C11—C17—O1 173.4 (10)
N2—C8—H8B···O2ii 0.97 2.53 3.475 (14) 166
C8—N2—C9—C10 55.7 (11)  C16—C11—C17—O1 −3.0 (15)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|--------|
| N2—H2N1···O2 | 0.89 | 1.90 | 2.780 (11) | 170 |
| N2—H2N2···O3 | 0.89 | 1.94 | 2.803 (12) | 164 |
| C8—H8A···O3i | 0.97 | 2.64 | 3.377 (14) | 133 |
| C8—H8B···O2ii | 0.97 | 2.53 | 3.475 (14) | 166 |
| C9—H9B···O3iii | 0.97 | 2.59 | 3.403 (14) | 142 |
4-Phenylpiperazin-1-ium 4-iodobenzoate (4)

Crystal data

C_{10}H_{15}N_{2}^+·C_{7}H_{4}I_{2}O_{2}^−

Mr = 410.24

Monoclinic, P 2_1/c

a = 10.8507 (4) Å

b = 23.4045 (7) Å

c = 13.3019 (4) Å

β = 102.491 (4)°

V = 3298.13 (19) Å³

Z = 8

F(000) = 1632

D_x = 1.652 Mg m⁻³

Cell parameters from 6801 reflections

θ = 2.6–27.8°

µ = 1.95 mm⁻¹

T = 293 K

Prism, colourless

0.48 × 0.48 × 0.40 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire

CCD diffractometer

Radiation source: Enhance (Mo) X-ray Source

Rotation method data acquisition using ω scans.

Absorption correction: multi-scan

(CrysAlisRED; Oxford Diffraction, 2007)

T min = 0.575, T max = 1.000

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.037

wR(F²) = 0.084

S = 1.02

7079 reflections

409 parameters

4 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(F²) + (0.0402P)²]

where P = (F² + 2Fc²)/3

(Δ/σ) max = 0.002

Δρ max = 0.77 e Å⁻³

Δρ min = −1.25 e Å⁻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 (Å²)

|     | x    | y    | z     | U_{iso} [Å²] |
|-----|------|------|-------|--------------|
| C1  | 0.6237 (3) | 0.57603 (14) | 0.0843 (2) | 0.0363 (8) |
| C2  | 0.4969 (3) | 0.58795 (15) | 0.0505 (3) | 0.0431 (9) |
| H2  | 0.437868 | 0.568638 | 0.079160 | 0.052* |
| C3  | 0.4565 (4) | 0.62827 (17) | −0.0255 (3) | 0.0535 (10) |
| H3  | 0.370693 | 0.635548 | −0.047848 | 0.064* |
| C4   | 0.5422 (4) | 0.65774 (17) | −0.0684 (3) | 0.0587 (11) |
|-----|------------|--------------|-------------|-------------|
| H4  | 0.514944   | 0.685086     | −0.119018   | 0.070*      |
| C5  | 0.6689 (4) | 0.64613 (17) | −0.0351 (3) | 0.0578 (11) |
| H5  | 0.727710   | 0.665869     | −0.063350   | 0.069*      |
| C6  | 0.7087 (3) | 0.60578 (16) | 0.0390 (3)  | 0.0488 (9)  |
| H6  | 0.794547   | 0.598015     | 0.059728    | 0.059*      |
| C7  | 0.5780 (3) | 0.49980 (14) | 0.1955 (2)  | 0.0399 (8)  |
| H7A | 0.522273   | 0.482727     | 0.136209    | 0.048*      |
| C7B | 0.527435   | 0.523672     | 0.230538    | 0.048*      |
| C8  | 0.6407 (3) | 0.45316 (15) | 0.2676 (3)  | 0.0461 (9)  |
| H8A | 0.576921   | 0.431322     | 0.291939    | 0.055*      |
| H8B | 0.685619   | 0.427387     | 0.231077    | 0.055*      |
| C9  | 0.8241 (3) | 0.51415 (16) | 0.3220 (3)  | 0.0506 (10) |
| H9A | 0.875290   | 0.490380     | 0.287377    | 0.061*      |
| H9B | 0.879334   | 0.531571     | 0.381165    | 0.061*      |
| C10 | 0.7615 (3) | 0.56009 (15) | 0.2497 (3)  | 0.0437 (9)  |
| H10A| 0.716702   | 0.586020     | 0.286126    | 0.052*      |
| H10B| 0.825224   | 0.581826     | 0.225187    | 0.052*      |
| C11 | 0.1383 (3) | 0.57882 (14) | 0.0931 (3)  | 0.0378 (8)  |
| C12 | 0.0736 (3) | 0.62745 (16) | 0.1107 (3)  | 0.0500 (10) |
| H12 | 0.060684   | 0.634674     | 0.176404    | 0.060*      |
| C13 | 0.0276 (4) | 0.66576 (16) | 0.0312 (3)  | 0.0604 (11) |
| H13 | 0.014418   | 0.698638     | 0.044310    | 0.072*      |
| C14 | 0.0443 (4) | 0.65500 (19) | −0.0669 (3) | 0.0609 (12) |
| H14 | 0.012708   | 0.680304     | −0.120126   | 0.073*      |
| C15 | 0.1071 (3) | 0.60727 (17) | −0.0854 (3) | 0.0519 (10) |
| H15 | 0.117968   | 0.600061     | −0.151708   | 0.062*      |
| C16 | 0.1549 (3) | 0.56928 (15) | −0.0072 (3) | 0.0435 (9)  |
| H16 | 0.198547   | 0.537080     | −0.021249   | 0.052*      |
| C17 | 0.1510 (4) | 0.48047 (15) | 0.1505 (3)  | 0.0540 (10) |
| H17A| 0.154730   | 0.470809     | 0.080323    | 0.065*      |
| H17B| 0.064339   | 0.476153     | 0.157480    | 0.065*      |
| C18 | 0.2346 (4) | 0.44063 (16) | 0.2238 (3)  | 0.0516 (10) |
| H18A| 0.203871   | 0.401837     | 0.210497    | 0.062*      |
| H18B| 0.319385   | 0.442244     | 0.211451    | 0.062*      |
| C19 | 0.1817 (3) | 0.55429 (15) | 0.2758 (3)  | 0.0441 (9)  |
| H19A| 0.094917   | 0.550003     | 0.282589    | 0.053*      |
| H19B| 0.206022   | 0.593865     | 0.289794    | 0.053*      |
| C20 | 0.2659 (3) | 0.51623 (15) | 0.3526 (3)  | 0.0480 (9)  |
| H20A| 0.353238   | 0.523724     | 0.350540    | 0.058*      |
| H20B| 0.254904   | 0.525406     | 0.421236    | 0.058*      |
| C21 | 0.5418 (3) | 0.35843 (13) | 0.5875 (2)  | 0.0330 (7)  |
| C22 | 0.6116 (3) | 0.31980 (14) | 0.5442 (3)  | 0.0403 (8)  |
| H22 | 0.609882   | 0.321699     | 0.474075    | 0.048*      |
| C23 | 0.6838 (3) | 0.27831 (14) | 0.6037 (3)  | 0.0421 (9)  |
| H23 | 0.730730   | 0.252638     | 0.573877    | 0.050*      |
| C24 | 0.6857 (3) | 0.27537 (14) | 0.7075 (3)  | 0.0378 (8)  |
| C25 | 0.6173 (3) | 0.31365 (15) | 0.7525 (3)  | 0.0422 (9)  |
H25 0.618742 0.311707 0.822587 0.051*  
C26 0.5467 (3) 0.35490 (15) 0.6916 (3) 0.0439 (9)  
H26 0.501084 0.381014 0.721785 0.053*  
C27 0.4575 (3) 0.40162 (15) 0.5219 (3) 0.0393 (8)  
C28 1.0539 (3) 0.35016 (15) 0.5371 (2) 0.0332 (7)  
C29 1.0084 (3) 0.32960 (15) 0.6197 (3) 0.0435 (9)  
H29 0.927288 0.339430 0.625776 0.052*  
C30 1.0812 (3) 0.29473 (14) 0.6934 (3) 0.0436 (9)  
H30 1.050319 0.282046 0.749431 0.052*  
C31 1.2002 (3) 0.27904 (13) 0.5219 (3) 0.03702 (10)  
C32 1.2455 (3) 0.29675 (14) 0.5995 (3) 0.0411 (8)  
H32 1.324481 0.284729 0.591371 0.049*  
C33 1.1730 (3) 0.33275 (14) 0.5275 (3) 0.0413 (8)  
H33 1.204660 0.345427 0.471774 0.050*  
C34 0.9773 (3) 0.39127 (14) 0.4615 (3) 0.0419 (9)  
I1 0.78561 (3) 0.21027 (2) 0.79917 (2) 0.05702 (10)  
I2 1.31203 (3) 0.22704 (2) 0.79616 (2) 0.05455 (10)  
N1 0.6722 (2) 0.53483 (12) 0.1613 (2) 0.0367 (7)  
N2 0.7303 (3) 0.47858 (13) 0.3568 (2) 0.0450 (8)  
H21N 0.684 (3) 0.4978 (14) 0.392 (2) 0.054*  
H22N 0.771 (3) 0.4508 (12) 0.397 (2) 0.054*  
N3 0.1911 (2) 0.53973 (11) 0.1718 (2) 0.0367 (7)  
N4 0.2388 (3) 0.45488 (14) 0.3322 (2) 0.0460 (8)  
H41N 0.300 (3) 0.4353 (14) 0.370 (2) 0.055*  
H42N 0.170 (2) 0.4466 (15) 0.350 (3) 0.055*  
O1 0.4122 (2) 0.44040 (11) 0.56598 (19) 0.0571 (7)  
O2 0.4359 (2) 0.39436 (11) 0.42592 (19) 0.0561 (7)  
O3 1.0238 (2) 0.41261 (12) 0.3931 (2) 0.0644 (8)  
O4 0.8680 (2) 0.40136 (11) 0.4733 (2) 0.0645 (8)  

Atomic displacement parameters (Å²)

| U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|-----|-----|-----|-----|-----|-----|
|   0.043 (2) | 0.033 (2) | 0.0308 (18) | −0.0001 (16) | 0.0052 (16) | −0.0052 (15) |
| 0.039 (2) | 0.046 (2) | 0.041 (2) | −0.0046 (17) | 0.0016 (17) | −0.0035 (17) |
| 0.051 (2) | 0.056 (3) | 0.047 (2) | 0.003 (2) | −0.0029 (19) | 0.004 (2) |
| 0.071 (3) | 0.055 (3) | 0.046 (2) | 0.009 (2) | 0.004 (2) | 0.0126 (19) |
| 0.059 (3) | 0.062 (3) | 0.055 (3) | −0.001 (2) | 0.018 (2) | 0.016 (2) |
| 0.045 (2) | 0.053 (2) | 0.047 (2) | 0.0058 (19) | 0.0084 (19) | 0.0039 (19) |
| 0.039 (2) | 0.040 (2) | 0.038 (2) | −0.0020 (16) | 0.0033 (16) | −0.0034 (16) |
| 0.049 (2) | 0.043 (2) | 0.047 (2) | −0.0008 (18) | 0.0116 (19) | 0.0044 (18) |
| 0.051 (2) | 0.045 (2) | 0.047 (2) | −0.0004 (19) | −0.0076 (19) | −0.0001 (18) |
| 0.045 (2) | 0.040 (2) | 0.041 (2) | −0.0041 (17) | −0.0035 (17) | −0.0029 (17) |
| 0.0287 (18) | 0.034 (2) | 0.045 (2) | −0.0064 (15) | −0.0052 (16) | 0.0021 (16) |
| 0.052 (2) | 0.041 (2) | 0.052 (2) | 0.0060 (18) | −0.0013 (19) | 0.0017 (18) |
| 0.055 (3) | 0.038 (2) | 0.079 (3) | 0.0053 (19) | −0.007 (2) | 0.008 (2) |
| 0.055 (3) | 0.056 (3) | 0.063 (3) | −0.005 (2) | −0.006 (2) | 0.025 (2) |
| 0.047 (2) | 0.055 (3) | 0.050 (2) | −0.011 (2) | 0.0033 (19) | 0.015 (2) |

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### Geometric parameters (Å, °)

| Bond                  | Length (Å) | Angle (°) |
|-----------------------|------------|-----------|
| C1—C2                 | 1.380 (4)  |           |
| C1—C6                 | 1.393 (5)  |           |
| C1—N1                 | 1.422 (4)  |           |
| C2—C3                 | 1.383 (5)  |           |
| C2—H2                 | 0.9300     |           |
| C3—C4                 | 1.376 (5)  |           |
| C3—H3                 | 0.9300     |           |
| C4—C5                 | 1.377 (5)  |           |
| C4—H4                 | 0.9300     |           |
| C5—C6                 | 1.367 (5)  |           |
| C5—H5                 | 0.9300     |           |
| C6—H6                 | 0.9300     |           |
| C7—N1                 | 1.458 (4)  |           |
| C7—H7A                | 0.9700     |           |
| C7—H7B                | 0.9700     |           |

| Bond                  | Length (Å) | Angle (°) |
|-----------------------|------------|-----------|
| C8—C2                 | 1.382 (4)  |           |
| C8—C9                 | 1.377 (5)  |           |
| C9—C10                | 1.353 (5)  |           |
| C9—H10                | 0.9300     |           |
| C10—C11               | 1.375 (5)  |           |
| C10—H10               | 0.9300     |           |
| C11—C12               | 1.375 (5)  |           |
| C11—H11               | 0.9300     |           |
| C12—C13               | 1.375 (5)  |           |
| C12—H12               | 0.9300     |           |
| C13—C14               | 1.375 (5)  |           |
| C13—H13               | 0.9300     |           |
| C14—C15               | 1.375 (5)  |           |
| C14—H14               | 0.9300     |           |
| C15—C16               | 1.375 (5)  |           |
| C15—H15               | 0.9300     |           |
| C16—C17               | 1.375 (5)  |           |
| C16—H16               | 0.9300     |           |
| C17—C18               | 1.375 (5)  |           |
| C17—H17               | 0.9300     |           |
| C18—C19               | 1.375 (5)  |           |
| C18—H18               | 0.9300     |           |
| C19—C20               | 1.375 (5)  |           |
| C19—H19               | 0.9300     |           |
| C20—C21               | 1.375 (5)  |           |
| C20—H20               | 0.9300     |           |
| C21—C22               | 1.375 (5)  |           |
| C21—H21               | 0.9300     |           |
| C22—C23               | 1.375 (5)  |           |
| C22—H22               | 0.9300     |           |
| C23—C24               | 1.375 (5)  |           |
| C23—H23               | 0.9300     |           |
C8—N2 1.485 (4) C23—H23 0.9300
C8—H8A 0.9700 C24—C25 1.380 (5)
C8—H8B 0.9700 C24—I1 2.101 (3)
C9—N2 1.465 (5) C25—C26 1.381 (4)
C9—C10 1.503 (5) C25—H25 0.9300
C9—H9A 0.9700 C26—H26 0.9300
C9—H9B 0.9700 C27—O1 1.238 (4)
C10—N1 1.477 (4) C27—O2 1.258 (4)
C10—H10A 0.9700 C28—C29 1.385 (4)
C10—H10B 0.9700 C28—C33 1.387 (4)
C11—C12 1.384 (5) C28—C34 1.506 (5)
C11—C16 1.403 (5) C29—C30 1.384 (5)
C11—N3 1.415 (4) C29—H29 0.9300
C12—C13 1.394 (5) C30—C31 1.380 (5)
C12—H12 0.9300 C30—H30 0.9300
C13—C14 1.378 (6) C31—C32 1.366 (4)
C13—H13 0.9300 C31—I2 2.109 (3)
C14—C15 1.358 (5) C32—C33 1.386 (4)
C14—H14 0.9300 C32—H32 0.9300
C15—C16 1.381 (5) C33—H33 0.9300
C15—H15 0.9300 C34—O3 1.237 (4)
C16—H16 0.9300 C34—O4 1.253 (4)
C17—N3 1.463 (4) N2—H21N 0.877 (18)
C17—C18 1.503 (5) N2—H22N 0.897 (18)
C17—H17A 0.9700 N4—H41N 0.869 (18)
C17—H17B 0.9700 N4—H42N 0.851 (18)

C2—C1—C6 117.7 (3) N3—C19—C20 110.5 (3)
C2—C1—N1 124.0 (3) N3—C19—H19A 109.5
C6—C1—N1 118.3 (3) C20—C19—H19A 109.5
C1—C2—C3 120.8 (3) N3—C19—H19B 109.5
C1—C2—H2 119.6 C20—C19—H19B 109.5
C3—C2—H2 119.6 H19A—C19—H19B 108.1
C4—C3—C2 120.6 (4) N4—C20—C19 112.5 (3)
C4—C3—H3 119.7 N4—C20—H20A 109.1
C2—C3—H3 119.7 C19—C20—H20A 109.1
C3—C4—C5 119.0 (4) N4—C20—H20B 109.1
C3—C4—H4 120.5 C19—C20—H20B 109.1
C5—C4—H4 120.5 H20A—C20—H20B 107.8
C6—C5—C4 120.4 (4) C26—C21—C22 118.3 (3)
C6—C5—H5 119.8 C26—C21—C27 120.6 (3)
C4—C5—H5 119.8 C22—C21—C27 121.0 (3)
C5—C6—C1 121.5 (3) C21—C22—C23 120.9 (3)
C5—C6—H6 119.3 C21—C22—H22 119.5
C1—C6—H6 119.3 C23—C22—H22 119.5
N1—C7—C8 110.7 (3) C24—C23—C22 119.5 (3)
N1—C7—H7A 109.5 C24—C23—H23 120.3
C8—C7—H7A 109.5 C22—C23—H23 120.3
| Bond          | Angle (°) | Bond          | Angle (°) | Bond          | Angle (°) |
|--------------|----------|--------------|----------|--------------|----------|
| N1—C7—H7B   | 109.5    | C23—C24—C25 | 120.6    | N2—C8—C7    | 110.1 (3) |
| C8—C7—H7B   | 109.5    | C23—C24—C25 | 120.8    | N2—C8—H8A   | 109.6     |
| H7A—C7—H7B  | 108.1    | C25—C24—C25 | 118.5    | N2—C8—H8B   | 109.6     |
| N2—C8—C7    | 110.1 (3)| C24—C25—C26 | 118.8    | N2—C8—H8A   | 109.6     |
| N2—C8—H8A   | 109.6    | C24—C25—H25 | 120.6    | C7—C8—H8B   | 109.6     |
| N2—C8—H8B   | 109.6    | C21—C26—C25 | 121.8    | C7—C8—H8B   | 109.6     |
| H8A—C8—H8B  | 108.2    | C25—C26—H26 | 119.1    | H8A—C8—H8B  | 108.2     |
| N2—C9—C10   | 111.1 (3)| O1—C27—O2   | 125.0    | N2—C9—H9A   | 109.4     |
| N2—C9—H9A   | 109.4    | O1—C27—C21  | 118.0    | C10—C9—H9A  | 109.4     |
| C10—C9—H9A  | 109.4    | O2—C27—C21  | 116.9    | N2—C9—H9B   | 109.4     |
| N2—C9—H9B   | 109.4    | C29—C28—C33 | 118.1    | C10—C9—H9B  | 109.4     |
| C10—C9—H9B  | 109.4    | C29—C28—C34 | 120.8    | H9A—C9—H9B  | 108.0     |
| N1—C10—C9   | 110.6 (3)| C30—C29—C28 | 121.3    | N1—C10—C9   | 110.6 (3) |
| N1—C10—H10A | 109.5    | C30—C29—H29 | 119.3    | C9—C10—H10A | 109.5     |
| N1—C10—H10A | 109.5    | C31—C30—C29 | 119.1    | H10A—C10—H10B | 108.1 |
| C9—C10—H10B | 109.5    | C31—C30—H30 | 120.5    | C12—C11—C16 | 117.8 (3) |
| H10A—C10—H10B | 108.1 | C29—C30—H30 | 120.5    | C12—C11—N3  | 123.1 (3) |
| C12—C11—C16 | 117.8 (3)| C32—C31—C30 | 120.8    | C16—C11—N3  | 119.1 (3) |
| C12—C11—N3  | 123.1 (3)| C32—C31—C30 | 120.8    | C11—C12—C13 | 120.8 (4) |
| C16—C11—N3  | 119.1 (3)| C30—C31—C32 | 119.0    | C11—C12—H12 | 119.6     |
| C11—C12—C13 | 120.8 (4)| C31—C32—C33 | 119.5    | C13—C12—H12 | 119.6     |
| C11—C12—H12 | 119.6    | C31—C32—C33 | 120.2    | C14—C13—C12 | 120.1 (4) |
| C13—C12—H12 | 119.6    | C33—C32—C33 | 120.2    | C14—C13—C12 | 120.1 (4) |
| C14—C13—C12 | 120.1 (4)| C32—C33—C28 | 121.1    | C14—C13—H13 | 119.9     |
| C14—C13—H13 | 119.9    | C32—C33—H33 | 119.5    | C15—C14—C13 | 119.7 (4) |
| C14—C15—C16 | 120.9 (4)| C1—N1—C7    | 115.5    | C15—C14—H14 | 120.1     |
| C14—C15—H15 | 119.5    | C1—N1—C10   | 112.3    | C13—C14—H14 | 120.1     |
| C16—C15—H15 | 119.5    | C7—N1—C10   | 111.1    | C14—C15—C16 | 120.9 (4) |
| C15—C16—C11 | 120.6 (4)| C9—N2—C8    | 110.8    | C15—C16—H16 | 119.7     |
| C15—C16—H16 | 119.7    | C9—N2—H21N  | 113 (2)  | C11—C16—H16 | 119.7     |
| N3—C17—C18  | 110.5 (3)| C8—N2—H22N  | 108 (2)  | N3—C17—C18  | 110.5 (3) |
| N3—C17—H17A | 109.5    | C8—N2—H22N  | 110 (2)  | C18—C17—H17A| 109.5     |
| C18—C17—H17A| 109.5    | H21N—N2—H22N| 109 (3)  | N3—C17—H17B | 109.5     |
| N3—C17—H17B | 109.5    | C11—N3—C19  | 116.9    | C18—C17—H17B| 109.5     |
| H17A—C17—H17B| 108.1 | C19—N3—C17  | 114.5    | N4—C18—C17  | 112.4 (3) |
| N4—C18—C17  | 112.4 (3)| C18—N4—C20  | 111.3    | N4—C18—H18A | 109.1     |
| N4—C18—H18A | 109.1    | C18—N4—H41N | 108 (2)  | C17—C18—H18A| 109.1     |
| Bond                  | Length (Å) | Angle (°) | Distance (Å) | Duration (s) |
|----------------------|------------|-----------|--------------|--------------|
| N4—C18—H18B         | 109.1      |           |              | 112          |
| C17—C18—H18B        | 109.1      |           |              | 109          |
| H18A—C18—H18B       | 107.9      |           |              | 109          |

