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Twelve 4-(4-methoxyphenyl)piperazin-1-ium salts containing organic anions: supramolecular assembly in one, two and three dimensions

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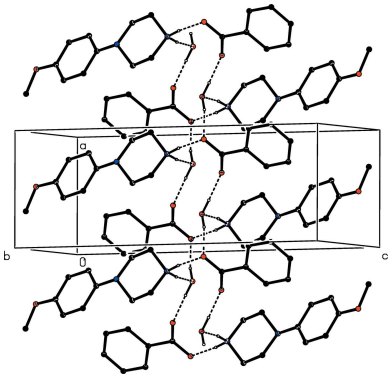
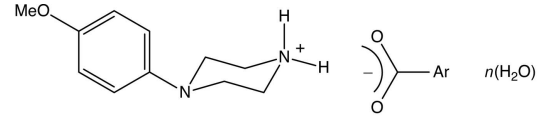
Twelve 4-(4-methoxyphenyl)piperazin-1-ium salts containing organic anions have been prepared and structurally characterized. The monohydrated benzoate, 4-fluorobenzoate, 4-chlorobenzoate and 4-bromobenzoate salts, $C_{11}H_{17}N_2O^+\cdot C_7H_5O_2^-\cdot H_2O$ (I), $C_{11}H_{17}N_2O^+\cdot C_7H_4FO_2^-\cdot H_2O$ (II), $C_{11}H_{17}N_2O^+\cdot C_7H_4ClO_2^-\cdot H_2O$ (III), and $C_{11}H_{17}N_2O^+\cdot C_7H_4BrO_2^-\cdot H_2O$ (IV), respectively, are isomorphous and all exhibit disorder in the 4-methoxyphenyl unit: the components are linked by N—H···O and O—H···O hydrogen bond to form chains of rings. The unsolvated 2-hydroxybenzoate, pyridine-3-carboxylate and 2-hydroxy-3,5-dinitrobenzoate salts, $C_{11}H_{17}N_2O^+\cdot C_7H_5O_3^-$ (V), $C_{11}H_{17}N_2O^+\cdot C_6H_4NO_2^-$ (VI) and $C_{11}H_{17}N_2O^+\cdot C_7H_3N_2O_7^-$ (VII), respectively, are all fully ordered: the components of (V) are linked by multiple N—H···O hydrogen bonds to form a chain of rings; those of (VI) are linked into a three-dimensional framework by a combination of N—H···O, C—H···O and C—H···N hydrogen bonds and those of (VII), where the anion has a structure reminiscent of the picrate anion, are linked into a three-dimensional array by N—H···O and C—H···O hydrogen bonds. The hydrogensuccinate and hydrogenfumarate salts, $C_{11}H_{17}N_2O^+\cdot C_4H_5O_4^-$ (VIII) and $C_{11}H_{17}N_2O^+\cdot C_4H_3O_3^-$ (IX), respectively, are isomorphous, and both exhibit disorder in the anionic component: N—H···O and O—H···O hydrogen bonds link the ions into sheets, which are further linked by C—H···π(arene) interactions. The anion of the hydrogenmaleate salt, $C_{11}H_{17}N_2O^+\cdot C_4H_3O_3^-$ (X), contains a very short and nearly symmetrical O···H···O hydrogen bond, and N—H···O hydrogen bonds link the anions into chains of rings. The ions in the trichloroacetate salt, $C_{11}H_{17}N_2O^+\cdot C_2Cl_3O_2^-$ (XI), are linked into simple chains by N—H···O hydrogen bonds. In the hydrated chloranilate salt, $2C_{11}H_{17}N_2O^+\cdot C_6Cl_2O_4^{2-}\cdot 2H_2O$ (XII), which crystallizes as a non-merohedral twin, the anion lies across a centre of inversion in space group $P2_1/n$, and a combination of N—H···O and O—H···O hydrogen bonds generates complex sheets. Comparisons are made with the structures of some related compounds.