### Hydrogen-bond geometry (Å, °)

|        | D—H     | H···A     | D···A      | D—H···A   |
|--------|---------|-----------|------------|-----------|
| C9—H9A—O3  | 0.97    | 2.63      | 3.218 (4)  | 119       |
| N2—H21N—O1i | 0.88 (2) | 1.94 (2)  | 2.780 (4)  | 160 (3)   |
| N2—H22N—O4  | 0.90 (2) | 1.74 (2)  | 2.627 (4)  | 173 (3)   |
| N4—H41N—O1   | 0.87 (2) | 2.63 (3)  | 3.285 (4)  | 133 (3)   |

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4-Phenylpiperazin-1-ium 4-nitrobenzoate (5)

Crystal data

C_{10}H_{15}N_{2}⁺·C_{7}H_{4}NO_{4}⁻
Mr = 329.35
Monoclinic, P_{2}1/c
a = 13.0683 (9) Å
b = 15.7868 (9) Å
c = 7.9255 (5) Å
β = 95.137 (6)°
V = 1628.52 (18) Å³
Z = 4

F(000) = 696
D_x = 1.343 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 4084 reflections
θ = 2.6–27.9°
µ = 0.10 mm⁻¹
T = 293 K
Prism, yellow
0.48 × 0.44 × 0.16 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire
CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Rotation method data acquisition using ω scans.
Absorption correction: multi-scan (CrysalisRED; Oxford Diffraction, 2007)
T_{min} = 0.790, T_{max} = 1.000
11699 measured reflections
3587 independent reflections
2088 reflections with I > 2σ(I)

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.054
wR(F²) = 0.117
S = 1.10
3587 reflections
251 parameters
83 restraints

Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

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 (Å²)

|        | x          | y          | z          | U_{eq} / U_{eq} | Occ. (<1) |
|--------|------------|------------|------------|-----------------|-----------|
| N1     | 0.31713 (11)| 0.63737 (9)| 0.06853 (18)| 0.0443 (4)      | 0.999     |
| N2     | 0.42384 (12)| 0.61812 (10)| 0.3978 (2) | 0.0497 (4)       | 0.999     |
| H21    | 0.4059 (14) | 0.5640 (10)| 0.412 (2)  | 0.060*          | 0.999     |
| H22    | 0.4650 (13) | 0.6358 (11)| 0.493 (2)  | 0.060*          | 0.999     |
| C1     | 0.25304 (14)| 0.61655 (11)| −0.0794 (2)| 0.0451 (5)      | 0.999     |
### Atomic displacement parameters (Å²)

|     | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|-----|-----|-----|-----|-----|-----|-----|
| N1  | 0.0417 (9) | 0.0431 (8) | 0.0468 (9) | 0.0018 (7) | −0.0038 (7) | 0.0015 (7) |
| N2  | 0.0525 (10) | 0.0434 (9) | 0.0505 (10) | 0.0009 (7) | −0.0110 (8) | −0.0029 (8) |
| C1  | 0.0461 (11) | 0.0442 (10) | 0.0437 (11) | −0.0081 (8) | −0.0027 (8) | 0.0094 (9) |

**Table 1**: Atomic displacement parameters (Å²) for the compounds

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|    |      |      |      |      |      |      |
|----|------|------|------|------|------|------|
| C2 | 0.0514 (12) | 0.0637 (13) | 0.0606 (13) | −0.0023 (10) | −0.0057 (10) | 0.0071 (11) |
| C3 | 0.0526 (14) | 0.0923 (17) | 0.0657 (16) | −0.0093 (12) | −0.0104 (11) | 0.0187 (14) |
| C4 | 0.0733 (17) | 0.112 (2) | 0.0476 (14) | −0.0251 (15) | −0.0141 (12) | 0.0100 (14) |
| C5 | 0.092 (2) | 0.0928 (18) | 0.0446 (13) | −0.0129 (14) | −0.0014 (12) | −0.0059 (12) |
| C6 | 0.0661 (14) | 0.0663 (13) | 0.0472 (12) | 0.0008 (10) | −0.0018 (10) | 0.0001 (11) |
| C7 | 0.0458 (11) | 0.0493 (10) | 0.0489 (12) | 0.0022 (9) | 0.0014 (8) | 0.0022 (9) |
| C8 | 0.0457 (12) | 0.0565 (12) | 0.0603 (13) | 0.0002 (9) | −0.0025 (10) | 0.0042 (10) |
| C9 | 0.0561 (12) | 0.0510 (11) | 0.0562 (12) | 0.0111 (9) | −0.0070 (9) | −0.0086 (10) |
| C10 | 0.0478 (12) | 0.0564 (12) | 0.0522 (12) | 0.0093 (9) | −0.0026 (9) | 0.0065 (9) |
| O1 | 0.0597 (9) | 0.0622 (8) | 0.0710 (10) | 0.0133 (7) | −0.0213 (7) | 0.0013 (7) |
| O2 | 0.0715 (10) | 0.0475 (7) | 0.0567 (9) | 0.0020 (7) | −0.0117 (7) | −0.0087 (7) |
| N3 | 0.068 (4) | 0.100 (5) | 0.065 (3) | −0.018 (4) | −0.019 (3) | 0.005 (3) |
| O3 | 0.106 (5) | 0.126 (5) | 0.084 (5) | −0.009 (4) | −0.036 (4) | −0.028 (4) |
| O4 | 0.056 (3) | 0.140 (6) | 0.084 (3) | 0.000 (4) | −0.0213 (18) | 0.014 (4) |
| N3A | 0.064 (5) | 0.105 (6) | 0.071 (5) | −0.007 (5) | −0.024 (5) | 0.007 (5) |
| O3A | 0.091 (7) | 0.124 (7) | 0.066 (5) | −0.011 (5) | −0.025 (4) | −0.011 (5) |
| O4A | 0.050 (4) | 0.146 (8) | 0.102 (5) | −0.018 (6) | −0.023 (3) | 0.020 (6) |
| C11 | 0.0450 (11) | 0.0361 (9) | 0.0444 (11) | −0.0045 (8) | −0.0029 (8) | 0.0032 (8) |
| C12 | 0.0491 (12) | 0.0475 (11) | 0.0538 (12) | 0.0021 (9) | −0.0014 (9) | 0.0022 (9) |
| C13 | 0.0690 (15) | 0.0557 (12) | 0.0510 (12) | −0.0014 (11) | −0.0046 (10) | 0.0014 (10) |
| C14 | 0.0520 (13) | 0.0599 (13) | 0.0550 (13) | −0.0116 (10) | −0.0127 (10) | 0.0058 (10) |
| C15 | 0.0414 (12) | 0.0722 (14) | 0.0664 (15) | 0.0017 (10) | −0.0008 (10) | 0.0060 (12) |
| C16 | 0.0500 (12) | 0.0564 (12) | 0.0500 (12) | 0.0033 (10) | 0.0016 (9) | −0.0033 (9) |
| C17 | 0.0498 (12) | 0.0389 (10) | 0.0492 (12) | −0.0040 (9) | −0.0044 (9) | 0.0045 (9) |

**Geometric parameters (Å, °)**

|     |       |       |       |       |       |       |
|-----|-------|-------|-------|-------|-------|-------|
| N1—C1 | 1.417 (2) |  |  |  |  |  |
| N1—C7 | 1.460 (2) |  |  |  |  |  |
| N1—C10 | 1.466 (2) |  |  |  |  |  |
| N2—C9 | 1.472 (2) |  |  |  |  |  |
| N2—C8 | 1.477 (3) |  |  |  |  |  |
| N2—H21 | 0.896 (14) |  |  |  |  |  |
| N2—H22 | 0.931 (14) |  |  |  |  |  |
| C1—C6 | 1.383 (3) |  |  |  |  |  |
| C1—C2 | 1.395 (3) |  |  |  |  |  |
| C2—C3 | 1.376 (3) |  |  |  |  |  |
| C2—H2 | 0.9300 |  |  |  |  |  |
| C3—C4 | 1.363 (3) |  |  |  |  |  |
| C3—H3 | 0.9300 |  |  |  |  |  |
| C4—C5 | 1.367 (3) |  |  |  |  |  |
| C4—H4 | 0.9300 |  |  |  |  |  |
| C5—C6 | 1.383 (3) |  |  |  |  |  |
| C5—H5 | 0.9300 |  |  |  |  |  |
| C6—H6 | 0.9300 |  |  |  |  |  |
| C7—C8 | 1.510 (2) |  |  |  |  |  |
| C7—H7A | 0.9700 |  |  |  |  |  |
| C7—H7B | 0.9700 |  |  |  |  |  |
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| C8—H8A       | 0.9700       | C15—H15       | 0.9300       |
| C8—H8B       | 0.9700       | C16—H16       | 0.9300       |
| C9—C10       | 1.504 (2)    |               |              |
| C1—N1—C7     | 115.50 (14)  | N2—C9—H9A     | 109.7        |
| C1—N1—C10    | 114.03 (14)  | C10—C9—H9A    | 109.7        |
| C7—N1—C10    | 112.51 (13)  | N2—C9—H9B     | 109.7        |
| C9—N2—C8     | 109.43 (15)  | C10—C9—H9B    | 109.7        |
| C9—N2—H21    | 110.4 (12)   | H9A—C9—H9B    | 108.2        |
| C8—N2—H21    | 107.1 (13)   | N1—C10—C9     | 112.01 (16)  |
| C9—N2—H22    | 110.0 (11)   | N1—C10—H10A   | 109.2        |
| C8—N2—H22    | 110.9 (12)   | C9—C10—H10A   | 109.2        |
| H21—N2—H22   | 108.9 (16)   | N1—C10—H10B   | 109.2        |
| C6—C1—C2     | 117.37 (17)  | C9—C10—H10B   | 109.2        |
| C6—C1—N1     | 122.71 (16)  | H10A—C10—H10B | 107.9        |
| C2—C1—N1     | 119.91 (17)  | O4—N3—O3      | 124.7 (4)    |
| C3—C2—C1     | 120.9 (2)    | O4—N3—C14     | 118.9 (9)    |
| C3—C2—H2     | 119.6        | O3—N3—C14     | 116.4 (9)    |
| C1—C2—H2     | 119.6        | O4A—N3A—O3A   | 124.6 (5)    |
| C4—C3—C2     | 121.0 (2)    | O4A—N3A—C14   | 115.4 (12)   |
| C4—C3—H3     | 119.5        | O3A—N3A—C14   | 120.0 (12)   |
| C2—C3—H3     | 119.5        | C16—C11—C12   | 119.07 (16)  |
| C3—C4—C5     | 118.9 (2)    | C16—C11—C17   | 120.49 (17)  |
| C3—C4—H4     | 120.5        | C12—C11—C17   | 120.42 (17)  |
| C5—C4—H4     | 120.5        | C11—C12—C13   | 120.68 (18)  |
| C4—C5—C6     | 120.9 (2)    | C11—C12—H12   | 119.7        |
| C4—C5—H5     | 119.5        | C13—C12—H12   | 119.7        |
| C6—C5—H5     | 119.5        | C14—C13—C12   | 118.33 (19)  |
| C5—C6—C1     | 120.9 (2)    | C14—C13—H13   | 120.8        |
| C5—C6—H6     | 119.6        | C12—C13—H13   | 120.8        |
| C1—C6—H6     | 119.6        | C13—C14—C15   | 122.52 (18)  |
| N1—C7—C8     | 111.92 (15)  | C13—C14—N3A   | 113.8 (8)    |
| N1—C7—H7A    | 109.2        | C15—C14—N3A   | 123.7 (8)    |
| C8—C7—H7A    | 109.2        | C13—C14—N3    | 121.9 (5)    |
| N1—C7—H7B    | 109.2        | C15—C14—N3    | 115.6 (5)    |
| C8—C7—H7B    | 109.2        | C14—C15—C16   | 118.29 (19)  |
| H7A—C7—H7B   | 107.9        | C14—C15—H15   | 120.9        |
| N2—C8—C7     | 110.09 (16)  | C16—C15—H15   | 120.9        |
| N2—C8—H8A    | 109.6        | C15—C16—C11   | 121.07 (19)  |
| C7—C8—H8A    | 109.6        | C15—C16—H16   | 119.5        |
| N2—C8—H8B    | 109.6        | C11—C16—H16   | 119.5        |
| C7—C8—H8B    | 109.6        | O2—C17—O1     | 124.86 (16)  |
| H8A—C8—H8B   | 108.2        | O2—C17—C11    | 117.72 (16)  |
| N2—C9—C10    | 109.78 (15)  | O1—C17—C11    | 117.41 (17)  |
| C7—N1—C1—C6  | 1.1 (2)      | C11—C12—C13—C14 | 1.5 (3) |
| C10—N1—C1—C6 | −131.49 (19) | C12—C13—C14—C15 | 0.6 (3) |
| C7—N1—C1—C2  | −177.35 (16) | C12—C13—C14—N3A | −179 (2) |
C10—N1—C1—C2 50.0 (2) C12—C13—C14—N3 −179.8 (14)
C6—C1—C2—C3 0.6 (3) O4A—N3A—C14—C13 −160 (3)
N1—C1—C2—C3 179.11 (18) O3A—N3A—C14—C15 −161 (3)
C1—C2—C3—C4 0.6 (3) O3—N3—C14—C13 −7 (3)
C2—C3—C4—C5 0.7 (3) O4—N3—C14—C15 −9 (3)
C3—C4—C5—C6 1.0 (3) O3—N3—C14—C15 173.1 (18)
N1—C1—C6—C5 179.50 (18) C13—C14—C15—C16 −1.5 (3)
C6—C1—C6—C5 0.6 (3) C12—C11—C16—C15 1.5 (3)
N1—C1—C10—C9 173.98 (14) C17—C11—C16—C15 176.86 (17)
C7—N1—C10—C9 52.0 (2) C12—C11—C17—O2 −157.93 (17)
C9—N2—C10—N1 −173.98 (14) C16—C11—C17—O2 20.4 (3)
C10—N1—C7—C8 175.30 (15) C14—C15—C16—C11 0.4 (3)
C8—N2—C9—C8 60.4 (2) C12—C11—C16—C15 1.5 (3)
N2—C9—C10—N1 −137.98 (14) C17—C11—C16—C15 −176.86 (17)
C8—N2—C9—C10 60.4 (2) C16—C11—C17—O2 20.4 (3)
C9—N2—C8—C7 −56.4 (2) C12—C11—C17—O2 −157.93 (17)
N2—C9—C8—C7 56.4 (2) C16—C11—C17—O1 −160.75 (18)
C16—C11—C12—C13 −2.5 (3) C17—C11—C17—O1 20.4 (3)
C17—C11—C12—C13 175.88 (17) C12—C11—C17—O1 20.4 (3)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|--------|
| N2—H21···O2i | 0.90 (1) | 1.96 (2) | 2.846 (2) | 173 (2) |
| N2—H22···O1 | 0.93 (1) | 1.78 (2) | 2.7135 (19) | 179 (2) |
| N2—H22···O2 | 0.93 (1) | 2.49 (2) | 3.057 (2) | 120 (1) |
| C8—H8B···O1ii | 0.97 | 2.50 | 3.468 (2) | 126 |
| C10—H10B···O4Aiii | 0.97 | 2.61 | 3.276 (15) | 126 |

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

4-Phenylpiperazin-1-ium 2-hydroxy-4,6-dinitrophenolate (6)

Crystal data

C_{16}H_{15}N_{2}C_{7}H_{3}N_{2}O_{7}^−

M_r = 390.35

F(000) = 816

Monoclinic, P2_1/c

\(a = 7.779\) (3) Å
\(b = 7.411\) (3) Å
\(c = 31.357\) (9) Å
\(\beta = 96.82\) (3)°
\(V = 1794.9\) (11) Å³

Z = 4

Data collection

Oxford Diffraction Xcalibur with Sapphire
CCD
diffractometer

Absorption correction: multi-scan

(CrystalisRED; Oxford Diffraction, 2007)

\(T_{\text{min}} = 0.959, T_{\text{max}} = 1.000\)
7737 measured reflections
3882 independent reflections
1590 reflections with \(I > 2\sigma(I)\)
\( R_{int} = 0.055 \)  
\( \theta_{\text{max}} = 28.0^\circ, \theta_{\text{min}} = 2.6^\circ \)  
\( h = -9 \rightarrow 9 \)  
\( k = -9 \rightarrow 9 \)  
\( l = -40 \rightarrow 26 \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full  
\( R[F^2 > 2\sigma(F^2)] = 0.085 \)  
\( wR(F^2) = 0.155 \)  
\( S = 1.03 \)

3882 reflections  
321 parameters  
288 restraints  
Primary atom site location: dual  
Secondary atom site location: difference Fourier map  
Hydrogen site location: mixed  
H atoms treated by a mixture of independent and constrained refinement

\[ w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.7929P] \]

\( (\Delta/\sigma)_{\text{max}} < 0.001 \)  
\( \Delta \rho_{\text{max}} = 0.18 \text{ e Å}^{-3} \)  
\( \Delta \rho_{\text{min}} = -0.20 \text{ e Å}^{-3} \)

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 (Å²)

|    | \( x \)   | \( y \)   | \( z \)   | \( U_{iso}^{*}/U_{eq} \) | Occ. (\(<1\)) |
|----|-----------|-----------|-----------|--------------------------|--------------|
| O1 | 0.2174 (3) | 0.5690 (4) | 0.40623 (8) | 0.0678 (9)               |              |
| O2 | 0.3815 (3) | 0.5542 (4) | 0.46760 (8) | 0.0644 (9)               |              |
| H2O | 0.372 (5)  | 0.581 (6)  | 0.4933 (7)  | 0.077*                   |              |
| O3 | 0.2737 (3) | 0.6604 (4) | 0.53481 (7) | 0.0538 (8)               |              |
| N3 | 0.0028 (7) | 0.8237 (11)| 0.57913 (17)| 0.0504 (16)              | 0.690 (11)   |
| O4 | 0.1059 (7) | 0.7315 (9) | 0.60356 (18)| 0.069 (2)                | 0.690 (11)   |
| O5 | −0.0948 (7)| 0.9353 (9) | 0.5930 (2)  | 0.0602 (19)              | 0.690 (11)   |
| N3A| −0.0015 (11)| 0.825 (2)| 0.5769 (3)  | 0.053 (3)                | 0.310 (11)   |
| O4A| 0.1438 (10)| 0.818 (2)  | 0.5983 (4)  | 0.065 (4)                | 0.310 (11)   |
| O5A| −0.1263 (11)| 0.898 (2)| 0.5910 (5)  | 0.053 (4)                | 0.310 (11)   |
| O6 | −0.4591 (3)| 0.9346 (4) | 0.45916 (8) | 0.0725 (9)               |              |
| O7 | −0.3746 (3)| 0.8095 (4) | 0.40327 (8) | 0.0738 (9)               |              |
| N4 | −0.3514 (4)| 0.8515 (5) | 0.44113 (10)| 0.0517 (9)               |              |
| C11| 0.0978 (4) | 0.6775 (5) | 0.46853 (11)| 0.0390 (9)               |              |
| C12| 0.1281 (4) | 0.7048 (5) | 0.51389 (11)| 0.0418 (9)               |              |
| C13| −0.0142 (4)| 0.7862 (5) | 0.53288 (10)| 0.0400 (9)               |              |
| C14| −0.1672 (4)| 0.8346 (5) | 0.50932 (11)| 0.0398 (9)               |              |
| H14| −0.254887| 0.888430  | 0.522579   | 0.048*                   |              |
| C15| −0.1890 (4)| 0.8024 (5) | 0.46600 (11)| 0.0393 (9)               |              |
| C16| −0.0579 (4)| 0.7232 (5) | 0.44552 (11)| 0.0413 (10)              |              |
| H16| −0.075920| 0.701222  | 0.416128   | 0.050*                   |              |
| C17| 0.2359 (5) | 0.5974 (5) | 0.44453 (12)| 0.0477 (10)              |              |
| N1 | 0.6156 (4) | 0.6931 (4) | 0.70321 (9) | 0.0467 (8)               |              |
| N2 | 0.4692 (4) | 0.6095 (6) | 0.61759 (11)| 0.0666 (11)              |              |
| H21| 0.387 (4)  | 0.620 (5)  | 0.5958 (9)  | 0.080*                   |              |
Atomic displacement parameters (Å²)

|   | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|---|------------|------------|------------|------------|------------|------------|
| O1 | 0.0641 (18) | 0.097 (2)  | 0.0424 (17) | 0.0242 (16) | 0.0060 (13) | 0.0135 (18) |
| O2 | 0.0490 (17) | 0.099 (2)  | 0.0463 (17) | 0.0219 (16) | 0.0089 (14) | 0.0024 (19) |
| O3 | 0.0412 (15) | 0.077 (2)  | 0.0425 (16) | 0.0074 (14) | 0.0000 (12) | 0.0002 (15) |
| N3 | 0.047 (3)   | 0.068 (4)  | 0.037 (3)   | −0.003 (3)  | 0.006 (3)   | −0.006 (3)  |
| O4 | 0.062 (3)   | 0.104 (5)  | 0.040 (3)   | 0.015 (3)   | 0.000 (2)   | 0.005 (3)   |
| O5 | 0.059 (3)   | 0.070 (4)  | 0.053 (3)   | −0.002 (3)  | 0.015 (3)   | −0.018 (3)  |
| N3A| 0.045 (5)   | 0.072 (6)  | 0.042 (6)   | −0.001 (5)  | 0.003 (5)   | −0.006 (6)  |
| O4A| 0.053 (5)   | 0.093 (8)  | 0.045 (6)   | 0.009 (6)   | −0.008 (5)  | −0.005 (6)  |
| O5A| 0.049 (5)   | 0.078 (8)  | 0.032 (6)   | −0.002 (5)  | 0.006 (5)   | −0.021 (6)  |