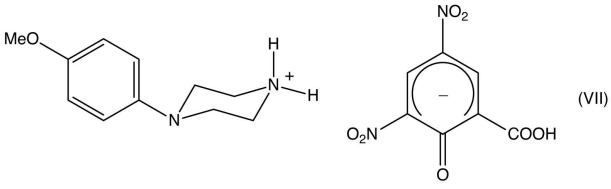
1. Chemical context

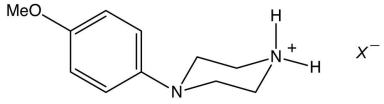
In recent years, *N*-(4-methoxyphenyl)piperazine (MeOPP) has emerged as a new addition to the range of designer recreational drugs, and considerable effort has been invested in the development of methods for the detection both of MeOPP itself and of its metabolites *N*-(4-hydroxyphenyl)piperazine and 4-hydroxyaniline (Arbo *et al.*, 2012) in human fluids (Staack & Maurer, 2003; Staack *et al.*, 2004). MeOPP has euphoric stimulant properties and its action on human physiology is similar to that of amphetamines (Staack

& Maurer, 2005; Wohlfarth *et al.*, 2010), but it has a significantly lower potential for abuse (Nagai *et al.*, 2007). However, no therapeutic applications of MeOPP have been reported to date. In view of the reported properties of MeOPP, coupled with the broad range of biological activities exhibited by piperazine derivatives (Asif, 2015; Brito *et al.*, 2019), we have recently initiated a programme of study centred on *N*-(4-methoxyphenyl)piperazine derivatives, and we have recently reported the synthesis and structures of a series of 1-aroyl-4-(4-methoxyphenyl)piperazines (Kiran Kumar *et al.*, 2019). In a continuation of that work, we have now prepared a series of 4-methoxyphenyl)piperazin-1-ium salts of simple organic acids, (I)–(XII), in order to study the various patterns of hydrogen-bonding interactions present in these salts, which may eventually be of value in pharmacological and pharmaceutical applications (Kavitha *et al.*, 2014; Kaur *et al.*, 2015; Shaibah, Yathirajan *et al.*, 2017; Shaibah, Sagar *et al.*, 2017; Shaibah *et al.*, 2019). Salts of this type are readily prepared by co-crystallizations of the piperazine and the acids in methanol solution and, in total, 28 different acids representing a wide range of chemical types were investigated (see Section 5): however, only twelve of these provided crystals suitable for single-crystal X-ray diffraction, and thus we report here the molecular and supramolecular structures of (I)–(XII) (Figs. 1–12).

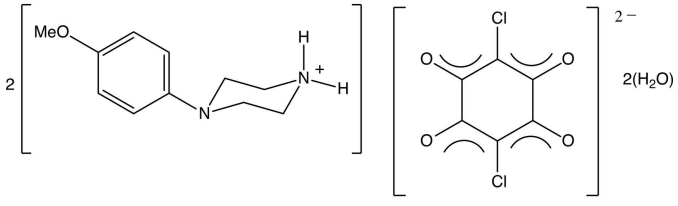


(I) Ar = C_6H_5, n = 1
(II) Ar = 4-FC_6H_4, n = 1
(III) Ar = 4-ClC_6H_4, n = 1
(IV) Ar = 4-BrC_6H_4, n = 1
(V) Ar = 2-HOC_6H_4, n = nil
(VI) Ar = 3-C_5H_4N, n = nil





(VIII) X = hydrogensuccinate
(IX) X = hydrogenfumarate
(X) X = hydrogenmaleate
(XI) X = trichloroacetate



(XII)

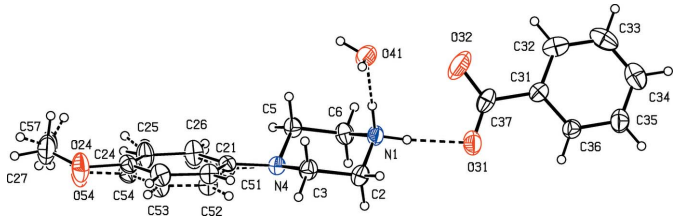


Figure 1
The independent components of compound (I), showing the atom-labelling scheme, the disorder of the 4-methoxyphenyl group, and the hydrogen bonds within the selected asymmetric unit. The major disorder component is drawn using full lines and the minor disorder component is drawn using dashed lines. Displacement ellipsoids are drawn at the 30% probability level and, for the sake of clarity, a few of the atom labels have been omitted.