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|      | U1 (Å²)      | U2 (Å²)      | U3 (Å²)      | U12 (Å²)     | U13 (Å²)     | U23 (Å²)     |
|------|--------------|--------------|--------------|--------------|--------------|--------------|
| O6   | 0.0612 (18)  | 0.096 (2)    | 0.0589 (19)  | 0.0335 (17)  | 0.0024 (14)  | −0.0098 (18) |
| O7   | 0.074 (2)    | 0.103 (3)    | 0.0416 (17)  | 0.0259 (17)  | −0.0089 (13) | −0.0162 (18) |
| N4   | 0.049 (2)    | 0.059 (2)    | 0.047 (2)    | 0.0105 (18)  | 0.0045 (16)  | −0.004 (2)   |
| C11  | 0.041 (2)    | 0.039 (2)    | 0.037 (2)    | 0.0007 (18)  | 0.0059 (17)  | 0.001 (2)    |
| C12  | 0.040 (2)    | 0.044 (2)    | 0.042 (2)    | −0.0043 (19) | 0.0037 (17)  | −0.001 (2)   |
| C13  | 0.048 (2)    | 0.043 (3)    | 0.030 (2)    | −0.0043 (19) | 0.0082 (17)  | −0.007 (2)   |
| C14  | 0.041 (2)    | 0.036 (2)    | 0.044 (2)    | 0.0019 (18)  | 0.0103 (17)  | −0.002 (2)   |
| C15  | 0.038 (2)    | 0.043 (2)    | 0.037 (2)    | 0.0041 (18)  | 0.0025 (16)  | −0.002 (2)   |
| C16  | 0.051 (2)    | 0.040 (3)    | 0.032 (2)    | 0.0016 (19)  | 0.0056 (17)  | −0.0001 (19) |
| C17  | 0.042 (2)    | 0.056 (3)    | 0.046 (3)    | 0.006 (2)    | 0.0065 (19)  | 0.001 (2)    |
| N1   | 0.0485 (18)  | 0.055 (2)    | 0.0368 (18)  | −0.0090 (17) | 0.0049 (14)  | 0.0003 (18)  |
| N2   | 0.054 (2)    | 0.103 (3)    | 0.042 (2)    | 0.022 (2)    | −0.0011 (16) | −0.015 (2)   |
| C1   | 0.047 (3)    | 0.067 (3)    | 0.038 (3)    | −0.006 (3)   | 0.010 (2)    | −0.006 (3)   |
| C2   | 0.061 (3)    | 0.076 (4)    | 0.050 (3)    | −0.016 (3)   | −0.004 (3)   | 0.007 (3)    |
| C3   | 0.065 (3)    | 0.080 (4)    | 0.055 (3)    | −0.019 (3)   | −0.001 (3)   | 0.008 (3)    |
| C4   | 0.069 (3)    | 0.076 (4)    | 0.038 (3)    | −0.015 (3)   | 0.003 (2)    | −0.004 (3)   |
| C5   | 0.064 (3)    | 0.089 (4)    | 0.043 (3)    | −0.020 (3)   | 0.011 (3)    | 0.009 (3)    |
| C6   | 0.057 (3)    | 0.081 (3)    | 0.038 (3)    | −0.014 (3)   | 0.008 (2)    | 0.007 (3)    |
| C1A  | 0.051 (4)    | 0.075 (4)    | 0.037 (4)    | −0.011 (4)   | 0.011 (4)    | 0.003 (4)    |
| C2A  | 0.058 (4)    | 0.081 (5)    | 0.049 (4)    | −0.014 (4)   | 0.010 (4)    | −0.004 (4)   |
| C3A  | 0.062 (4)    | 0.084 (5)    | 0.053 (4)    | −0.013 (4)   | 0.007 (4)    | −0.001 (4)   |
| C4A  | 0.064 (4)    | 0.084 (5)    | 0.043 (4)    | −0.025 (4)   | 0.011 (4)    | 0.002 (4)    |
| C5A  | 0.060 (4)    | 0.080 (4)    | 0.037 (4)    | −0.023 (4)   | 0.008 (4)    | 0.009 (4)    |
| C6A  | 0.057 (4)    | 0.079 (4)    | 0.041 (4)    | −0.020 (4)   | 0.005 (4)    | 0.005 (4)    |
| C7   | 0.073 (3)    | 0.067 (3)    | 0.046 (3)    | −0.008 (2)   | −0.001 (2)   | 0.003 (2)    |
| C8   | 0.069 (3)    | 0.081 (4)    | 0.051 (3)    | −0.013 (2)   | 0.002 (2)    | −0.009 (3)   |
| C9   | 0.059 (3)    | 0.086 (4)    | 0.050 (3)    | −0.001 (3)   | 0.0037 (19)  | 0.018 (3)    |
| C10  | 0.058 (3)    | 0.089 (4)    | 0.045 (2)    | −0.013 (2)   | 0.0022 (19)  | 0.015 (3)    |

**Geometric parameters (Å, °)**

| Bond/Angle | Distance (Å) | Angle (°) |
|------------|--------------|-----------|
| C1—C7      | 1.211 (4)    |           |
| C1—C6      | 1.3900       | C2—C3     | 1.3900     |
| C2—C3      | 0.841 (18)   | C2—H2A    | 0.9300     |
| C3—C4      | 1.283 (4)    | C3—C4     | 1.3900     |
| N3—O5      | 1.236 (4)    | C3—H3A    | 0.9300     |
| N3—O4      | 1.246 (5)    | C4—C5     | 1.3900     |
| N3—C13     | 1.467 (6)    | C4—H4A    | 0.9300     |
| N3A—O5A    | 1.237 (4)    | C5—C6     | 1.3900     |
| N3A—O4A    | 1.246 (5)    | C5—H5A    | 0.9300     |
| N3A—C13    | 1.401 (10)   | C6—H6A    | 0.9300     |
| O6—N4      | 1.230 (3)    | C1A—C2A   | 1.3900     |
| O7—N4      | 1.220 (3)    | C1A—C6A   | 1.3900     |
| N4—C15     | 1.450 (4)    | C2A—C3A   | 1.3900     |
| C11—C16    | 1.376 (4)    | C2A—H2AA  | 0.9300     |
| C11—C12    | 1.428 (4)    | C3A—C4A   | 1.3900     |
| C11—C17    | 1.505 (5)    | C3A—H3AA  | 0.9300     |
| C12—C13    | 1.449 (5)    | C4A—C5A   | 1.3900     |

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| Bond/Distance                  | Length (Å) | Bond/Distance                  | Length (Å) |
|-------------------------------|------------|-------------------------------|------------|
| C13—C14                       | 1.372 (4)  | C4A—H4AA                      | 0.9300     |
| C14—C15                       | 1.370 (4)  | C5A—C6A                       | 1.3900     |
| C14—H14                       | 0.9300     | C5A—H5AA                      | 0.9300     |
| C15—C16                       | 1.398 (4)  | C6A—H6AA                      | 0.9300     |
| C16—H16                       | 0.9300     | C7—C8                         | 1.501 (5)  |
| N1—C1A                        | 1.399 (9)  | C7—H7A                        | 0.9700     |
| N1—C1                         | 1.448 (5)  | C7—H7B                        | 0.9700     |
| N1—C7                         | 1.453 (5)  | C8—H8A                        | 0.9700     |
| N1—C10                        | 1.465 (4)  | C8—H8B                        | 0.9700     |
| N2—C9                         | 1.476 (5)  | C9—C10                        | 1.503 (5)  |
| N2—C8                         | 1.482 (5)  | C9—H9A                        | 0.9700     |
| N2—H21                        | 0.884 (18) | C9—H9B                        | 0.9700     |
| N2—H22                        | 0.874 (18) | C10—H10A                      | 0.9700     |
| C1—C2                         | 1.3900     | C10—H10B                      | 0.9700     |
| C17—O2—H2O                    | 108 (3)    | C4—C3—H3A                     | 120.0      |
| O5—N3—O4                      | 121.9 (4)  | C5—C4—C3                      | 120.0      |
| O5—N3—C13                     | 119.2 (5)  | C5—C4—H4A                     | 120.0      |
| O4—N3—C13                     | 118.7 (5)  | C3—C4—H4A                     | 120.0      |
| O5A—N3A—O4A                   | 121.8 (6)  | C6—C5—C4                      | 120.0      |
| O5A—N3A—C13                   | 118.4 (8)  | C6—C5—H5A                     | 120.0      |
| O4A—N3A—C13                   | 118.4 (8)  | C4—C5—H5A                     | 120.0      |
| O7—N4—O6                      | 123.1 (3)  | C5—C6—C1                      | 120.0      |
| O7—N4—C15                     | 118.5 (3)  | C5—C6—H6A                     | 120.0      |
| O6—N4—C15                     | 118.4 (3)  | C1—C6—H6A                     | 120.0      |
| C16—C11—C12                   | 121.2 (3)  | C2A—C1A—C6A                   | 120.0      |
| C16—C11—C17                   | 118.1 (3)  | C2A—C1A—N1                    | 116.8 (8)  |
| C12—C11—C17                   | 120.7 (3)  | C6A—C1A—N1                    | 123.1 (8)  |
| O3—C12—C11                    | 120.3 (3)  | C1A—C2A—C3A                   | 120.0      |
| O3—C12—C13                    | 124.6 (3)  | C1A—C2A—H2AA                  | 120.0      |
| C11—C12—C13                   | 115.1 (3)  | C3A—C2A—H2AA                  | 120.0      |
| C14—C13—N3A                   | 115.6 (4)  | C4A—C3A—C2A                   | 120.0      |
| C14—C13—C12                   | 122.9 (3)  | C4A—C3A—H3AA                  | 120.0      |
| N3A—C13—C12                   | 121.5 (4)  | C2A—C3A—H3AA                  | 120.0      |
| C14—C13—N3                    | 117.0 (3)  | C3A—C4A—C5A                   | 120.0      |
| C12—C13—N3                    | 120.1 (3)  | C3A—C4A—H4AA                  | 120.0      |
| C15—C14—C13                   | 119.1 (3)  | C5A—C4A—H4AA                  | 120.0      |
| C15—C14—H14                   | 120.5      | C4A—C5A—C6A                   | 120.0      |
| C13—C14—H14                   | 120.5      | C4A—C5A—H5AA                  | 120.0      |
| C14—C15—C16                   | 121.2 (3)  | C6A—C5A—H5AA                  | 120.0      |
| C14—C15—N4                    | 119.1 (3)  | C5A—C6A—C1A                   | 120.0      |
| C16—C15—N4                    | 119.7 (3)  | C5A—C6A—H6AA                  | 120.0      |
| C11—C16—C15                   | 120.5 (3)  | C1A—C6A—H6AA                  | 120.0      |
| C11—C16—H16                   | 119.8      | N1—C7—C8                      | 111.2 (3)  |
| C15—C16—H16                   | 119.8      | N1—C7—H7A                     | 109.4      |
| O1—C17—O2                     | 119.9 (3)  | C8—C7—H7A                     | 109.4      |
| O1—C17—C11                    | 123.8 (3)  | N1—C7—H7B                     | 109.4      |
| O2—C17—C11                    | 116.2 (3)  | C8—C7—H7B                     | 109.4      |

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| Bond                  | Length (Å)  | Torsion (°)  |
|-----------------------|-------------|--------------|
| C1A—N1—C7            | 120.5 (6)   | H7A—C7—H7B  |
| C1—N1—C7             | 114.3 (3)   | N2—C8—C7    |
| C1A—N1—C10           | 112.9 (5)   | N2—C8—H8A   |
| C1—N1—C10            | 116.6 (3)   | C7—C8—H8A   |
| C7—N1—C10            | 110.8 (3)   | C7—C8—H8B   |
| C9—N2—C8             | 109.8 (3)   | H8A—C8—H8B  |
| C9—N2—H21            | 109 (3)     | N2—C9—C10   |
| C8—N2—H21            | 110 (3)     | N2—C9—C10   |
| C9—N2—H22            | 109 (3)     | N2—C9—H9A   |
| C8—N2—H22            | 111 (3)     | C10—C9—H9A  |
| H21—N2—H22           | 107 (4)     | N2—C9—H9B   |
| C2—C1—C6             | 120.0       | C10—C9—H9B  |
| C2—C1—N1             | 119.9 (3)   | C9—C10—H10A |
| C6—C1—N1             | 120.1 (3)   | N1—C10—C9   |
| C3—C2—C1             | 120.0       | N1—C10—H10A |
| C3—C2—H2A            | 120.0       | C9—C10—H10A |
| C1—C2—H2A            | 120.0       | N1—C10—H10B |
| C2—C3—C4             | 120.0       | C9—C10—H10B |
| C2—C3—H3A            | 120.0       | H10A—C10—H10B |
| C16—C11—C12—O3      | 179.6 (3)   | C7—N1—C1—C2 |
| C17—C11—C12—O3      | −0.4 (5)    | C10—N1—C1—C2 |
| C16—C11—C12—C13     | −1.2 (5)    | C7—N1—C1—C6 |
| C17—C11—C12—C13     | 178.8 (3)   | C10—N1—C1—C6 |
| O5A—N3A—C13—C14     | 0.4 (19)    | C6—C1—C2—C3 |
| O4A—N3A—C13—C14     | −166.2 (13) | N1—C1—C2—C3 |
| O5A—N3A—C13—C12     | 178.7 (12)  | C1—C2—C3—C4 |
| O4A—N3A—C13—C12     | 12 (2)      | C2—C3—C4—C5 |
| O3—C12—C13—C14      | 179.0 (4)   | C3—C4—C5—C6 |
| C11—C12—C13—C14     | −0.2 (5)    | C4—C5—C6—C1 |
| O3—C12—C13—N3A      | 0.8 (10)    | C2—C1—C6—C5 |
| C11—C12—C13—N3A     | −178.4 (9)  | N1—C1—C6—C5 |
| O3—C12—C13—N3       | 0.2 (6)     | C7—N1—C1A—C2A |
| C11—C12—C13—N3      | −179.0 (5)  | C10—N1—C1A—C2A |
| O5—N3—C13—C14       | −18.9 (9)   | C7—N1—C1A—C6A |
| O4—N3—C13—C14       | 155.4 (6)   | C10—N1—C1A—C6A |
| O5—N3—C13—C12       | 160.0 (6)   | C6A—C1A—C2A—C3A |
| O4—N3—C13—C12       | −25.7 (9)   | N1—C1A—C2A—C3A |
| N3A—C13—C14—C15     | 179.4 (9)   | C1A—C2A—C3A—C4A |
| C12—C13—C14—C15     | 1.1 (5)     | C2A—C3A—C4A—C5A |
| N3—C13—C14—C15      | 179.9 (5)   | C3A—C4A—C5A—C6A |
| C13—C14—C15—C16     | −0.6 (6)    | C4A—C5A—C6A—C1A |
| C13—C14—C15—N4      | 179.3 (3)   | C2A—C1A—C6A—C5A |
| O7—N4—C15—C14   | −174.3 (4)  | N1—C1A—C6A—C5A |
| O6—N4—C15—C14   | 6.1 (5)     | C1A—N1—C7—C8 |
| O7—N4—C15—C16     | 5.6 (5)     | C1—N1—C7—C8 |
| O6—N4—C15—C16     | −174.0 (3)  | C10—N1—C7—C8 |
| C12—C11—C16—C15     | 1.7 (5)     | C9—N2—C8—C7 |

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C17—C11—C16—C15 −178.3 (3) N1—C7—C8—N2 58.3 (5) C12—C17—O1 179.4 (3) N2—C9—C10—N1 −57.0 (5)
C14—C15—C16—C11 −0.8 (6) C8—N2—C9—C10 58.3 (4) C1A—N1—C10—C9 −165.4 (6)
N4—C15—C16—C11 179.3 (3) C1A—N1—C10—C9 −165.4 (6)
C16—C11—C17—O1 −0.9 (6) C1—N1—C10—C9 −170.9 (4) C7—N1—C10—C9 56.1 (5)
C12—C11—C17—O2 179.1 (4) C1—N1—C10—C9 −170.9 (4) C7—N1—C10—C9 56.1 (5)
C16—C11—C17—O2 −179.4 (3) N2—C9—C10—N1 −57.0 (5) C12—C17—O2 0.6 (5)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|---------|
| O2—H2O···O3 | 0.84 (2) | 1.69 (2) | 2.487 (3) | 156 (4) |
| N2—H2···O3 | 0.88 (2) | 2.03 (2) | 2.873 (4) | 159 (3) |
| N2—H2···O4 | 0.88 (2) | 2.37 (3) | 2.950 (6) | 123 (3) |
| N2—H2···O4A | 0.88 (2) | 2.40 (4) | 2.966 (10) | 122 (3) |
| N2—H2···O1i | 0.87 (2) | 2.10 (2) | 2.947 (4) | 164 (4) |
| N2—H2···O2i | 0.87 (2) | 2.62 (3) | 3.270 (4) | 132 (3) |
| C8—H8···O7ii | 0.97 | 2.36 | 3.134 (5) | 137 |
| C8—H8···O4 | 0.97 | 2.44 | 3.000 (6) | 116 |
| C9—H9···O4 | 0.97 | 2.58 | 3.111 (8) | 132 |
| C9—H9···O5ii | 0.97 | 2.60 | 3.166 (8) | 118 |
| C9—H9···O5A | 0.97 | 2.29 | 3.040 (13) | 133 |
| C9—H9···O5A | 0.97 | 2.29 | 3.040 (13) | 133 |

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

4-Phenylpiperazin-1-ium 2-hydroxy-4,6-dinitrophenolate (7)

Crystal data

C_{10}H_{15}N_{2}+·C_{7}H_{3}N_{2}O_{6}−

M_r = 374.35

Triclinic, P1

a = 5.707 (2) Å

b = 12.505 (3) Å

c = 13.116 (3) Å

α = 97.41 (2)°

β = 93.28 (2)°

γ = 102.82 (2)°

V = 901.5 (4) Å³

Z = 2

F(000) = 392

\( D_\lambda = 1.379 \text{ Mg m}^{-3} \)

Mo Kα radiation, \( \lambda = 0.71073 \text{ Å} \)

Cell parameters from 838 reflections

θ max = 28.1°, θ min = 3.2°

\\( μ = 0.11 \text{ mm}^{-1} \)

T = 293 K

Needle, yellow

0.48 × 0.08 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire

CCD
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Rotation method data acquisition using ω scans.

Absorption correction: multi-scan (CrysallisRED; Oxford Diffraction, 2007)

\( R_{int} = 0.087 \)

\( θ_{max} = 28.1°, θ_{min} = 3.2° \)

\( h = −7→7 \)

\( k = −16→15 \)

\( l = −16→17 \)

T min = 0.647, T max = 1.000

7800 measured reflections

7800 independent reflections

2647 reflections with \( I > 2σ(I) \)

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Refinement

Refinement on $F^2$

Least-squares matrix: full

$R(F^2) = 0.147$

$S = 1.13$

7800 reflections

251 parameters

2 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.297$

$S = 1.13$

$7800$ reflections

$251$ parameters

$2$ restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 3.195P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

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

$\Delta \rho_{\text{min}} = -0.30$ e Å$^{-3}$

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. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)

| C1  | 1.122 (2) | 0.6276 (12) | 0.8824 (9) | 0.051 (4) |
|-----|-----------|-------------|------------|-----------|
| C2  | 1.091 (2) | 0.7342 (12) | 0.9003 (10) | 0.062 (4) |
| H2  | 0.954536 | 0.750440 | 0.869306 | 0.074* |
| C3  | 1.256 (3) | 0.8180 (14) | 0.9629 (11) | 0.089 (5) |
| H3  | 1.229141 | 0.889054 | 0.974939 | 0.107* |
| C4  | 1.462 (3) | 0.7954 (17) | 1.0076 (11) | 0.090 (6) |
| H4  | 1.577146 | 0.850571 | 1.049126 | 0.108* |
| C5  | 1.491 (3) | 0.6892 (17) | 0.9888 (11) | 0.084 (5) |
| H5  | 1.626416 | 0.672664 | 1.019709 | 0.101* |
| C6  | 1.329 (2) | 0.6064 (13) | 0.9265 (10) | 0.066 (4) |
| H6  | 1.358012 | 0.535803 | 0.913969 | 0.079* |
| C7  | 0.956 (2) | 0.4298 (10) | 0.8199 (9) | 0.055 (4) |
| H7A | 0.973803 | 0.416389 | 0.890828 | 0.066* |
| C8  | 0.729 (2) | 0.3532 (10) | 0.7652 (9) | 0.056 (4) |
| H8A | 0.738219 | 0.276750 | 0.765936 | 0.067* |
| H8B | 0.590703 | 0.365439 | 0.800390 | 0.067* |
| C9  | 0.700 (2) | 0.4918 (11) | 0.6524 (9) | 0.063 (4) |
| H9A | 0.557086 | 0.508210 | 0.681256 | 0.076* |
| H9B | 0.694830 | 0.504487 | 0.580979 | 0.076* |
| C10 | 0.920 (2) | 0.5662 (10) | 0.7114 (9) | 0.055 (4) |
| H10A| 1.061481 | 0.555114 | 0.677531 | 0.066* |
| H10B| 0.911569 | 0.642726 | 0.711107 | 0.066* |
| C11 | −0.018 (2) | 0.1731 (10) | 0.4335 (9) | 0.041 (3) |
| C12 | 0.037 (2) | 0.0713 (10) | 0.4039 (8) | 0.046 (3) |
| H12 | 0.169558 | 0.053646 | 0.436202 | 0.055* |
| C13 | −0.106 (2) | −0.0027 (11) | 0.3270 (10) | 0.046 (3) |
C14  -0.307 (2)  0.0161 (10)  0.2780 (9)  0.054 (4)  
H14  -0.406231  -0.036584  0.227934  0.065*  
C15  -0.353 (2)  0.1182 (12)  0.3079 (10)  0.052 (4)  
C16  -0.219 (2)  0.1950 (10)  0.3858 (9)  0.047 (3)  
H16  -0.264440  0.261054  0.406096  0.065*  
C17  0.144 (3)  0.2554 (12)  0.5164 (10)  0.056 (4)  
N1   0.9454 (16)  0.5450 (8)  0.8180 (7)  0.046 (3)  
N2   0.7030 (19)  0.3750 (10)  0.6575 (9)  0.060 (3)  
H21  0.585 (14)  0.323 (8)  0.625 (8)  0.072*  
H22  0.817 (15)  0.354 (9)  0.624 (8)  0.072*  
N3   −0.040 (2)  −0.1092 (10)  0.2942 (9)  0.063 (3)  
N4   −0.560 (2)  0.1460 (14)  0.2536 (10)  0.075 (4)  
O1   0.0892 (15)  0.3455 (7)  0.5441 (7)  0.069 (3)  
O2   0.3327 (15)  0.2290 (7)  0.5475 (7)  0.071 (3)  
O3   0.1442 (18)  −0.1237 (7)  0.3359 (7)  0.076 (3)  
O4   −0.1697 (18)  −0.1757 (8)  0.2251 (7)  0.099 (4)  
O5   −0.5922 (18)  0.2403 (11)  0.2752 (8)  0.094 (4)  
O6   −0.6948 (17)  0.0739 (10)  0.1901 (8)  0.090 (4)  

Atomic displacement parameters (Å²)

|     | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|-----|-----|-----|-----|-----|-----|-----|
| C1  | 0.045 (9) | 0.059 (11) | 0.043 (8) | 0.005 (8) | −0.004 (7) | −0.001 (7) |
| C2  | 0.068 (10) | 0.053 (11) | 0.064 (10) | 0.012 (9) | 0.006 (8) | 0.005 (8) |
| C3  | 0.102 (14) | 0.073 (13) | 0.072 (11) | −0.006 (12) | 0.001 (10) | −0.014 (9) |
| C4  | 0.074 (13) | 0.108 (17) | 0.057 (10) | −0.029 (12) | −0.011 (9) | −0.012 (11) |
| C5  | 0.082 (13) | 0.111 (16) | 0.055 (10) | 0.012 (13) | 0.004 (9) | 0.017 (10) |
| C6  | 0.054 (10) | 0.080 (13) | 0.053 (9) | 0.002 (9) | −0.004 (8) | −0.001 (8) |
| C7  | 0.058 (9) | 0.061 (11) | 0.052 (8) | 0.023 (8) | 0.007 (7) | 0.012 (7) |
| C8  | 0.064 (10) | 0.039 (9) | 0.062 (9) | 0.008 (7) | 0.011 (8) | 0.000 (7) |
| C9  | 0.069 (10) | 0.055 (11) | 0.062 (9) | 0.011 (8) | −0.010 (8) | 0.006 (7) |
| C10 | 0.055 (9) | 0.047 (9) | 0.058 (9) | 0.013 (7) | −0.005 (7) | −0.005 (7) |
| C11 | 0.035 (7) | 0.026 (8) | 0.058 (8) | 0.002 (6) | 0.010 (7) | 0.006 (6) |
| C12 | 0.048 (8) | 0.048 (9) | 0.036 (8) | 0.000 (7) | −0.004 (7) | 0.013 (6) |
| C13 | 0.035 (8) | 0.055 (10) | 0.050 (8) | 0.015 (7) | −0.001 (7) | 0.010 (7) |
| C14 | 0.050 (9) | 0.038 (10) | 0.061 (9) | −0.012 (8) | 0.004 (8) | 0.000 (7) |
| C15 | 0.039 (9) | 0.067 (11) | 0.047 (8) | 0.001 (8) | −0.006 (7) | 0.018 (8) |
| C16 | 0.038 (8) | 0.042 (9) | 0.068 (9) | 0.019 (7) | 0.016 (7) | 0.010 (7) |
| C17 | 0.058 (10) | 0.050 (11) | 0.052 (9) | 0.004 (8) | 0.016 (8) | −0.008 (8) |
| N1  | 0.048 (7) | 0.045 (8) | 0.045 (7) | 0.015 (6) | 0.001 (6) | 0.004 (5) |
| N2  | 0.050 (8) | 0.058 (10) | 0.061 (9) | 0.005 (6) | 0.005 (6) | −0.015 (6) |
| N3  | 0.078 (10) | 0.053 (9) | 0.062 (8) | 0.026 (8) | 0.003 (7) | −0.002 (7) |
| N4  | 0.055 (9) | 0.111 (14) | 0.069 (9) | 0.028 (10) | 0.012 (8) | 0.028 (9) |
| O1  | 0.070 (7) | 0.048 (7) | 0.083 (7) | 0.008 (5) | 0.019 (5) | −0.009 (5) |
| O2  | 0.051 (6) | 0.063 (7) | 0.087 (7) | 0.012 (5) | −0.013 (6) | −0.021 (5) |
| O3  | 0.079 (8) | 0.056 (7) | 0.096 (8) | 0.028 (6) | 0.000 (6) | 0.001 (5) |
| O4  | 0.136 (9) | 0.061 (8) | 0.083 (7) | 0.022 (7) | −0.022 (7) | −0.032 (6) |
| O5  | 0.077 (8) | 0.130 (12) | 0.100 (9) | 0.060 (8) | 0.019 (6) | 0.042 (8) |
Geometric parameters (Å, º)

| Bond/Angle | Distance/n (Å/º) |
|------------|------------------|
| C1—C6      | 1.377 (15)       |
| C1—C2      | 1.377 (16)       |
| C1—N1      | 1.418 (14)       |
| C2—C3      | 1.384 (17)       |
| C2—H2      | 0.9300           |
| C3—C4      | 1.385 (19)       |
| C3—H3      | 0.9300           |
| C4—C5      | 1.37 (2)         |
| C4—H4      | 0.9300           |
| C5—C6      | 1.365 (18)       |
| C5—H5      | 0.9300           |
| C6—H6      | 0.9300           |
| C7—N1      | 1.459 (13)       |
| C7—H7A     | 0.9700           |
| C7—H7B     | 0.9700           |
| C8—N2      | 1.479 (15)       |
| C8—H8A     | 0.9700           |
| C8—H8B     | 0.9700           |
| C9—N2      | 1.475 (16)       |
| C9—C10     | 1.492 (14)       |
| C9—H9A     | 0.9700           |
| C9—H9B     | 0.9700           |
| C6—C1—C2   | 118.0 (13)       |
| C6—C1—N1   | 122.7 (14)       |
| C2—C1—N1   | 119.3 (13)       |
| C1—C2—C3   | 121.9 (15)       |
| C1—C2—H2   | 119.1            |
| C3—C2—H2   | 119.1            |
| C2—C3—C4   | 119.5 (17)       |
| C2—C3—H3   | 120.2            |
| C4—C3—H3   | 120.2            |
| C5—C4—C3   | 117.8 (16)       |
| C5—C4—H4   | 121.1            |
| C3—C4—H4   | 121.1            |
| C6—C5—C4   | 122.9 (17)       |
| C6—C5—H5   | 118.5            |
| C4—C5—H5   | 118.5            |
| C5—C6—C1   | 119.8 (15)       |
| C5—C6—H6   | 120.1            |
| C1—C6—H6   | 120.1            |
| N1—C7—C8   | 110.1 (10)       |
| N1—C7—H7A  | 109.6            |
C8—C7—H7A 109.6  C11—C16—H16 120.4
N1—C7—H7B 109.6  O1—C17—O2 125.5 (13)
C8—C7—H7B 109.6  O1—C17—C11 118.5 (14)
H7A—C7—H7B 108.2  C1—N1—C7 117.2 (11)
N2—C8—C7 109.2 (10)  C1—N1—C10 113.8 (10)
N2—C8—H8A 109.8  C7—N1—C10 110.0 (9)
C7—C8—H8A 109.8  C9—N2—C8 111.8 (9)
N2—C8—H8B 109.8  C9—N2—H21 119 (9)
C7—C8—H8B 109.8  O2—C17—C11 115.8 (13)
H8A—C8—H8B 108.3  C1—N1—C10 113.8 (10)
N2—C9—C10 111.9 (11)  C7—N1—C10 110.0 (9)
N1—C10—H10A 109.2  O3—N3—O4 124.1 (13)
C9—C10—H10A 109.2  O3—N3—C13 117.2 (12)
C6—C1—C2—C3 −2 (2)  C16—C11—C17—O1 1.7 (18)
N1—C1—C2—C3 179.6 (12)  C12—C11—C17—O1 −178.2 (12)
C1—C2—C3—C4 1 (2)  C16—C11—C17—O2 −174.2 (12)
C2—C3—C4—C5 −1 (2)  C12—C11—C17—O2 5.8 (17)
C3—C4—C5—C6 1 (3)  C6—C1—N1—C7 15.3 (16)
C4—C5—C6—C1 −2 (2)  C2—C1—N1—C7 −166.4 (11)
C2—C1—C6—C5 2.3 (19)  C6—C1—N1—C10 −115.1 (13)
N1—C1—C6—C5 −179.3 (12)  C2—C1—N1—C10 63.3 (15)
N1—C7—C8—N2 58.8 (12)  C9—C10—N1—C9 −167.8 (10)
N2—C9—C10—N1 −55.4 (13)  C9—C10—N1—C9 56.9 (13)
C16—C11—C12—C13 1.7 (17)  C16—C11—C12—C13 −178.4 (11)
C17—C11—C12—C13 −178.4 (11)  C11—C12—C13—N3 178.0 (11)
C11—C12—C13—C14 −1.8 (18)  C10—C9—N2—C8 55.0 (13)
C11—C12—C13—N3 178.0 (11)  C7—C8—N2—C9 −56.9 (13)
C12—C13—C14—C15 2.8 (18)  C4—C3—C2—C1 −177.5 (11)
N3—C13—C14—C15 −177.0 (12)  C12—C13—C14—C15 −2.3 (17)
C13—C14—C15—C16 −4.0 (19)  C12—C13—C14—C15 −0.4 (18)
C13—C14—C15—N4 176.5 (11)  C12—C13—C14—C15 179.8 (12)
C14—C15—C16—C11 4.2 (19)  C16—C15—N4—O5 5.4 (18)
N4—C15—C16—C11 −176.4 (11)  C14—C15—N4—O5 −175.0 (14)
C12—C11—C16—C15 −2.8 (16)  C16—C15—N4—O6 −173.4 (13)
C17—C11—C16—C15 177.3 (11)  C14—C15—N4—O6 6.1 (17)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|---------|
| C8—H8A···O3 | 0.97 | 2.43 | 3.250 (14) | 142 |
| C10—H10B···O5 | 0.97 | 2.58 | 3.366 (16) | 138 |

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N2—H21···O2 0.87 (3) 1.81 (4) 2.672 (13) 172 (13)
N2—H22···O1iii 0.87 (3) 1.94 (4) 2.792 (13) 166 (12)

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

4-Phenylpiperazin-1-ium 2,4,6-trinitrophenolate (8)

Crystal data
C_{10}H_{15}N_{2}^+·C_{6}H_{2}N_{3}O_{7}^−
Mr = 391.34
Monoclinic, P2_1/c
a = 8.517 (1) Å
b = 6.825 (1) Å
c = 30.265 (4) Å
β = 95.33 (1)°
V = 1751.7 (4) Å³
Z = 4
F(000) = 816
D_x = 1.484 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 2640 reflections
θ = 2.6–27.9°
µ = 0.12 mm⁻¹
T = 293 K
Prism, yellow
0.50 × 0.36 × 0.20 mm

Data collection
Oxford Diffraction Xcalibur with Sapphire
CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
ω and φ scans
Absorption correction: multi-scan
(CrystalisRED; Oxford Diffraction, 2007)
T_min = 0.835, T_max = 1.000
12427 measured reflections
3893 independent reflections
2389 reflections with I > 2σ(I)
R(int) = 0.076
θ_max = 28.0°, θ_min = 2.6°
h = −10→10
k = −8→4
l = −34→38

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.064
wR(F²) = 0.149
S = 1.05
3893 reflections
260 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(Fo²) + (0.0504P)² + 0.8725P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)max < 0.001
Δρ_max = 0.26 e Å⁻³
Δρ_min = −0.20 e Å⁻³
Extinction correction: SHELXL-2018/3
(Sheldrick 2018),
Extinction coefficient: 0.0131 (17)

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 (Å²)

|    | x     | y     | z     | U_{eq}  |
|----|-------|-------|-------|---------|
| C1 | 0.7177 (3) | 0.4179 (4) | 0.26101 (7) | 0.0433 (6) |
| C2 | 0.7900 (3) | 0.5991 (4) | 0.25921 (9) | 0.0570 (7) |
| H2 | 0.780507 | 0.690261 | 0.281649 | 0.068* |

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C3  0.8768 (3)  0.6449 (5)  0.22386 (10)  0.0688 (9)  
H3  0.923005  0.768012  0.222678  0.083*  
C4  0.8954 (3)  0.5133 (6)  0.19100 (10)  0.0694 (9)  
H4  0.953581  0.545868  0.167535  0.083*  
C5  0.8277 (3)  0.3334 (5)  0.19292 (9)  0.0669 (8)  
H5  0.841487  0.241929  0.170835  0.080*  
C6  0.7388 (3)  0.2847 (4)  0.22725 (8)  0.0556 (7)  
H6  0.692475  0.161451  0.227796  0.067*  
C7  0.6520 (3)  0.1721 (4)  0.31432 (9)  0.0593 (7)  
H7A  0.75327  0.171429  0.331875  0.071*  
H7B  0.656412  0.077286  0.290590  0.071*  
C8  0.5257 (3)  0.1140 (4)  0.34299 (9)  0.0608 (8)  
H8A  0.425199  0.106259  0.325154  0.073*  
H8B  0.549272  −0.014205  0.355756  0.073*  
C9  0.4869 (3)  0.4552 (5)  0.35981 (10)  0.0659 (8)  
H9A  0.485333  0.550341  0.383577  0.079*  
H9B  0.384923  0.457927  0.342652  0.079*  
C10  0.6136 (3)  0.5090 (4)  0.33044 (9)  0.0574 (7)  
H10A  0.591245  0.637189  0.317528  0.069*  
H10B  0.714497  0.515872  0.348122  0.069*  
C11  −0.1176 (3)  0.2879 (3)  0.46054 (8)  0.0401 (5)  
C12  0.0517 (3)  0.2586 (3)  0.46416 (7)  0.0378 (5)  
C13  0.1453 (3)  0.2289 (3)  0.50261 (8)  0.0403 (5)  
H13  0.253635  0.212835  0.502247  0.048*  
C14  0.0762 (3)  0.2232 (3)  0.54215 (7)  0.0393 (5)  
C15  −0.0855 (3)  0.2447 (3)  0.54264 (8)  0.0406 (6)  
H15  −0.131175  0.242523  0.569377  0.049*  
C16  −0.1766 (3)  0.2689 (3)  0.50371 (8)  0.0395 (5)  
N1  0.6227 (2)  0.3663 (3)  0.29532 (6)  0.0426 (5)  
N2  0.5157 (3)  0.2589 (4)  0.37874 (8)  0.0600 (7)  
H21  0.446 (4)  0.227 (4)  0.3950 (10)  0.072*  
H22  0.614 (4)  0.265 (4)  0.3984 (10)  0.072*  
N3  0.1308 (3)  0.2645 (3)  0.42356 (7)  0.0491 (5)  
N4  0.1728 (3)  0.1928 (3)  0.58323 (7)  0.0551 (6)  
N5  −0.3455 (3)  0.2877 (4)  0.50670 (8)  0.0561 (6)  
O1  −0.1980 (2)  0.3022 (3)  0.42443 (6)  0.0645 (6)  
O2  0.2413 (2)  0.1487 (3)  0.42128 (6)  0.0648 (6)  
O3  0.0884 (3)  0.3800 (3)  0.39444 (6)  0.0705 (6)  
O4  0.3160 (3)  0.1892 (4)  0.58218 (7)  0.0770 (7)  
O5  0.1098 (3)  0.1737 (3)  0.61764 (6)  0.0763 (7)  
O6  −0.3873 (3)  0.3692 (4)  0.53943 (8)  0.0982 (9)  
O7  −0.4365 (2)  0.2218 (4)  0.47735 (8)  0.0836 (7)  

**Atomic displacement parameters (Å²)**

|   | U₁₁  | U₁₂  | U₁₃  | U₂₂  | U₂₃  | U₃₃  |
|---|------|------|------|------|------|------|
| C1| 0.0335 (12) | 0.0615 (16) | 0.0346 (12) | 0.0028 (11) | 0.0017 (10) | 0.0009 (11) |
| C2| 0.0524 (16) | 0.0688 (19) | 0.0505 (16) | −0.0122 (14) | 0.0088 (13) | −0.0012 (14) |

*Acta Cryst. (2022), E78, 1016-1027*
**Geometric parameters (Å, °)**

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C1—C2 | 1.385 (4) | C10—N1 | 1.449 (3) |
| C1—C6 | 1.392 (3) | C10—H10A | 0.9700 |
| C1—N1 | 1.419 (3) | C10—H10B | 0.9700 |
| C2—C3 | 1.391 (4) | C11—O1 | 1.244 (3) |
| C2—H2 | 0.9300 | C11—C12 | 1.443 (3) |
| C3—C4 | 1.361 (4) | C11—C16 | 1.445 (3) |
| C3—H3 | 0.9300 | C12—C13 | 1.363 (3) |
| C4—C5 | 1.359 (4) | C12—N3 | 1.456 (3) |
| C4—H4 | 0.9300 | C13—C14 | 1.382 (3) |
| C5—C6 | 1.382 (4) | C13—H13 | 0.9300 |
| C5—H5 | 0.9300 | C14—C15 | 1.386 (3) |
| C6—H6 | 0.9300 | C14—N4 | 1.441 (3) |
| C7—N1 | 1.457 (3) | C15—C16 | 1.360 (3) |
| C7—C8 | 1.497 (4) | C15—H15 | 0.9300 |
| C7—H7A | 0.9700 | C16—N5 | 1.455 (3) |
| C7—H7B | 0.9700 | N2—H21 | 0.83 (3) |
| C8—N2 | 1.474 (4) | N2—H22 | 0.98 (3) |
| C8—H8A | 0.9700 | N3—O3 | 1.212 (3) |
| C8—H8B | 0.9700 | N3—O2 | 1.236 (3) |
C9—N2 1.469 (4) N4—O5 1.222 (3)
C9—C10 1.506 (3) N4—O4 1.223 (3)
C9—H9A 0.9700 N5—O7 1.210 (3)
C9—H9B 0.9700 N5—O6 1.218 (3)