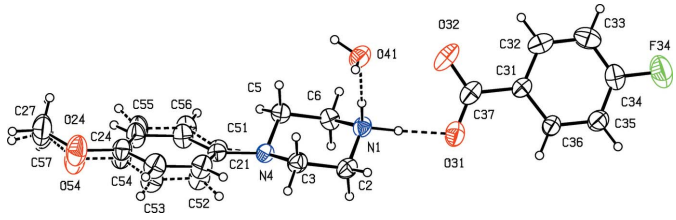


Figure 2
The independent components of compound (II), showing the atom-labelling scheme, the disorder of the 4-methoxyphenyl group, and the hydrogen bonds within the selected asymmetric unit. The major disorder component is drawn using full lines and the minor disorder component is drawn using dashed lines. Displacement ellipsoids are drawn at the 30% probability level and, for the sake of clarity, a few of the atom labels have been omitted.

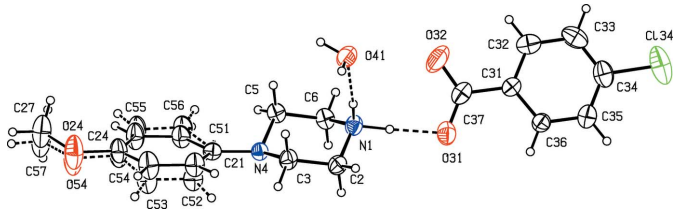


Figure 3
The independent components of compound (III), showing the atom-labelling scheme, the disorder of the 4-methoxyphenyl group, and the hydrogen bonds within the selected asymmetric unit. The major disorder component is drawn using full lines and the minor disorder component is drawn using dashed lines. Displacement ellipsoids are drawn at the 30% probability level and, for the sake of clarity, a few of the atom labels have been omitted.

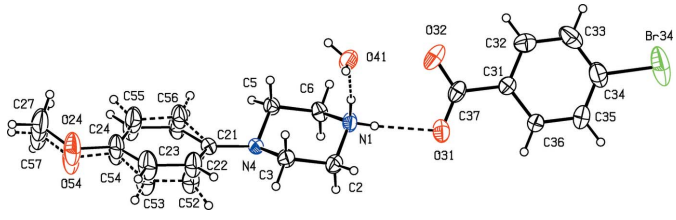


Figure 4
The independent components of compound (IV), showing the atom-labelling scheme, the disorder of the 4-methoxyphenyl group, and the hydrogen bonds within the selected asymmetric unit. The major disorder component is drawn using full lines and the minor disorder component is drawn dashed broken lines. Displacement ellipsoids are drawn at the 30% probability level and, for the sake of clarity, a few of the atom labels have been omitted.

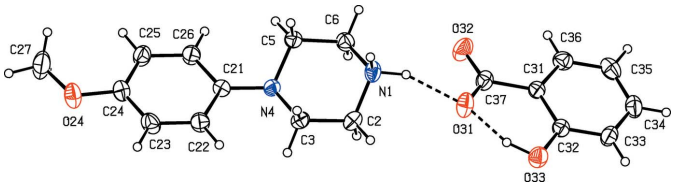


Figure 5
The independent components of compound (V), showing the atom-labelling scheme and the hydrogen bonds within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