C2—C1—C6 117.8 (2) N1—C10—H10B 109.4
C2—C1—N1 122.4 (2) C9—C10—H10B 109.4
C6—C1—N1 119.8 (2) H10A—C10—H10B 108.0
C1—C2—C3 120.1 (3) O1—C11—C12 122.9 (2)
C1—C2—H2 120.0 C1—C11—C16 126.2 (2)
C3—C2—H2 120.0 C12—C11—C16 110.8 (2)
C4—C3—C2 121.3 (3) C13—C12—C11 125.5 (2)
C4—C3—H3 119.3 C13—C12—N3 116.4 (2)
C2—C3—H3 119.3 C11—C12—N3 118.1 (2)
C5—C4—C3 119.1 (3) C12—C13—C14 118.7 (2)
C5—C4—H4 120.4 C12—C13—H13 120.6
C3—C4—H4 120.4 C14—C13—H13 120.6
C4—C5—C6 120.9 (3) C13—C14—C15 120.6 (2)
C4—C5—H5 119.6 C13—C14—N4 119.7 (2)
C6—C5—H5 119.6 C15—C14—N4 119.6 (2)
C5—C6—C1 120.8 (3) C16—C15—C14 119.4 (2)
C5—C6—H6 119.6 C16—C15—H15 120.3
C1—C6—H6 119.6 C14—C15—H15 120.3
N1—C7—C8 111.3 (2) C15—C16—C11 124.8 (2)
N1—C7—H7A 109.4 C15—C16—N5 116.4 (2)
C8—C7—H7A 109.4 C11—C16—N5 118.7 (2)
N1—C7—H7B 109.4 C1—N1—C10 116.3 (2)
C8—C7—H7B 109.4 C1—N1—C7 115.2 (2)
N1—C7—C8 110.0 (2) C15—C16—C11 124.8 (2)
N2—C8—C7 110.0 (2) C9—N2—C8 110.2 (2)
N2—C8—H8A 109.7 C9—N2—H21 112 (2)
C7—C8—H8A 109.7 C8—N2—H21 111 (2)
N2—C8—H8B 109.7 C9—N2—H22 107.5 (17)
C7—C8—H8B 109.7 C8—N2—H22 111.7 (17)
H8A—C8—H8B 108.2 H21—N2—H22 105 (3)
N2—C9—C10 110.5 (2) O3—N3—O2 123.5 (2)
N2—C9—H9A 109.6 O3—N3—C12 120.1 (2)
C10—C9—H9A 109.6 O2—N3—C12 116.3 (2)
N2—C9—H9B 109.6 O5—N4—O4 122.5 (2)
C10—C9—H9B 109.6 O5—N4—C14 119.4 (2)
H9A—C9—H9B 108.1 O4—N4—C14 118.1 (2)
N1—C10—C9 111.0 (2) O7—N5—O6 123.4 (2)
N1—C10—H10A 109.4 O7—N5—C16 119.4 (2)
C9—C10—H10A 109.4 O6—N5—C16 117.1 (2)

C6—C1—C2—C3 1.7 (4) O1—C11—C16—N5 −0.6 (4)
N1—C1—C2—C3 −177.4 (2) C12—C11—C16—N5 179.8 (2)
C1—C2—C3—C4 −1.3 (4) C2—C1—N1—C10 −4.1 (3)
Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|------|---------|
| C8—H8B···O4^i | 0.97 | 2.42  | 3.265 (4) | 145 |
| C9—H9A···O4^ii | 0.97 | 2.60  | 3.353 (4) | 134 |
| C9—H9A···O6^iii | 0.97 | 2.61  | 3.455 (4) | 146 |
| N2—H21···O2 | 0.83 (3) | 2.06 (3) | 2.871 (3) | 166 (3) |
| N2—H21···O7^iv | 0.83 (3) | 2.60 (3) | 2.985 (3) | 110 (2) |
| N2—H22···O1^iv | 0.98 (3) | 1.74 (3) | 2.705 (3) | 168 (3) |
| N2—H21···O7^iv | 0.83 (3) | 2.60 (3) | 2.985 (3) | 110 (2) |

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

4-Phenylpiperazin-1-ium benzoate monohydrate (9)

Crystal data

C_{10}H_{15}N_{2}^+·C_{7}H_{5}O_{2}^-·H_{2}O

F(000) = 648

M_r = 302.36

Monoclinic, P2_1/c

α = 6.202 (2) Å

β = 93.83 (2)°

γ = 111.46 (2)°

V = 1625.1 (8) Å³

Z = 4

D_x = 1.236 Mg m⁻³

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 885 reflections

θ = 2.7–27.8°

µ = 0.09 mm⁻¹

T = 293 K

Rod, colourless

0.32 × 0.20 × 0.16 mm
**Data collection**

Oxford Diffraction Xcalibur with Sapphire

CCD diffractometer

Radiation source: Enhance (Mo) X-ray Source

ω and φ scans

Absorption correction: multi-scan

(CrystalisRED; Oxford Diffraction, 2007)

\[ T_{\text{min}} = 0.985, T_{\text{max}} = 1.000 \]

**Refinement**

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.065 \)

\( wR(F^2) = 0.144 \)

\( S = 0.95 \)

3492 reflections

211 parameters

4 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

\( \Delta \rho_{\text{max}} = 0.24 \text{ e Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.16 \text{ e Å}^{-3} \)

**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 (Å²)**

|      | x     | y     | z     | \( U_{\text{iso}} \) or \( U_{\text{eq}} \) |
|------|-------|-------|-------|----------------------------------|
| N1   | 0.2813 (3) | 0.60989 (6) | 0.7704 (3) | 0.0434 (6) |
| N2   | 0.2143 (4) | 0.52769 (7) | 0.7340 (3) | 0.0540 (7) |
| H21  | 0.175 (4)  | 0.5046 (6)  | 0.776 (3)  | 0.065*     |
| H22  | 0.244 (4)  | 0.5249 (8)  | 0.621 (2)  | 0.065*     |
| C1   | 0.3322 (4) | 0.64902 (8) | 0.7364 (3) | 0.0458 (7) |
| C2   | 0.1985 (5) | 0.67263 (9) | 0.6301 (4) | 0.0732 (9) |
| H2   | 0.073519   | 0.662304   | 0.574143   | 0.088*     |
| C3   | 0.2469 (6) | 0.71136 (9) | 0.6050 (5) | 0.0890 (11)|
| H3   | 0.153321   | 0.726509   | 0.533416   | 0.107*     |
| C4   | 0.4287 (7) | 0.72754 (10)| 0.6834 (5) | 0.0871 (11)|
| H4   | 0.460834   | 0.753486   | 0.666273   | 0.105*     |
| C5   | 0.5623 (6) | 0.70463 (10)| 0.7878 (5) | 0.0849 (11)|
| H5   | 0.687062   | 0.715266   | 0.842693   | 0.102*     |
| C6   | 0.5172 (5) | 0.66585 (9) | 0.8144 (4) | 0.0684 (9) |
| H6   | 0.612551   | 0.650963   | 0.885571   | 0.082*     |
| C7   | 0.4623 (4) | 0.58257 (7) | 0.7779 (4) | 0.0500 (7) |
| H7A  | 0.579852   | 0.592960   | 0.854289   | 0.060*     |
| H7B  | 0.513636   | 0.579710   | 0.660752   | 0.060*     |
| C8   | 0.4003 (4) | 0.54349 (7) | 0.8453 (4) | 0.0554 (8) |
| H8A  | 0.522296   | 0.525995   | 0.842923   | 0.067*     |
| Atomic coordinates (Å)                  |                                |                                |                                |                                |                                |                                |
|----------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| H8B                                    | 0.361408                        | 0.545749                        | 0.966498                        | 0.067*                          |                                  |                                  |
| C9                                     | 0.0303 (4)                      | 0.55502 (8)                     | 0.7319 (4)                      | 0.0586 (8)                      |                                  |                                  |
| H9A                                    | −0.018777                       | 0.557418                        | 0.849982                        | 0.070*                          |                                  |                                  |
| H9B                                    | −0.088519                       | 0.545041                        | 0.655591                        | 0.070*                          |                                  |                                  |
| C10                                    | 0.0951 (4)                      | 0.594168                        | 0.6670 (4)                      | 0.0544 (7)                      |                                  |                                  |
| H10A                                   | 0.129289                        | 0.592100                        | 0.544591                        | 0.065*                          |                                  |                                  |
| H10B                                   | −0.025699                       | 0.611834                        | 0.672570                        | 0.065*                          |                                  |                                  |
| O1                                     | 0.0826 (4)                      | 0.453526                        | 0.8352 (3)                      | 0.0739 (6)                      |                                  |                                  |
| C9                                     | 0.3636 (4)                      | 0.442718                        | 0.6833 (4)                      | 0.1271 (11)                     |                                  |                                  |
| H11                                    | 0.1746 (4)                      | 0.388369                        | 0.7732 (3)                      | 0.0488 (7)                      |                                  |                                  |
| C12                                    | 0.3518 (5)                      | 0.362811                        | 0.6979 (4)                      | 0.0710 (9)                      |                                  |                                  |
| H12                                    | 0.434100                        | 0.372529                        | 0.643180                        | 0.085*                          |                                  |                                  |
| C13                                    | 0.2834 (6)                      | 0.323512                        | 0.7030 (4)                      | 0.0850 (11)                     |                                  |                                  |
| C14                                    | 0.378578                        | 0.306980                        | 0.650576                        | 0.102*                          |                                  |                                  |
| C15                                    | 0.1131 (7)                      | 0.308670                        | 0.7841 (5)                      | 0.0841 (10)                     |                                  |                                  |
| H14                                    | 0.097272                        | 0.282041                        | 0.788617                        | 0.101*                          |                                  |                                  |
| O2                                     | −0.0285 (5)                     | 0.333051                        | 0.8592 (4)                      | 0.0758 (10)                     |                                  |                                  |
| C16                                    | 0.0017 (4)                      | 0.372828                        | 0.8532 (4)                      | 0.0566 (8)                      |                                  |                                  |
| H16                                    | −0.096028                       | 0.389140                        | 0.903761                        | 0.068*                          |                                  |                                  |
| C17                                    | 0.2108 (5)                      | 0.431330                        | 0.7647 (4)                      | 0.0605 (8)                      |                                  |                                  |
| O3                                     | 0.7231 (3)                      | 0.477947                        | 0.6283 (3)                      | 0.0737 (7)                      |                                  |                                  |
| H31                                    | 0.816 (5)                       | 0.467911                        | 0.697 (4)                       | 0.111*                          |                                  |                                  |
| H32                                    | 0.609 (4)                       | 0.46659                         | 0.645 (5)                       | 0.111*                          |                                  |                                  |

**Atomic displacement parameters (Å²)**

|                  | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| N1               | 0.0406 (13)| 0.0418 (14)| 0.0472 (14)| −0.0004 (11)| −0.0012 (10)| −0.0001 (11)|
| N2               | 0.0689 (17)| 0.0449 (15)| 0.0493 (16)| −0.0092 (14)| 0.0112 (14)| 0.0018 (14)|
| C1               | 0.0524 (17)| 0.0389 (16)| 0.0463 (17)| −0.0012 (14)| 0.0049 (13)| −0.0033 (14)|
| C2               | 0.074 (2)  | 0.050 (2)  | 0.092 (2)  | −0.0010 (17)| −0.0224 (19)| 0.0050 (19)|
| C3               | 0.109 (3)  | 0.048 (2)  | 0.106 (3)  | 0.004 (2)   | −0.026 (2)  | 0.010 (2)  |
| C4               | 0.133 (3)  | 0.044 (2)  | 0.082 (3)  | −0.014 (2)  | −0.012 (2)  | 0.000 (2)  |
| C5               | 0.105 (3)  | 0.060 (2)  | 0.086 (3)  | −0.031 (2)  | −0.024 (2)  | 0.000 (2)  |
| C6               | 0.074 (2)  | 0.054 (2)  | 0.075 (2)  | −0.0112 (18)| −0.0153 (17)| 0.0072 (17)|
| C7               | 0.0442 (16)| 0.0485 (18)| 0.0566 (18)| −0.0019 (14)| −0.0008 (13)| −0.0016 (15)|
| C8               | 0.0595 (18)| 0.0498 (18)| 0.0556 (18)| 0.0000 (15) | −0.0066 (15)| 0.0025 (15)|
| C9               | 0.0512 (17)| 0.0590 (19)| 0.0659 (19)| −0.0085 (16)| 0.0071 (14)| −0.0031 (17)|
| C10              | 0.0434 (16)| 0.0507 (18)| 0.068 (2)  | −0.0008 (14)| −0.0024 (14)| 0.0025 (16)|
| O1               | 0.0960 (16)| 0.0529 (14)| 0.0741 (15)| −0.0102 (12)| 0.0157 (13)| 0.0002 (12)|
| O2               | 0.0889 (17)| 0.104 (2)  | 0.195 (3)  | −0.0264 (15)| 0.0568 (19)| 0.035 (2)  |
| C11              | 0.0447 (16)| 0.0594 (19)| 0.0417 (16)| 0.0016 (15) | −0.0014 (13)| 0.0053 (15)|
| C12              | 0.062 (2)  | 0.089 (3)  | 0.063 (2)  | 0.017 (2)   | 0.0069 (16)| 0.0160 (19)|
| C13              | 0.106 (3)  | 0.077 (3)  | 0.072 (2)  | 0.040 (2)   | 0.007 (2)  | 0.002 (2)  |
| C14              | 0.125 (3)  | 0.053 (2)  | 0.073 (2)  | 0.003 (2)   | −0.009 (2) | −0.004 (2) |
| C15              | 0.087 (2)  | 0.062 (2)  | 0.079 (2)  | −0.023 (2)  | 0.0130 (19)| 0.000 (2)  |
| C16              | 0.0602 (18)| 0.055 (2)  | 0.0557 (18)| −0.0061 (16)| 0.0122 (15)| −0.0043 (15)|
Geometric parameters (Å, °)

|          |                  |                  |                  |                  |                  |                  |                  |
|----------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| C1—C6   | 1.384 (3)         | O2—C17           | 1.251 (3)        |
| C1—C2   | 1.384 (3)         | C11—C16          | 1.376 (3)        |
| C2—C3   | 1.388 (4)         | C11—C12          | 1.393 (4)        |
| C2—H2   | 0.9300            | C11—C17          | 1.504 (4)        |
| C3—C4   | 1.360 (4)         | C12—C13          | 1.375 (4)        |
| C3—H3   | 0.9300            | C12—H12          | 0.9300           |
| C4—C5   | 1.362 (4)         | C13—C14          | 1.358 (4)        |
| C4—H4   | 0.9300            | C13—H13          | 0.9300           |
| C5—C6   | 1.387 (4)         | C14—C15          | 1.369 (4)        |
| C5—H5   | 0.9300            | C14—H14          | 0.9300           |
| C6—C7   | 1.504 (3)         | C15—C16          | 1.389 (4)        |
| C6—C7   | 1.504 (3)         | C15—H15          | 0.9300           |
| C7—H7A  | 0.9700            | C16—H16          | 0.9300           |
| C7—H7B  | 0.9700            | O3—H31           | 0.830 (18)       |
| C8—H8A  | 0.9700            | O3—H32           | 0.826 (18)       |

C1—N1—C10 115.8 (2) C7—C8—H8B 109.7
C1—N1—C7 116.32 (19) H8A—C8—H8B 108.2
C10—N1—C7 110.9 (2) N2—C9—C10 110.8 (2)
C9—N2—C8 109.8 (2) N2—C9—H9A 109.5
C9—N2—H21 110.3 (17) C10—C9—H9A 109.5
C8—N2—H21 110.0 (17) N2—C9—H9B 109.5
C9—N2—H22 105.5 (17) C10—C9—H9B 109.5
C8—N2—H22 112.5 (17) H9A—C9—H9B 108.1
H21—N2—H22 109 (3) N1—C10—C9 112.3 (2)
C6—C1—C2 116.7 (3) N1—C10—H10A 109.2
C6—C1—N1 120.8 (2) C9—C10—H10A 109.2
C2—C1—N1 122.5 (3) N1—C10—H10B 109.2
C1—C2—C3 121.5 (3) C9—C10—H10B 109.2
C1—C2—H2 119.3 H10A—C10—H10B 107.9
C3—C2—H2 119.3 C16—C11—C12 117.6 (3)
C4—C3—C2 121.2 (3) C16—C11—C17 121.8 (3)
C4—C3—H3 119.4 C12—C11—C17 120.6 (3)
C2—C3—H3 119.4 C13—C12—C11 121.2 (3)
C3—C4—C5 118.0 (3) C13—C12—H12 119.4
C3—C4—H4 121.0 C11—C12—H12 119.4
Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H  | H···A | D···A  | D—H···A |
|-------------|------|------|--------|---------|
| N2—H21···O1 | 0.90 (2) | 1.92 (2) | 2.813 (3) | 173 (2) |
| N2—H21···O2 | 0.90 (2) | 2.56 (2) | 3.112 (4) | 121 (2) |
| N2—H22···O3 i | 0.89 (2) | 1.92 (2) | 2.812 (3) | 173 (2) |
| C9—H9d···O1 ii | 0.97 | 2.48 | 3.420 (4) | 164 |
| C9—H9B···O3 iii | 0.97 | 2.60 | 3.340 (4) | 133 |
| O3—H31···O1 iv | 0.83 (2) | 1.96 (2) | 2.772 (3) | 166 (4) |
| O3—H32···O2 | 0.83 (2) | 1.77 (2) | 2.599 (3) | 179 (4) |

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x, −y+1, −z+2; (iii) x−1, y, z; (iv) x+1, y, z.
4-Phenylpiperazin-1-ium 4-methylbenzenesulfonate (10)

Crystal data

C₁₀H₁₅N₂⁺·C₇H₇O₃S⁻

$F(000) = 712$

$D_r = 1.325 \text{ Mg m}^{-3}$

Monoclinic, $P2_1$

Cell parameters from 2252 reflections

$\theta = 2.9^{\circ} - 27.6^{\circ}$

$\mu = 0.21 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Plate, colourless

$0.50 \times 0.36 \times 0.14 \text{ mm}$

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

(CrystalisRED; Oxford Diffraction, 2007)

$T_{\text{min}} = 0.696$, $T_{\text{max}} = 1.000$

Refinement

Refinement on $F^2$

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.126$

$wR(F^2) = 0.298$

$S = 1.12$

$4918$ independent reflections

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Absolute structure: Flack $x$ determined using

597 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons et al., 2013)

Absolute structure parameter: 0.00 (11)

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. Refined as a 2-component twin.

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

|    | $x$       | $y$       | $z$       | $U_{eq}$ | Occ. (<1) |
|----|-----------|-----------|-----------|----------|-----------|
| N1 | 0.3198 (15)| 0.0451 (12)| 0.1981 (8) | 0.044 (3) |           |
| N2 | 0.3315 (13)| −0.0070 (11)| 0.0453 (8) | 0.041 (3) |           |
| H21N | 0.301100 | 0.008772 | −0.000733 | 0.050*    |           |
| H22N | 0.400866 | −0.068854 | 0.045658 | 0.050*    |           |
| C1  | 0.345 (5)  | 0.050 (4)  | 0.2756 (14)| 0.056 (4) | 0.49 (7)  |
| C2  | 0.244 (4)  | −0.010 (4) | 0.322 (2)  | 0.058 (4) | 0.49 (7)  |
| Atom | X   | Y     | Z     | E   | Biso |
|------|-----|-------|-------|-----|-----|
| H2   | 0.163707 | -0.061632 | 0.302457 | 0.069* | 0.49 (7) |
| C3   | 0.263 (4) | 0.006 (5) | 0.3965 (19) | 0.060 (4) | 0.49 (7) |
| H3   | 0.195547 | -0.034965 | 0.427260 | 0.073* | 0.49 (7) |
| C4   | 0.383 (5) | 0.082 (4) | 0.4252 (14) | 0.062 (4) | 0.49 (7) |
| H4   | 0.398 (7) | 0.092749 | 0.475215 | 0.074* | 0.49 (7) |
| C5   | 0.484 (6) | 0.143 (3) | 0.3791 (18) | 0.061 (4) | 0.49 (7) |
| H5   | 0.564573 | 0.193797 | 0.398368 | 0.074* | 0.49 (7) |
| C6   | 0.465 (5) | 0.127 (4) | 0.3044 (17) | 0.058 (4) | 0.49 (7) |
| H6   | 0.532736 | 0.167132 | 0.273565 | 0.070* | 0.49 (7) |
| C1A  | 0.338 (4) | 0.047 (3) | 0.2748 (13) | 0.055 (3) | 0.51 (7) |
| C2A  | 0.259 (5) | -0.042 (4) | 0.3132 (19) | 0.057 (4) | 0.51 (7) |
| H2A  | 0.204660 | -0.104759 | 0.288426 | 0.069* | 0.51 (7) |
| C3A  | 0.261 (4) | -0.038 (4) | 0.3887 (19) | 0.061 (4) | 0.51 (7) |
| H3A  | 0.207972 | -0.097323 | 0.414372 | 0.073* | 0.51 (7) |
| C4A  | 0.342 (5) | 0.056 (4) | 0.4258 (13) | 0.062 (4) | 0.51 (7) |
| H4A  | 0.342913 | 0.059306 | 0.476246 | 0.075* | 0.51 (7) |
| C5A  | 0.420 (7) | 0.146 (2) | 0.3874 (18) | 0.060 (4) | 0.51 (7) |
| H5A  | 0.474543 | 0.208501 | 0.412173 | 0.072* | 0.51 (7) |
| C6A  | 0.418 (5) | 0.141 (3) | 0.3119 (18) | 0.059 (4) | 0.51 (7) |
| C7A  | 0.471233 | 0.201067 | 0.286226 | 0.070* | 0.51 (7) |
| C8   | 0.4521 (18) | 0.0840 (15) | 0.1564 (9) | 0.049 (4) | 0.51 (7) |
| H7A  | 0.537245 | 0.023733 | 0.161521 | 0.059* | 0.51 (7) |
| C9   | 0.493647 | 0.160291 | 0.176389 | 0.059* | 0.51 (7) |
| H9A  | 0.411 (2) | 0.1017 (15) | 0.0780 (9) | 0.052 (4) | 0.51 (7) |
| C10  | 0.339429 | 0.171509 | 0.071858 | 0.063* | 0.51 (7) |
| H10A | 0.507744 | 0.119164 | 0.052790 | 0.063* | 0.51 (7) |
| C11  | 0.1907 (17) | -0.0413 (16) | 0.0857 (9) | 0.046 (4) | 0.51 (7) |
| H9B  | 0.144478 | -0.115915 | 0.065528 | 0.056* | 0.51 (7) |
| C12  | 0.10126 | 0.022516 | 0.080775 | 0.056* | 0.51 (7) |
| C13  | 0.2369 (19) | -0.0603 (15) | 0.1653 (10) | 0.049 (4) | 0.51 (7) |
| H10B | 0.140631 | -0.076696 | 0.191354 | 0.059* | 0.51 (7) |
| H11B | 0.306204 | -0.131345 | 0.170331 | 0.059* | 0.51 (7) |
| S1   | 0.1579 (4) | 0.7481 (4) | -0.1011 (2) | 0.0439 (10) | 0.51 (7) |
| O1   | 0.1787 (12) | 0.6159 (9) | -0.0944 (6) | 0.049 (3) | 0.51 (7) |
| O2   | 0.2928 (18) | 0.8175 (11) | -0.0705 (7) | 0.076 (4) | 0.51 (7) |
| C11  | 0.1506 (16) | 0.7750 (13) | -0.1938 (8) | 0.036 (3) | 0.51 (7) |
| C12  | 0.2354 (19) | 0.8746 (17) | -0.2240 (10) | 0.054 (4) | 0.51 (7) |
| H12  | 0.388418 | 0.925481 | -0.193938 | 0.065* | 0.51 (7) |
| C13  | 0.224 (2) | 0.8952 (19) | -0.2971 (11) | 0.067 (5) | 0.51 (7) |
| H13  | 0.283222 | 0.959399 | -0.315160 | 0.081* | 0.51 (7) |
| C14  | 0.133 (2) | 0.830 (2) | -0.3450 (11) | 0.070 (5) | 0.51 (7) |
| C15  | 0.042 (2) | 0.735 (2) | -0.3146 (10) | 0.069 (5) | 0.51 (7) |
| H15  | 0.022524 | 0.687927 | -0.344707 | 0.083* | 0.51 (7) |
| C16  | 0.051 (2) | 0.7130 (15) | -0.2414 (9) | 0.060 (5) | 0.51 (7) |
| H16  | 0.013532 | 0.652069 | -0.223331 | 0.072* | 0.51 (7) |
| C17  | 0.121 (3) | 0.853 (3) | -0.4249 (11) | 0.101 (8) | 0.51 (7) |
| H17A | 0.138438 | 0.778329 | -0.450528 | 0.152* | 0.51 (7) |
|      |        |        |       |        |
|------|--------|--------|-------|--------|
| H17B | 0.200838 | 0.911924 | -0.437227 | 0.152* |
| H17C | 0.015970 | 0.884299 | -0.438319 | 0.152* |
| N3   | 0.2216 (15) | 0.5462 (13) | 0.1956 (8) | 0.046 (3) |
| N4   | 0.1795 (13) | 0.4911 (11) | 0.0439 (8) | 0.041 (3) |
| H41N | 0.110853 | 0.428961 | 0.045763 | 0.049* |
| H42N | 0.200180 | 0.504089 | -0.002420 | 0.049* |
| C18  | 0.212 (4) | 0.553 (3) | 0.2730 (13) | 0.052 (3) |
| C19  | 0.321 (4) | 0.490 (4) | 0.3187 (18) | 0.055 (4) |
| H19  | 0.395669 | 0.437535 | 0.299289 | 0.066* |
| C2  | 0.319 (3) | 0.506 (4) | 0.3935 (17) | 0.058 (4) |
| H20  | 0.392116 | 0.464559 | 0.424139 | 0.070* |
| C21  | 0.208 (5) | 0.585 (3) | 0.4226 (13) | 0.060 (4) |
| H21  | 0.206786 | 0.596177 | 0.472606 | 0.071* |
| C22  | 0.099 (6) | 0.648 (3) | 0.3768 (17) | 0.058 (4) |
| H22  | 0.025007 | 0.700772 | 0.396224 | 0.070* |
| C23  | 0.101 (5) | 0.632 (3) | 0.3020 (16) | 0.056 (4) |
| H23  | 0.028557 | 0.673749 | 0.271374 | 0.067* |
| C18A | 0.222 (5) | 0.547 (4) | 0.2737 (15) | 0.053 (3) |
| C19A | 0.308 (5) | 0.459 (4) | 0.313 (2) | 0.054 (4) |
| H19A | 0.355887 | 0.394865 | 0.289012 | 0.065* |
| C20A | 0.322 (4) | 0.466 (4) | 0.388 (2) | 0.057 (4) |
| H20A | 0.379451 | 0.406632 | 0.414826 | 0.069* |
| C21A | 0.250 (6) | 0.562 (4) | 0.4245 (15) | 0.059 (4) |
| H21A | 0.259318 | 0.566251 | 0.474911 | 0.071* |
| C22A | 0.164 (7) | 0.650 (3) | 0.385 (2) | 0.058 (4) |
| H22A | 0.115621 | 0.714105 | 0.409183 | 0.070* |
| C23A | 0.150 (6) | 0.643 (3) | 0.310 (2) | 0.057 (4) |
| H23A | 0.092056 | 0.702341 | 0.283368 | 0.068* |
| C24  | 0.2995 (19) | 0.4424 (17) | 0.1647 (10) | 0.053 (4) |
| H24A | 0.233128 | 0.370513 | 0.170301 | 0.064* |
| H24B | 0.401590 | 0.428310 | 0.190816 | 0.064* |
| C25  | 0.3281 (16) | 0.4609 (14) | 0.0851 (9) | 0.042 (3) |
| H25A | 0.405263 | 0.526314 | 0.079855 | 0.051* |
| H25B | 0.373358 | 0.386948 | 0.065500 | 0.051* |
| C26  | 0.107 (2) | 0.6013 (14) | 0.0745 (9) | 0.049 (4) |
| H26A | 0.005379 | 0.618567 | 0.048646 | 0.058* |
| H26B | 0.177715 | 0.670632 | 0.068350 | 0.058* |
| C27  | 0.0796 (19) | 0.5836 (16) | 0.1541 (9) | 0.050 (4) |
| H27A | 0.040882 | 0.659632 | 0.173988 | 0.059* |
| H27B | 0.003443 | 0.522492 | 0.159258 | 0.059* |
| S2   | 0.3197 (4) | 0.2483 (4) | -0.1000 (2) | 0.0434 (10) |
| O4   | 0.4827 (15) | 0.2874 (13) | -0.0758 (7) | 0.082 (5) |
| O5   | 0.1897 (18) | 0.3143 (12) | -0.0704 (7) | 0.076 (4) |
| O6   | 0.3029 (13) | 0.1184 (10) | -0.0925 (6) | 0.055 (3) |
| C28  | 0.3101 (15) | 0.2744 (12) | -0.1926 (7) | 0.030 (3) |
| C29  | 0.398 (2) | 0.2104 (14) | -0.2397 (9) | 0.056 (4) |
| H29  | 0.464748 | 0.148626 | -0.221269 | 0.067* |
| C30  | 0.393 (2) | 0.2318 (19) | -0.3126 (9) | 0.069 (5) |
### Atomic displacement parameters (Å²)

|   | \(U_{11}\)   | \(U_{22}\)   | \(U_{33}\)   | \(U_{12}\)   | \(U_{13}\)   | \(U_{23}\)   |
|---|-------------|-------------|-------------|-------------|-------------|-------------|
| N1| 0.035 (6)   | 0.025 (6)   | 0.073 (6)   | −0.004 (5)  | 0.003 (5)   | 0.004 (5)   |
| N2| 0.022 (6)   | 0.028 (7)   | 0.075 (9)   | −0.001 (5)  | 0.003 (5)   | −0.001 (6)  |
| C1| 0.057 (8)   | 0.041 (8)   | 0.070 (6)   | −0.002 (7)  | 0.006 (6)   | 0.002 (6)   |
| C2| 0.060 (8)   | 0.043 (8)   | 0.070 (7)   | −0.006 (7)  | 0.006 (6)   | 0.000 (7)   |
| C3| 0.065 (8)   | 0.046 (9)   | 0.071 (7)   | −0.008 (8)  | 0.007 (6)   | −0.001 (7)  |
| C4| 0.065 (9)   | 0.049 (9)   | 0.072 (7)   | −0.009 (8)  | 0.005 (7)   | 0.000 (7)   |
| C5| 0.062 (9)   | 0.049 (8)   | 0.073 (7)   | −0.007 (8)  | 0.006 (7)   | −0.002 (7)  |
| C6| 0.059 (9)   | 0.045 (8)   | 0.071 (6)   | −0.004 (7)  | 0.007 (7)   | −0.001 (7)  |
| C1A| 0.056 (8)| 0.041 (7)| 0.070 (6) | −0.002 (7) | 0.007 (6) | 0.002 (6) |
| C2A| 0.058 (8)| 0.044 (8)| 0.071 (6) | −0.004 (7) | 0.007 (6) | 0.001 (7) |
| C3A| 0.065 (8)| 0.046 (9)| 0.071 (7) | −0.009 (8) | 0.007 (7) | 0.001 (7) |
| C4A| 0.065 (9)| 0.050 (8)| 0.072 (7) | −0.009 (8) | 0.005 (7) | 0.001 (7) |
| C5A| 0.061 (9)| 0.048 (8)| 0.072 (7) | −0.007 (8) | 0.006 (7) | −0.001 (7) |
| C6A| 0.059 (9)| 0.046 (8)| 0.071 (6) | −0.006 (7) | 0.007 (7) | 0.000 (6) |
| C7| 0.033 (7)| 0.041 (10)| 0.073 (7) | −0.010 (7) | 0.004 (6) | −0.009 (8) |
| C8| 0.051 (9)| 0.029 (8)| 0.077 (8) | −0.016 (7) | 0.004 (7) | 0.005 (8) |
| C9| 0.031 (7)| 0.036 (9)| 0.073 (8) | −0.007 (6) | 0.009 (6) | −0.010 (8) |
| C10| 0.038 (9)| 0.035 (9)| 0.076 (8) | −0.012 (7) | 0.012 (7) | 0.003 (7) |
| S1| 0.042 (2)| 0.029 (2)| 0.061 (3) | 0.009 (2) | 0.0026 (17) | −0.003 (2) |
| O1| 0.046 (7)| 0.018 (5)| 0.083 (8) | 0.002 (5) | 0.006 (5) | 0.004 (5) |
| O2| 0.114 (10)| 0.036 (7)| 0.076 (9) | −0.037 (7)| −0.030 (8) | 0.007 (7) |
| O3| 0.077 (8)| 0.095 (11)| 0.078 (8) | 0.057 (8) | 0.038 (7) | 0.019 (8) |
| C11| 0.031 (4)| 0.034 (4)| 0.043 (4) | 0.001 (3)| 0.002 (3) | −0.003 (3) |
| C12| 0.037 (9)| 0.057 (10)| 0.068 (8) | −0.018 (8)| 0.000 (7) | 0.005 (8) |
| C13| 0.064 (12)| 0.068 (13)| 0.070 (9) | −0.016 (9)| 0.011 (8) | 0.013 (9) |
| C14| 0.067 (12)| 0.080 (13)| 0.062 (9) | 0.005 (9)| 0.002 (8) | 0.000 (9) |
| C15| 0.076 (11)| 0.064 (12)| 0.067 (8) | −0.009 (10)| −0.017 (8) | −0.012 (9) |
| C16| 0.069 (10)| 0.039 (11)| 0.069 (8) | −0.017 (8)| −0.013 (8) | −0.002 (7) |
| C17| 0.108 (19)| 0.13 (2)| 0.068 (10) | 0.026 (17) | 0.009 (11) | 0.013 (12) |
| N3| 0.033 (6)| 0.037 (7)| 0.067 (5) | −0.005 (5)| −0.002 (5) | 0.001 (6) |
| N4| 0.024 (6)| 0.023 (6)| 0.076 (8) | −0.006 (5)| 0.006 (5) | 0.005 (6) |
| C18| 0.048 (8)| 0.040 (7)| 0.067 (6) | −0.001 (7)| −0.002 (5) | 0.004 (6) |
| C19| 0.052 (7)| 0.044 (8)| 0.068 (6) | 0.004 (7)| −0.003 (6) | 0.002 (7) |
| C20| 0.058 (8)| 0.046 (9)| 0.069 (6) | 0.007 (8)| −0.002 (6) | 0.003 (7) |
|      | 0.058 (9) | 0.049 (8) | 0.071 (7) | 0.008 (8) | −0.002 (6) | 0.003 (7) |
| C21  | 0.055 (9) | 0.048 (8) | 0.071 (7) | 0.007 (8) | −0.003 (7) | 0.000 (7) |
| C22  | 0.051 (8) | 0.045 (7) | 0.071 (6) | 0.005 (7) | −0.003 (6) | 0.001 (7) |
| C23  | 0.049 (8) | 0.041 (7) | 0.067 (6) | −0.001 (7) | −0.002 (6) | 0.003 (6) |
| C18A | 0.051 (8) | 0.043 (8) | 0.068 (6) | 0.002 (7) | −0.002 (6) | 0.003 (7) |
| C20A | 0.057 (8) | 0.045 (9) | 0.069 (6) | 0.008 (8) | −0.003 (6) | 0.003 (7) |
| C21A | 0.058 (9) | 0.048 (8) | 0.071 (7) | 0.009 (8) | −0.001 (7) | 0.002 (7) |
| C22A | 0.056 (9) | 0.047 (8) | 0.072 (7) | 0.007 (8) | −0.002 (7) | 0.000 (7) |
| C23A | 0.053 (9) | 0.045 (7) | 0.071 (6) | 0.003 (8) | −0.003 (7) | 0.000 (6) |
| C24  | 0.029 (8) | 0.052 (10) | 0.079 (8) | 0.010 (7) | 0.000 (7) | 0.004 (8) |
| C25  | 0.022 (6) | 0.022 (8) | 0.083 (8) | −0.004 (6) | 0.003 (6) | −0.005 (7) |
| C26  | 0.052 (9) | 0.021 (7) | 0.073 (8) | 0.012 (7) | 0.003 (7) | 0.008 (7) |
| C27  | 0.047 (4) | 0.047 (5) | 0.054 (4) | 0.005 (3) | 0.001 (3) | −0.002 (3) |
| S2   | 0.041 (2) | 0.030 (2) | 0.059 (3) | −0.014 (2) | 0.0019 (17) | −0.002 (2) |
| O4   | 0.072 (7) | 0.087 (11) | 0.082 (9) | −0.056 (7) | −0.035 (6) | 0.031 (8) |
| O5   | 0.107 (10) | 0.048 (8) | 0.076 (9) | 0.008 (7) | 0.035 (8) | 0.000 (7) |
| O6   | 0.058 (7) | 0.026 (6) | 0.082 (9) | −0.017 (5) | −0.004 (6) | 0.009 (6) |
| C28  | 0.025 (4) | 0.025 (4) | 0.039 (4) | −0.008 (3) | 0.002 (3) | −0.003 (3) |
| C29  | 0.075 (11) | 0.033 (10) | 0.061 (8) | 0.011 (7) | 0.011 (8) | −0.004 (7) |
| C30  | 0.097 (13) | 0.053 (12) | 0.059 (8) | 0.003 (9) | 0.018 (8) | −0.015 (8) |
| C31  | 0.069 (12) | 0.063 (12) | 0.068 (9) | −0.021 (8) | −0.005 (8) | 0.005 (8) |
| C32  | 0.058 (12) | 0.044 (11) | 0.087 (9) | 0.000 (8) | −0.008 (8) | 0.019 (9) |
| C33  | 0.035 (8) | 0.031 (8) | 0.087 (9) | 0.005 (6) | 0.001 (8) | 0.007 (8) |
| C34  | 0.11 (2) | 0.13 (2) | 0.076 (10) | −0.039 (18) | −0.012 (11) | 0.022 (13) |

**Geometric parameters (Å, °)**

|      | 1.41 (3) | N3—C18 | 1.43 (3) |
| N1—C1A | 1.44 (3) | N3—C27 | 1.437 (19) |
| N1—C7 | 1.437 (19) | N3—C18A | 1.44 (3) |
| N1—C10 | 1.461 (19) | N3—C24 | 1.44 (2) |
| N2—C9 | 1.467 (18) | N4—C25 | 1.459 (19) |
| N2—C8 | 1.475 (19) | N4—C26 | 1.473 (18) |
| N2—H21N | 0.8900 | N4—H41N | 0.8900 |
| N2—H22N | 0.8900 | N4—H42N | 0.8900 |
| C1—C2 | 1.3900 | C18—C19 | 1.3900 |
| C1—C6 | 1.3900 | C18—C23 | 1.3900 |
| C2—C3 | 1.3900 | C19—C20 | 1.3900 |
| C2—H2 | 0.9300 | C19—H19 | 0.9300 |
| C3—C4 | 1.3900 | C20—C21 | 1.3900 |
| C3—H3 | 0.9300 | C20—H20 | 0.9300 |
| C4—C5 | 1.3900 | C21—C22 | 1.3900 |
| C4—H4 | 0.9300 | C21—H21 | 0.9300 |
| C5—C6 | 1.3900 | C22—C23 | 1.3900 |
| C5—H5 | 0.9300 | C22—H22 | 0.9300 |
| C6—H6 | 0.9300 | C23—H23 | 0.9300 |
| C1A—C2A | 1.3900 | C18A—C19A | 1.3900 |
| C1A—C6A | 1.3900 | C18A—C23A | 1.3900 |
C2A—C3A 1.3900  C19A—C20A 1.3900
C2A—H2A 0.9300  C19A—H19A 0.9300
C3A—C4A 1.3900  C20A—C21A 1.3900
C3A—H3A 0.9300  C20A—H20A 0.9300
C4A—C5A 1.3900  C21A—C22A 1.3900
C4A—H4A 0.9300  C21A—H21A 0.9300
C5A—C6A 1.3900  C22A—C23A 1.3900
C5A—H5A 0.9300  C22A—H22A 0.9300
C6A—H6A 0.9300  C23A—H23A 0.9300
C7—C8 1.48 (2)  C24—C25 1.51 (2)
C7—H7A 0.9700  C24—H24A 0.9700
C7—H7B 0.9700  C24—H24B 0.9700
C8—H8A 0.9700  C25—H25A 0.9700
C8—H8B 0.9700  C25—H25B 0.9700
C9—C10 1.51 (2)  C26—C27 1.51 (2)
C9—H9A 0.9700  C26—H26A 0.9700
C9—H9B 0.9700  C26—H26B 0.9700
C10—H10A 0.9700  C27—H27A 0.9700
C10—H10B 0.9700  C27—H27B 0.9700
S1—O2 1.448 (12)  S2—O5 1.430 (13)
S1—O3 1.451 (12)  S2—O6 1.436 (11)
S1—O1 1.462 (11)  S2—O4 1.473 (11)
S1—C11 1.731 (15)  S2—C28 1.728 (14)
C11—C16 1.358 (19)  C28—C29 1.355 (19)
C11—C12 1.43 (2)  C28—C33 1.42 (2)
C12—C13 1.36 (2)  C29—C30 1.36 (2)
C12—H12 0.9300  C29—H29 0.9300
C13—C14 1.34 (3)  C30—C31 1.38 (3)
C13—H13 0.9300  C30—H30 0.9300
C14—C15 1.41 (3)  C31—C32 1.38 (3)
C14—C17 1.49 (3)  C31—C34 1.48 (3)
C15—C16 1.37 (2)  C32—C33 1.39 (3)
C15—H15 0.9300  C32—H32 0.9300
C16—H16 0.9300  C33—H33 0.9300
C17—H17A 0.9600  C34—H34A 0.9600
C17—H17B 0.9600  C34—H34B 0.9600
C17—H17C 0.9600  C34—H34C 0.9600
C1A—N1—C7 118.8 (19)  C18—N3—C27 115.7 (18)
C1—N1—C7 116.1 (19)  C27—N3—C18A 119 (2)
C1A—N1—C10 116.9 (19)  C27—N3—C24 118.7 (19)
C1—N1—C10 119.1 (19)  C27—N3—C24 112.9 (14)
C7—N1—C10 111.9 (13)  C18A—N3—C24 115 (2)
C9—N2—C8 110.6 (13)  C25—N4—C26 109.8 (13)
C9—N2—H21N 109.5  C25—N4—H41N 109.7
C8—N2—H21N 109.5  C26—N4—H41N 109.7
C9—N2—H22N 109.5  C25—N4—H42N 109.7
C8—N2—H22N 109.5  C26—N4—H42N 109.7
H21N—N2—H22N 108.1
H41N—N4—H42N 108.2
C2—C1—C6 120.0  C19—C18—C23 120.0
C2—C1—N1 122 (2)  C19—C18—N3 121 (2)
C6—C1—N1 118 (2)  C23—C18—N3 119 (2)
C3—C2—C1 120.0  C20—C19—C18 120.0
C3—C2—H2 120.0  C20—C19—H19 120.0
C1—C2—H2 120.0  C18—C19—H19 120.0
C2—C3—C4 120.0  C21—C20—C19 120.0
C2—C3—H3 120.0  C21—C20—H19 120.0
C4—C3—H3 120.0  C22—C21—C20 120.0
C3—C4—H4 120.0  C22—C21—H21 120.0
C5—C4—H4 120.0  C20—C21—H21 120.0
C6—C5—C4 120.0  C21—C22—C23 120.0
C6—C5—H5 120.0  C21—C22—H22 120.0
C4—C5—H5 120.0  C23—C22—H22 120.0
C5—C6—C1 120.0  C22—C23—C18 120.0
C5—C6—H6 120.0  C22—C23—H23 120.0
C1—C6—H6 120.0  C18—C23—H23 120.0
C2A—C1A—C6A 120.0  C19A—C18A—C23A 120.0
C2A—C1A—N1 118 (2)  C19A—C18A—N3 119 (3)
C6A—C1A—N1 122 (2)  C23A—C18A—N3 120 (3)
C1A—C2A—C3A 120.0  C20A—C19A—C18A 120.0
C1A—C2A—H2A 120.0  C20A—C19A—H19A 120.0
C3A—C2A—H2A 120.0  C18A—C19A—H19A 120.0
C4A—C3A—C2A 120.0  C19A—C20A—C21A 120.0
C4A—C3A—H3A 120.0  C19A—C20A—H20A 120.0
C2A—C3A—H3A 120.0  C21A—C20A—H20A 120.0
C3A—C4A—C5A 120.0  C20A—C21A—C22A 120.0
C3A—C4A—H4A 120.0  C20A—C21A—H21A 120.0
C5A—C4A—H4A 120.0  C22A—C21A—H21A 120.0
C6A—C5A—C4A 120.0  C23A—C22A—C21A 120.0
C6A—C5A—H5A 120.0  C23A—C22A—H22A 120.0
C4A—C5A—H5A 120.0  C21A—C22A—H22A 120.0
C5A—C6A—C1A 120.0  C22A—C23A—C18A 120.0
C5A—C6A—H6A 120.0  C22A—C23A—H23A 120.0
C1A—C6A—H6A 120.0  C18A—C23A—H23A 120.0
N1—C7—C8 114.2 (13)  N3—C24—C25 111.9 (14)
N1—C7—H7A 108.7  N3—C24—H24A 109.2
C8—C7—H7A 108.7  C25—C24—H24A 109.2
N1—C7—H7B 108.7  N3—C24—H24B 109.2
C8—C7—H7B 108.7  C25—C24—H24B 109.2
H7A—C7—H7B 107.6  H24A—C24—H24B 107.9
N2—C8—C7 111.8 (13)  N4—C25—C24 111.5 (12)
N2—C8—H8A 109.3  N4—C25—H25A 109.3
C7—C8—H8A 109.3  C24—C25—H25A 109.3
N2—C8—H8B 109.3  N4—C25—H25B 109.3
C7—C8—H8B 109.3  C24—C25—H25B 109.3
H8A—C8—H8B | 107.9 | H25A—C25—H25B | 108.0
N2—C9—C10 | 110.8 (12) | N4—C26—C27 | 110.5 (13)
N2—C9—H9A | 109.5 | N4—C26—H26A | 109.6
C10—C9—H9A | 109.5 | C27—C26—H26A | 109.6
N2—C9—H9B | 109.5 | N4—C26—H26B | 109.6
C10—C9—H9B | 109.5 | C27—C26—H26B | 109.6
H9A—C9—H9B | 108.1 | H26A—C26—H26B | 108.1
N1—C10—C9 | 112.7 (13) | N3—C27—C26 | 113.3 (13)
N1—C10—H10A | 109.1 | N3—C27—H27A | 108.9
C9—C10—H10A | 109.1 | C26—C27—H27A | 108.9
N1—C10—H10B | 109.1 | N3—C27—H27B | 108.9
C9—C10—H10B | 109.1 | C26—C27—H27B | 108.9
H10A—C10—H10B | 107.8 | H27A—C27—H27B | 107.7
O2—S1—O3 | 114.3 (10) | O5—S2—O6 | 112.7 (8)
O2—S1—O1 | 113.6 (8) | O5—S2—O4 | 116.2 (9)
O3—S1—O1 | 111.2 (8) | O6—S2—O4 | 110.6 (8)
O2—S1—C11 | 106.6 (7) | O5—S2—C28 | 106.9 (8)
O3—S1—C11 | 105.8 (7) | O6—S2—C28 | 105.0 (7)
O1—S1—C11 | 104.5 (7) | O4—S2—C28 | 104.5 (7)
C16—C11—C12 | 115.3 (15) | C29—C28—C33 | 116.1 (14)
C16—C11—S1 | 123.0 (12) | C29—C28—S2 | 123.0 (12)
C12—C11—S1 | 121.3 (12) | C33—C28—S2 | 120.7 (12)
C13—C12—C11 | 119.8 (17) | C28—C29—C30 | 123.4 (16)
C13—C12—H12 | 120.1 | C28—C29—H29 | 118.3
C11—C12—H12 | 120.1 | C30—C29—H29 | 118.3
C14—C13—C12 | 124.9 (19) | C29—C30—C31 | 122.3 (18)
C14—C13—H13 | 117.5 | C29—C30—H30 | 118.9
C12—C13—H13 | 117.5 | C31—C30—H30 | 118.9
C13—C14—C15 | 115.2 (19) | C30—C31—C32 | 115.3 (19)
C13—C14—C17 | 124 (2) | C30—C31—C34 | 123 (2)
C15—C14—C17 | 120 (2) | C32—C31—C34 | 121 (2)
C16—C15—C14 | 121.0 (18) | C31—C32—C33 | 123.4 (18)
C16—C15—H15 | 119.5 | C31—C32—H32 | 118.3
C14—C15—H15 | 119.5 | C33—C32—H32 | 118.3
C11—C16—C15 | 123.5 (17) | C32—C33—C28 | 119.5 (16)
C11—C16—H16 | 118.3 | C32—C33—H33 | 120.2
C15—C16—H16 | 118.3 | C28—C33—H33 | 120.2
C14—C17—H17A | 109.5 | C31—C34—H34A | 109.5
C14—C17—H17B | 109.5 | C31—C34—H34B | 109.5
H17A—C17—H17B | 109.5 | H34A—C34—H34B | 109.5
C14—C17—H17C | 109.5 | C31—C34—H34C | 109.5
H17A—C17—H17C | 109.5 | H34A—C34—H34C | 109.5
H17B—C17—H17C | 109.5 | H34B—C34—H34C | 109.5
C7—N1—C1—C2 | −165 (2) | C27—N3—C18—C19 | 163 (2)
C10—N1—C1—C2 | −26 (3) | C24—N3—C18—C19 | 23 (3)
C7—N1—C1—C6 | 21 (3) | C27—N3—C18—C23 | −23 (3)
C10—N1—C1—C6 | 159 (2) | C24—N3—C18—C23 | −162 (2)
Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A     | D—H···A |
|-------------|------|-------|-----------|---------|
| N2—H21N···O6 | 0.89 | 2.07  | 2.884 (18) | 151     |
| N2—H22N···O4i | 0.89 | 1.92  | 2.774 (17) | 161     |
| C9—H9B···O1ii | 0.97 | 2.64  | 3.534 (19) | 154     |
| N4—H41N···O3ii | 0.89 | 1.92  | 2.788 (17) | 163     |
| N4—H42N···O1 | 0.89 | 2.09  | 2.890 (18) | 149     |
| N4—H42N···O5 | 0.89 | 2.43  | 2.865 (18) | 111     |
| C25—H25···O6iii | 0.97 | 2.63  | 3.520 (18) | 153     |

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

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4-Phenylpiperazin-1-ium 4-carboxy-2,3-dihydroxybutanoate monohydrate (11)

Crystal data

C10H15N2⁺·C4H5O6⁻·H2O

Mr = 330.33

Orthorhombic, P2_12_12_1

a = 7.1185 (7) Å
b = 7.5255 (8) Å

c = 29.955 (3) Å

V = 1604.7 (3) Å³

Z = 4

F(000) = 704

D_x = 1.367 Mg m⁻³

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 3790 reflections

θ = 2.9–27.8°

µ = 0.11 mm⁻¹

T = 293 K

Prism, colourless

0.42 × 0.32 × 0.24 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire

CCD diffractometer

Radiation source: Enhance (Mo) X-ray Source

Rotation method data acquisition using ω scans.

Absorption correction: multi-scan (CrysalisRED; Oxford Diffraction, 2007)

T_min = 0.883, T_max = 1.000

6773 measured reflections

3354 independent reflections

2808 reflections with I > 2σ(I)

R(int) = 0.019

θ_max = 27.8°, θ_min = 2.9°

h = −9→9

k = −6→9

l = −36→38

Refinement

Refinement on F²

Least-squares matrix: full

R(F²) = 0.045

wR(F²) = 0.100

S = 1.09

3354 reflections

260 parameters

211 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(Fo)² + (0.0359P)² + 0.5036P]

where P = (Fo² + 2Fc²)/3

(Δ/σ)max < 0.001

Δρ_max = 0.20 e Å⁻³

Δρ_min = −0.16 e Å⁻³

Absolute structure: Flack x determined using 912 quotients [(I)−(I)⁰] / [(I) + (I)⁰] (Parsons et al., 2013)

Absolute structure parameter: −0.2 (5)

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sup-50
**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 (Å²)**

|   | x       | y       | z       | U(eq) | Occ. (<1) |
|---|---------|---------|---------|-------|-----------|
| N1 | 0.2138 (4) | 0.3376 (4) | 0.69293 (7) | 0.0428 (6) |           |
| N2 | 0.0481 (4) | 0.3028 (5) | 0.60649 (9) | 0.0515 (8) |           |
| H21 | 0.057 (6) | 0.189 (3) | 0.6004 (13) | 0.062* |           |
| H22 | −0.007 (5) | 0.338 (5) | 0.5825 (9) | 0.062* |           |
| C1 | 0.3025 (8) | 0.3071 (7) | 0.7352 (2) | 0.0393 (16) | 0.611 (13) |
| C2 | 0.4926 (8) | 0.2687 (11) | 0.73967 (16) | 0.0489 (16) | 0.611 (13) |
| H2 | 0.566167 | 0.250879 | 0.714417 | 0.059* | 0.611 (13) |
| C3 | 0.5726 (8) | 0.2568 (12) | 0.78189 (19) | 0.0596 (18) | 0.611 (13) |
| H5 | 0.399769 | 0.231094 | 0.784885 | 0.071* | 0.611 (13) |
| C4 | 0.4626 (12) | 0.2834 (8) | 0.81965 (16) | 0.0629 (19) | 0.611 (13) |
| H4 | 0.516140 | 0.275436 | 0.847893 | 0.076* | 0.611 (13) |
| C5 | 0.2725 (11) | 0.3218 (11) | 0.8152 (2) | 0.0565 (19) | 0.611 (13) |
| H5 | 0.198908 | 0.339564 | 0.840434 | 0.068* | 0.611 (13) |
| C6 | 0.1925 (8) | 0.3336 (10) | 0.7730 (3) | 0.0469 (17) | 0.611 (13) |
| H6 | 0.065303 | 0.359351 | 0.769967 | 0.056* | 0.611 (13) |
| C1A | 0.3005 (14) | 0.3277 (13) | 0.7366 (4) | 0.044 (2) | 0.389 (13) |
| C2A | 0.4913 (13) | 0.3634 (19) | 0.7408 (3) | 0.054 (2) | 0.389 (13) |
| H2A | 0.561166 | 0.395753 | 0.715828 | 0.065* | 0.389 (13) |
| C3A | 0.5777 (13) | 0.3508 (18) | 0.7823 (3) | 0.058 (2) | 0.389 (13) |
| H3A | 0.705291 | 0.374729 | 0.785092 | 0.069* | 0.389 (13) |
| C4A | 0.4732 (18) | 0.3026 (13) | 0.8196 (3) | 0.060 (3) | 0.389 (13) |
| H4A | 0.531021 | 0.294126 | 0.847328 | 0.073* | 0.389 (13) |
| C5A | 0.2825 (18) | 0.2669 (16) | 0.8154 (4) | 0.052 (2) | 0.389 (13) |
| H5A | 0.219626 | 0.234547 | 0.840300 | 0.062* | 0.389 (13) |
| C6A | 0.1961 (13) | 0.2795 (15) | 0.7739 (5) | 0.044 (2) | 0.389 (13) |
| H6A | 0.068497 | 0.255570 | 0.771037 | 0.053* | 0.389 (13) |
| C7 | 0.0322 (4) | 0.2513 (6) | 0.68665 (10) | 0.0600 (10) |           |
| H7A | −0.044378 | 0.269546 | 0.713032 | 0.072* |           |
| H7B | 0.051046 | 0.124480 | 0.683019 | 0.072* |           |
| C8 | −0.0694 (5) | 0.3230 (6) | 0.64654 (11) | 0.0615 (11) |           |
| H8A | −0.186632 | 0.259277 | 0.642510 | 0.074* |           |
| H8B | −0.098445 | 0.447573 | 0.651123 | 0.074* |           |
| C9 | 0.2345 (5) | 0.3864 (6) | 0.61270 (11) | 0.0626 (11) |           |
| H9A | 0.219400 | 0.513976 | 0.615495 | 0.075* |           |
| H9B | 0.311852 | 0.363336 | 0.586672 | 0.075* |           |
| C10 | 0.3310 (4) | 0.3153 (6) | 0.65361 (9) | 0.0516 (9) |           |
| H10A | 0.358743 | 0.190224 | 0.649445 | 0.062* |           |
| H10B | 0.448994 | 0.377545 | 0.657941 | 0.062* |           |
| O1 | 0.3807 (3) | 0.8465 (3) | 0.42742 (7) | 0.0391 (5) |           |
### Atomic displacement parameters (Å²)

|     | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|-----|---------|---------|---------|---------|---------|---------|
| N1  | 0.0367 (13) | 0.0643 (16) | 0.0275 (11) | -0.0036 (13) | -0.0040 (10) | 0.0023 (12) |
| N2  | 0.0418 (14) | 0.083 (2) | 0.0299 (13) | -0.0080 (17) | -0.0080 (11) | 0.0064 (15) |
| C1  | 0.042 (3) | 0.047 (3) | 0.029 (3) | 0.000 (3) | -0.004 (3) | -0.009 (3) |
| C2  | 0.044 (3) | 0.067 (4) | 0.037 (2) | 0.012 (3) | -0.003 (2) | 0.001 (3) |
| C3  | 0.056 (3) | 0.075 (5) | 0.048 (3) | 0.012 (4) | -0.017 (2) | 0.003 (4) |
| C4  | 0.074 (4) | 0.079 (4) | 0.036 (3) | 0.007 (4) | -0.016 (3) | 0.002 (3) |
| C5  | 0.067 (3) | 0.069 (5) | 0.033 (3) | 0.005 (4) | -0.002 (3) | -0.002 (3) |
| C6  | 0.048 (3) | 0.056 (4) | 0.037 (3) | 0.009 (3) | -0.002 (2) | -0.005 (3) |
| C1A | 0.044 (4) | 0.051 (5) | 0.036 (4) | 0.003 (4) | -0.005 (4) | 0.010 (4) |
| C2A | 0.050 (4) | 0.072 (5) | 0.039 (4) | -0.001 (5) | -0.003 (3) | 0.006 (4) |
| C3A | 0.052 (4) | 0.078 (6) | 0.043 (4) | 0.000 (5) | -0.016 (3) | -0.001 (5) |
| C4A | 0.068 (5) | 0.078 (5) | 0.036 (4) | 0.001 (5) | -0.017 (4) | -0.002 (4) |
| C5A | 0.065 (4) | 0.058 (5) | 0.032 (4) | 0.005 (4) | 0.001 (4) | 0.001 (4) |
| C6A | 0.048 (4) | 0.048 (5) | 0.036 (4) | 0.002 (4) | -0.001 (3) | 0.003 (4) |
| C7  | 0.0388 (17) | 0.108 (3) | 0.0335 (16) | -0.015 (2) | 0.0016 (13) | 0.0005 (19) |
| C8  | 0.0405 (18) | 0.101 (3) | 0.0431 (18) | 0.007 (2) | -0.0058 (14) | -0.010 (2) |
| C9  | 0.051 (2) | 0.097 (3) | 0.0398 (17) | -0.023 (2) | -0.0084 (15) | 0.0173 (19) |
| C10 | 0.0357 (16) | 0.085 (3) | 0.0343 (15) | -0.0079 (18) | -0.0012 (12) | 0.0073 (17) |
| O1  | 0.0305 (10) | 0.0412 (11) | 0.0458 (11) | -0.0059 (9) | 0.0039 (9) | -0.0013 (10) |
| O2  | 0.0379 (12) | 0.0274 (10) | 0.0954 (18) | 0.0020 (9) | 0.0058 (12) | -0.0045 (12) |
| O3  | 0.0255 (10) | 0.0319 (10) | 0.0635 (14) | -0.0007 (9) | -0.0047 (10) | -0.0087 (11) |
| O4  | 0.0355 (11) | 0.0538 (12) | 0.0323 (10) | -0.0080 (11) | 0.0028 (9) | -0.0162 (10) |
| O5  | 0.0641 (15) | 0.0544 (13) | 0.0354 (11) | -0.0131 (12) | 0.0138 (10) | 0.0052 (10) |
| O6  | 0.0472 (12) | 0.0257 (9) | 0.0379 (10) | -0.0018 (9) | 0.0084 (9) | -0.0025 (9) |
| C11 | 0.0325 (14) | 0.0308 (14) | 0.0336 (14) | -0.0019 (13) | -0.0026 (12) | -0.0016 (12) |
| C12 | 0.0231 (12) | 0.0276 (13) | 0.0326 (13) | 0.0017 (11) | -0.0013 (11) | -0.0044 (12) |
| C13 | 0.0249 (13) | 0.0353 (14) | 0.0248 (12) | -0.0001 (12) | 0.0015 (11) | -0.0045 (11) |
C14 0.0291 (14) 0.0349 (14) 0.0293 (13) 0.0013 (12) 0.0002 (11) 0.0009 (12)
O7 0.0411 (13) 0.0784 (19) 0.0691 (16) 0.0049 (14) −0.0092 (12) −0.0320 (15)

Geometric parameters (Å, °)

| Bond | Distance (Å) | Angle (°) |
|------|-------------|-----------|
| N1—C1 | 1.434 (6) | C5A—H5A 0.9300 |
| N1—C1A | 1.448 (9) | C6A—H6A 0.9300 |
| N1—C10 | 1.453 (4) | C7—C8 1.502 (5) |
| N1—C7 | 1.459 (4) | C7—H7A 0.9700 |
| N2—C8 | 1.470 (4) | C7—H7B 0.9700 |
| N2—C9 | 1.480 (4) | C8—H8A 0.9700 |
| N2—H21 | 0.88 (2) | C8—H8B 0.9700 |
| N2—H22 | 0.86 (2) | C9—C10 1.503 (4) |
| C1—C2 | 1.3900 | C9—H9A 0.9700 |
| C1—C6 | 1.3900 | C9—H9B 0.9700 |
| C2—C3 | 1.3900 | C10—H10A 0.9700 |
| C2—H2 | 0.9300 | C10—H10B 0.9700 |
| C3—C4 | 1.3900 | O1—C11 1.255 (3) |
| C3—H3 | 0.9300 | O2—C11 1.247 (3) |
| C4—C5 | 1.3900 | O3—C12 1.417 (3) |
| C4—H4 | 0.9300 | O3—H3O 0.83 (2) |
| C5—C6 | 1.3900 | O4—C13 1.405 (3) |
| C5—H5 | 0.9300 | O4—H4O 0.79 (2) |
| C6—H6 | 0.9300 | O5—C14 1.205 (3) |
| C1A—C2A | 1.3900 | O6—C14 1.312 (3) |
| C1A—C6A | 1.3900 | O6—H6O 0.83 (2) |
| C2A—C3A | 1.3900 | C11—C12 1.528 (4) |
| C2A—H2A | 0.9300 | C12—C13 1.532 (4) |
| C3A—C4A | 1.3900 | C12—H12 0.9800 |
| C3A—H3A | 0.9300 | C13—C14 1.516 (4) |
| C4A—C5A | 1.3900 | C13—H13 0.9800 |
| C4A—H4A | 0.9300 | O7—H71O 0.84 (2) |
| C5A—C6A | 1.3900 | O7—H72O 0.85 (2) |
| C1—N1—C10 | 116.4 (3) | N1—C7—C8 111.7 (3) |
| C1A—N1—C10 | 118.8 (5) | N1—C7—H7A 109.3 |
| C1—N1—C7 | 115.6 (3) | C8—C7—H7A 109.3 |
| C1A—N1—C7 | 118.1 (5) | N1—C7—H7B 109.3 |
| C10—N1—C7 | 110.7 (2) | C8—C7—H7B 109.3 |
| C8—N2—C9 | 111.3 (3) | H7A—C7—H7B 107.9 |
| C8—N2—H21 | 108 (3) | N2—C8—C7 110.0 (3) |
| C9—N2—H21 | 112 (3) | N2—C8—H8A 109.7 |
| C8—N2—H22 | 113 (3) | C7—C8—H8A 109.7 |
| C9—N2—H22 | 112 (3) | N2—C8—H8B 109.7 |
| H21—N2—H22 | 99 (4) | C7—C8—H8B 109.7 |
| C2—C1—C6 | 120.0 | H8A—C8—H8B 108.2 |
| C2—C1—N1 | 123.2 (5) | N2—C9—C10 111.2 (3) |
| C6—C1—N1 | 116.6 (5) | N2—C9—H9A 109.4 |
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|-----------|----------------------|-----------|
| C1—C2—C3            | 120.0     | C10—C9—H9A          | 109.4     |
| C1—C2—H2            | 120.0     | N2—C9—H9B           | 109.4     |
| C3—C2—H2            | 120.0     | C10—C9—H9B          | 109.4     |
| C4—C3—C2            | 120.0     | H9A—C9—H9B          | 108.0     |
| C4—C3—H3            | 120.0     | N1—C10—C9           | 110.9 (3) |
| C2—C3—H3            | 120.0     | N1—C10—H10A         | 109.5     |
| C3—C4—C5            | 120.0     | C9—C10—H10A         | 109.5     |
| C3—C4—H4            | 120.0     | N1—C10—H10B         | 109.5     |
| C5—C4—H4            | 120.0     | C9—C10—H10B         | 109.5     |
| C4—C5—C6            | 120.0     | H10A—C10—H10B       | 108.0     |
| C4—C5—H5            | 120.0     | C12—O3—H3O          | 109.2     |
| C6—C5—H5            | 120.0     | C13—O4—H4O          | 111.3 (3) |
| C5—C6—C1            | 120.0     | C14—O6—H6O          | 112.3 (2) |
| C5—C6—H6            | 120.0     | O2—C11—O1           | 126.0 (3) |
| C1—C6—H6            | 120.0     | O2—C11—C12          | 116.2 (2) |
| C2A—C1A—C6A         | 120.0     | O1—C11—C12          | 117.8 (2) |
| C2A—C1A—N1          | 119.3 (7) | O3—C12—C11          | 111.7 (2) |
| C6A—C1A—N1          | 120.7 (7) | O3—C12—C13          | 109.3 (2) |
| C1A—C2A—C3A         | 120.0     | C11—C12—C13         | 110.2 (2) |
| C1A—C2A—H2A         | 120.0     | C12—H12—H3O         | 108.5     |
| C3A—C2A—H2A         | 120.0     | C11—C12—H12         | 108.5     |
| C4A—C3A—C2A         | 120.0     | C13—C12—H12         | 108.5     |
| C4A—C3A—H3A         | 120.0     | C14—C13—C14         | 112.1 (2) |
| C2A—C3A—H3A         | 120.0     | O4—C13—C12          | 110.9 (2) |
| C3A—C4A—C5A         | 120.0     | O4—C13—C12          | 109.7 (2) |
| C3A—C4A—H4A         | 120.0     | C14—C13—H13         | 108.0     |
| C5A—C4A—H4A         | 120.0     | C14—C13—H13         | 108.0     |
| C4A—C5A—C6A         | 120.0     | C12—C13—H13         | 108.0     |
| C4A—C5A—H5A         | 120.0     | O5—C14—O6           | 124.9 (3) |
| C6A—C5A—H5A         | 120.0     | O5—C14—C13          | 123.3 (2) |
| C5A—C6A—C1A         | 120.0     | O6—C14—C13          | 111.8 (2) |
| C5A—C6A—H6A         | 120.0     | H71O—O7—H72O        | 105.4 (4) |
| C1A—C6A—H6A         | 120.0     |                     |           |
| C10—N1—C1—C2        | 3.8 (6)   | N1—C1A—C6A—C5A      | 178.6 (8) |
| C7—N1—C1—C2         | 136.3 (5) | C1—N1—C7—C8         | 166.9 (4) |
| C10—N1—C1—C6        | 178.1 (4) | C1A—N1—C7—C8        | 160.3 (5) |
| C7—N1—C1—C6         | −49.5 (5) | C10—N1—C7—C8        | −58.0 (4) |
| C6—C1—C2—C3         | 0.0       | C9—N2—C8—C7         | −54.9 (5) |
| N1—C1—C2—C3         | 174.0 (5) | N1—C7—C8—N2         | 56.7 (5)  |
| C1—C2—C3—C4         | 0.0       | C8—N2—C9—C10        | 54.9 (5)  |
| C2—C3—C4—C5         | 0.0       | C1—N1—C10—C9        | −168.4 (4) |
| C3—C4—C5—C6         | 0.0       | C1A—N1—C10—C9       | −161.7 (5) |
| C4—C5—C6—C1         | 0.0       | C7—N1—C10—C9        | 56.8 (4)  |
| C2—C1—C6—C5         | 0.0       | N2—C9—C10—N1        | −55.5 (4) |
| N1—C1—C6—C5         | −174.4 (5)| O2—C11—C12—O3       | 6.3 (3)   |
| C10—N1—C1A—C2A      | 23.7 (8)  | O1—C11—C12—O3       | −173.2 (2) |
| C7—N1—C1A—C2A       | 162.3 (6) | O2—C11—C12—C13      | −115.4 (3) |
C10—N1—C1A—C6A −154.9 (6) O1—C11—C12—C13 65.1 (3)
C7—N1—C1A—C6A −16.3 (9) O3—C12—C13—O4 −66.8 (3)
C6A—C1A—C2A—C3A 0.0 C11—C12—C13—C14 56.4 (3)
N1—C1A—C2A—C3A −178.6 (8) O3—C12—C13—C14 −179.2 (2)
C1A—C2A—C3A—C4A 0.0 C11—C12—C13—C14 −179.2 (2)
C2A—C3A—C4A—C5A 0.0 O4—C13—C14—O5 0.4 (4)
C3A—C4A—C5A—C6A 0.0 O3—C12—C13—C14 −123.3 (3)
C4A—C5A—C6A—C1A 0.0 C12—C13—C14—O5 −123.3 (3)
C2A—C1A—C6A—C5A 0.0 C12—C13—C14—O6 179.5 (2)

Hydrogen-bond geometry (Å, º)

\[
\begin{array}{cccc}
D—H···A & D—H & H···A & D···A \\
N2—H21···O7i & 0.88 (2) & 1.95 (2) & 2.808 (5) & 164 (4) \\
N2—H22···O1ii & 0.86 (2) & 2.52 (3) & 3.069 (4) & 123 (2) \\
N2—H22···O5 & 0.86 (2) & 2.22 (3) & 2.820 (3) & 127 (3) \\
N2—H22···O6iii & 0.86 (2) & 2.41 (3) & 2.992 (3) & 125 (3) \\
C9—H9i···O2iv & 0.97 & 2.61 & 3.276 (4) & 126 \\
O3—H3···O1iv & 0.83 (2) & 2.17 (3) & 2.614 (3) & 114 (3) \\
O3—H3···O4ii & 0.83 (2) & 2.04 (2) & 2.789 (3) & 150 (3) \\
O4—H4···O1iv & 0.79 (2) & 2.06 (3) & 2.773 (3) & 151 (3) \\
O6—H6···O2v & 0.83 (2) & 1.67 (2) & 2.501 (3) & 174 (3) \\
O7—H7···O3v & 0.84 (2) & 1.95 (2) & 2.780 (3) & 171 (4) \\
O7—H7···O1vi & 0.85 (2) & 1.97 (2) & 2.821 (3) & 178 (4) \\
\end{array}
\]

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

4-Phenylpiperazin-1-ium fumarate (12)

**Crystal data**

\( \text{C}_{10}\text{H}_{15}\text{N}_{2}^{+}\cdot\text{C}_{4}\text{H}_{3}\text{O}_{4}^{-} \)

\( \text{Mr} = 278.30 \)

Orthorhombic, \( \text{Pca}2_1 \)

\( a = 26.702 (1) \) Å

\( b = 7.9626 (3) \) Å

\( c = 6.7571 (3) \) Å

\( V = 1436.68 (10) \) Å³

\( Z = 4 \)

\( F(000) = 592 \)

**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

(CrysAlisRED; Oxford Diffraction, 2007)

\( T_{\text{min}} = 0.894, T_{\text{max}} = 1.000 \)

\( D_d = 1.287 \text{ Mg m}^{-3} \)

\( \text{Mo } \text{Ka radiation, } \lambda = 0.71073 \) Å

\( \theta = 2.7–27.8° \)

\( \mu = 0.10 \text{ mm}^{-1} \)

\( T = 293 \) K

- Prism, light brown
- \( 0.48 \times 0.44 \times 0.40 \) mm

9534 measured reflections

3127 independent reflections

2770 reflections with \( I > 2\sigma(I) \)

\( R_{\text{free}} = 0.018, \theta_{\text{max}} = 27.9°, \theta_{\text{min}} = 3.0° \)

\( h = -33 \rightarrow 33 \)

\( k = -10 \rightarrow 5 \)

\( l = -8 \rightarrow 8 \)

**supporting information**

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sup-55
Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.077$

$S = 1.06$

3127 reflections

191 parameters

4 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

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 ($\overline{A}^2$)**

|    | x     | y     | z     | $U_{iso}/U_{eq}$ |
|----|-------|-------|-------|------------------|
| N1 | 0.07139 (6) | 0.0974 (2) | 0.4560 (3) | 0.0396 (4) |
| N2 | 0.15289 (7) | 0.1889 (2) | 0.2018 (3) | 0.0359 (4) |
| H21 | 0.1639 (9) | 0.258 (3) | 0.111 (3) | 0.043* |
| H22 | 0.1758 (8) | 0.112 (3) | 0.231 (4) | 0.043* |
| C1 | 0.02675 (7) | 0.1920 (3) | 0.4495 (3) | 0.0341 (5) |
| H2 | −0.01118 (8) | 0.1565 (3) | 0.3155 (4) | 0.0460 (5) |
| C3 | −0.06524 | 0.072842 | 0.221209 | 0.055* |
| C4 | −0.05581 (9) | 0.2442 (3) | 0.3210 (5) | 0.0554 (6) |
| H3 | −0.08037 | 0.217775 | 0.230469 | 0.066* |
| C5 | −0.06407 (10) | 0.3685 (3) | 0.4555 (5) | 0.0581 (8) |
| H4 | −0.094144 | 0.427343 | 0.457231 | 0.070* |
| C6 | −0.02681 (11) | 0.4041 (4) | 0.5880 (5) | 0.0605 (8) |
| H5 | −0.031873 | 0.488166 | 0.681492 | 0.073* |
| C7 | 0.01794 (9) | 0.3187 (3) | 0.5862 (4) | 0.0493 (6) |
| H6 | 0.042619 | 0.346194 | 0.677785 | 0.059* |
| C8 | 0.11662 (9) | 0.1763 (4) | 0.5335 (4) | 0.0516 (7) |
| C9 | 0.140074 | 0.089729 | 0.573846 | 0.062* |
| C10 | 0.108145 | 0.242129 | 0.649545 | 0.062* |
| C11 | 0.14116 (9) | 0.2881 (3) | 0.3825 (4) | 0.0453 (6) |
| C12 | 0.118887 | 0.380029 | 0.348976 | 0.054* |
| C13 | 0.171722 | 0.335098 | 0.436782 | 0.054* |
| C14 | 0.10846 (8) | 0.0982 (3) | 0.1241 (3) | 0.0406 (5) |
| C15 | 0.118462 | 0.025512 | 0.015935 | 0.049* |
| C16 | 0.084244 | 0.178364 | 0.073747 | 0.049* |
| C17 | 0.08503 (8) | −0.0048 (3) | 0.2859 (4) | 0.0458 (6) |
| Atomic displacement parameters ($\overline{A}^2$) | \(U^{11}\) | \(U^{22}\) | \(U^{33}\) | \(U^{12}\) | \(U^{13}\) | \(U^{23}\) |
|---------------------------------|--------|--------|--------|--------|--------|--------|
| N1                              | 0.0316 (9) | 0.0426 (10) | 0.0447 (11) | 0.0009 (8) | 0.0062 (8) | 0.0066 (9) |
| N2                              | 0.0285 (9) | 0.0317 (9) | 0.0504 (12) | 0.0015 (7) | 0.0070 (8) | 0.0071 (9) |
| C1                              | 0.0292 (10) | 0.0343 (10) | 0.0389 (11) | −0.0044 (8) | 0.0063 (9) | 0.0047 (10) |
| C2                              | 0.0385 (11) | 0.0495 (12) | 0.0502 (14) | −0.0029 (10) | 0.0001 (12) | −0.0091 (13) |
| C3                              | 0.0355 (11) | 0.0636 (15) | 0.0670 (17) | −0.0042 (11) | −0.0095 (14) | 0.0038 (16) |
| C4                              | 0.0364 (13) | 0.0466 (14) | 0.091 (2) | 0.0085 (11) | 0.0081 (15) | 0.0066 (16) |
| C5                              | 0.0538 (16) | 0.0474 (15) | 0.080 (2) | 0.0057 (12) | 0.0095 (15) | −0.0165 (15) |
| C6                              | 0.0423 (13) | 0.0489 (14) | 0.0567 (16) | −0.0027 (11) | −0.0030 (12) | −0.0138 (13) |
| C7                              | 0.0339 (13) | 0.0817 (19) | 0.0391 (13) | 0.0062 (13) | −0.0057 (10) | 0.0027 (14) |
| C8                              | 0.0279 (10) | 0.0477 (13) | 0.0604 (16) | −0.0049 (10) | −0.0010 (10) | −0.0136 (12) |
| C9                              | 0.0338 (12) | 0.0459 (13) | 0.0419 (13) | −0.0004 (10) | 0.0034 (10) | −0.0075 (11) |
| C10                             | 0.0368 (11) | 0.0295 (10) | 0.0709 (17) | −0.0033 (9) | 0.0130 (12) | −0.0028 (12) |
| O1                              | 0.0309 (7) | 0.0259 (7) | 0.0802 (13) | −0.0035 (6) | 0.0087 (9) | 0.0026 (9) |
| O2                              | 0.0367 (7) | 0.0188 (6) | 0.0654 (11) | 0.0011 (6) | 0.0051 (8) | 0.0038 (8) |
| O3                              | 0.0374 (8) | 0.0208 (6) | 0.0604 (11) | 0.0016 (6) | 0.0103 (7) | −0.0015 (7) |
| O4                              | 0.0305 (8) | 0.0258 (7) | 0.0671 (11) | 0.0008 (6) | 0.0107 (7) | 0.0088 (7) |
| C11                             | 0.0332 (10) | 0.0224 (9) | 0.0338 (11) | −0.0009 (7) | 0.0011 (9) | 0.0004 (9) |
| C12                             | 0.0297 (9) | 0.0231 (8) | 0.0443 (12) | −0.0037 (8) | 0.0045 (9) | 0.0019 (9) |
| C13                             | 0.0297 (9) | 0.0224 (8) | 0.0369 (11) | −0.0028 (7) | 0.0024 (9) | 0.0029 (9) |
| C14                             | 0.0283 (9) | 0.0201 (8) | 0.0365 (10) | 0.0003 (7) | −0.0024 (9) | 0.0033 (9) |

Geometric parameters (Å, °)

| N1—C1       | 1.411 (3) | C7—H7A    | 0.9700 |
| N1—C10      | 1.455 (3) | C7—H7B    | 0.9700 |
| N1—C7       | 1.459 (3) | C8—H8A    | 0.9700 |
| N2—C9       | 1.485 (3) | C8—H8B    | 0.9700 |
| N2—C8       | 1.487 (3) | C9—C10    | 1.504 (3) |
| N2—H21      | 0.87 (2)  | C9—H9A    | 0.9700 |
| N2—H22      | 0.89 (2)  | C9—H9B    | 0.9700 |
| C1—C2       | 1.388 (3) | C10—H10A  | 0.9700 |
| Bond          | Length (Å) | Bond          | Length (Å) | Angle (°) |
|---------------|------------|---------------|------------|-----------|
| C1—C6         | 1.388 (3)  | C10—H10B      | 0.9700     |
| C2—C3         | 1.382 (3)  | O1—C11        | 1.223 (2)  |
| C2—H2         | 0.9300     | O2—C11        | 1.286 (2)  |
| C3—C4         | 1.361 (4)  | O2—H2O        | 0.921 (19) |
| C3—H3         | 0.9300     | O3—C14        | 1.273 (2)  |
| C4—C5         | 1.368 (4)  | O4—C14        | 1.234 (2)  |
| C4—H4         | 0.9300     | C11—C12       | 1.485 (2)  |
| C5—C6         | 1.375 (4)  | C12—C13       | 1.306 (3)  |
| C5—H5         | 0.9300     | C12—H12       | 0.9300     |
| C6—H6         | 0.9300     | C13—C14       | 1.490 (2)  |
| C7—C8         | 1.505 (4)  | C13—H13       | 0.9300     |
| C1—N1—C10     | 119.1 (2)  | H7A—C7—H7B    | 107.9      |
| C1—N1—C7      | 118.8 (2)  | N2—C8—C7      | 109.53 (19)|
| C10—N1—C7     | 108.50 (18)| N2—C8—H8A     | 109.8      |
| C9—N2—C8      | 112.35 (16)| N2—C8—H8B     | 109.8      |
| C9—N2—H21     | 109.1 (17) | N2—C8—H8B     | 109.8      |
| C8—N2—H21     | 108.3 (17) | C7—C8—H8B     | 109.8      |
| C9—N2—H22     | 107.1 (16) | H8A—C8—H8B    | 108.2      |
| C8—N2—H22     | 109.1 (17) | N2—C9—C10     | 109.9 (2)  |
| H21—N2—H22    | 111 (2)    | N2—C9—H9A     | 109.7      |
| C2—C1—C6      | 117.3 (2)  | C10—C9—H9A    | 109.7      |
| C2—C1—N1      | 121.9 (2)  | N2—C9—H9B     | 109.7      |
| C6—C1—N1      | 120.7 (2)  | C10—C9—H9B    | 109.7      |
| C3—C2—C1      | 120.6 (2)  | H9A—C9—H9B    | 108.2      |
| C3—C2—H2      | 119.7      | N1—C10—C9     | 111.91 (17)|
| C1—C2—H2      | 119.7      | N1—C10—H10A   | 109.2      |
| C4—C3—C2      | 121.7 (3)  | C9—C10—H10A   | 109.2      |
| C4—C3—H3      | 119.2      | N1—C10—H10B   | 109.2      |
| C2—C3—H3      | 119.2      | C9—C10—H10B   | 109.2      |
| C3—C4—C5      | 118.0 (2)  | H10A—C10—H10B | 107.9      |
| C3—C4—H4      | 121.0      | C11—O2—H2O    | 111.3 (14) |
| C5—C4—H4      | 121.0      | O1—C11—O2     | 125.17 (17)|
| C4—C5—C6      | 121.6 (3)  | O1—C11—C12    | 120.99 (17)|
| C4—C5—H5      | 119.2      | O2—C11—C12    | 113.83 (16)|
| C6—C5—H5      | 119.2      | C13—C12—C11   | 122.85 (17)|
| C5—C6—C1      | 120.8 (2)  | C13—C12—H12   | 118.6      |
| C5—C6—H6      | 119.6      | C11—C12—H12   | 118.6      |
| C1—C6—H6      | 119.6      | C12—C13—C14   | 123.57 (17)|
| N1—C7—C8      | 111.8 (2)  | C12—C13—H13   | 118.2      |
| N1—C7—H7A     | 109.3      | C14—C13—H13   | 118.2      |
| C8—C7—H7A     | 109.3      | O4—C14—O3     | 124.92 (16)|
| N1—C7—H7B     | 109.3      | O4—C14—C13    | 120.10 (17)|
| C8—C7—H7B     | 109.3      | O3—C14—C13    | 114.97 (16)|
| C10—N1—C1—C2  | 18.6 (3)   | C10—N1—C7—C8  | 60.7 (3)   |
| C7—N1—C1—C2   | 154.6 (2)  | C9—N2—C8—C7   | 53.1 (3)   |
| C10—N1—C1—C6  | −165.3 (2) | N1—C7—C8—N2   | −57.3 (3)  |
### Supporting Information

| Bond                  | Angle (°) (esd) |
|-----------------------|-----------------|
| C7—N1—C1—C6          | −29.3 (3)       |
| C6—C1—C2—C3          | −0.4 (4)        |
| N1—C1—C2—C3          | 175.8 (2)       |
| C1—C2—C3—C4          | 0.5 (4)         |
| C2—C3—C4—C5          | −0.5 (4)        |
| C3—C4—C5—C6          | 0.4 (5)         |
| C4—C5—C6—C1          | −0.3 (5)        |
| N1—C1—C6—C5          | −176.0 (3)      |
| C1—N1—C7—C8          | −79.5 (3)       |
| C8—N2—C9—C10         | −52.9 (2)       |
| C1—N1—C10—C9         | 79.8 (2)        |
| C7—N1—C10—C9         | −60.2 (3)       |
| N2—C9—C10—N1         | 56.7 (2)        |
| O1—C11—C12—C13       | −10.5 (4)       |
| O2—C11—C12—C13       | 168.7 (2)       |
| C12—C13—C14—O4       | −9.5 (3)        |
| C12—C13—C14—O3       | 170.9 (2)       |

### Hydrogen-bond geometry (Å, °)

| Bond                  | D—H | H···A | D···A | D—H···A |
|-----------------------|------|-------|-------|---------|
| N2—H21···O4           | 0.87 (2) | 1.88 (2) | 2.741 (2) | 168 (2) |
| N2—H22···O1i          | 0.89 (2) | 1.89 (2) | 2.775 (2) | 172 (2) |
| C7—H7A···O2ii         | 0.97  | 2.51  | 3.317 (3) | 141     |
| C8—H8B···O3iii        | 0.97  | 2.55  | 3.203 (3) | 124     |
| C9—H9A···O2iv         | 0.97  | 2.66  | 3.318 (3) | 126     |
| O2—H2O···O3v          | 0.92 (2) | 1.54 (2) | 2.4610 (18) | 174 (2) |

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