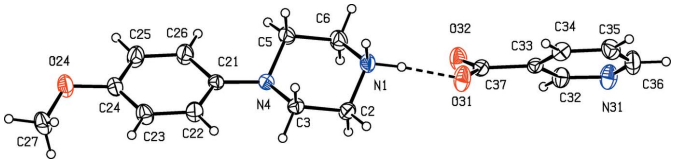


Figure 6
The independent components of compound (VI), showing the atom-labelling scheme and the hydrogen bonds within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

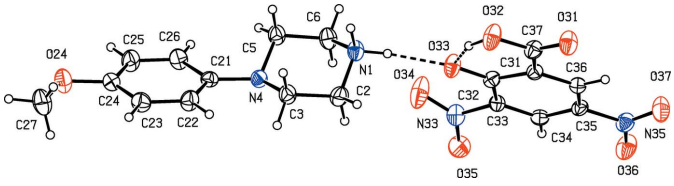


Figure 7
The independent components of compound (VII), showing the atom-labelling scheme and the hydrogen bond within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

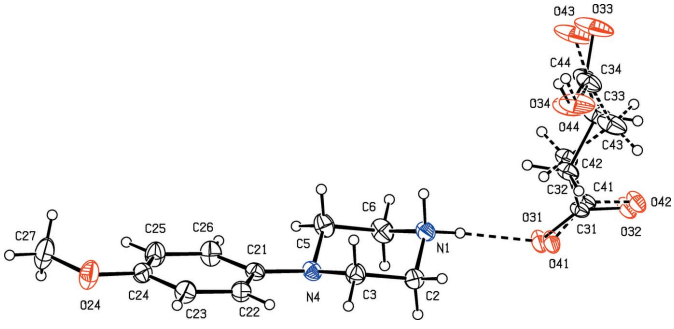


Figure 8
The independent components of compound (VIII), showing the atom-labelling scheme, the disorder of anion, and the hydrogen bonds within the selected asymmetric unit. The major disorder component is drawn using full lines and the minor disorder component is drawn using dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

2. Structural commentary

Compounds (I)–(XI) are all 1:1 salts, but in (XII), where the dianion lies across a centre of inversion while the cation lies in a general position, the cation:anion ratio is 2:1. Compounds (I)–(IV) and (XII) all crystallize as hydrates, but compounds (V)–(XI) all crystallize in solvent-free form. Compounds (I)–(IV) are isomorphous (Table 2), in each of which the 4-methoxyphenyl groups is disordered over two sets of atomic sites (Figs. 1–4), having occupancies 0.66 (2) and 0.34 (2) in (I), 0.81 (3) and 0.19 (3) in (II), 0.73 (2) and 0.27 (2) in (III) and 0.80 (2) and 0.20 (2) in (IV). Similarly, compounds (VIII) and (IX) are isomorphous, and in both of them the anion exhibits disorder, with occupancies of 0.660 (15) and 0.340 (15) in (VIII), and 0.906 (9) and 0.094 (9) in (IX) (Figs. 8 and 9).

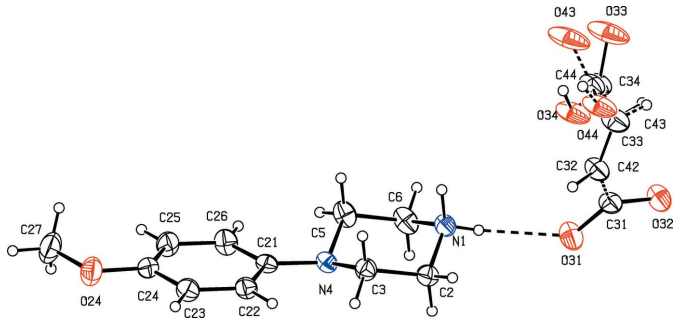


Figure 9
The independent components of compound (IX), showing the atom-labelling scheme, the disorder of anion, and the hydrogen bonds within the selected asymmetric unit. The major disorder component is drawn using full lines and the minor disorder component is drawn using dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

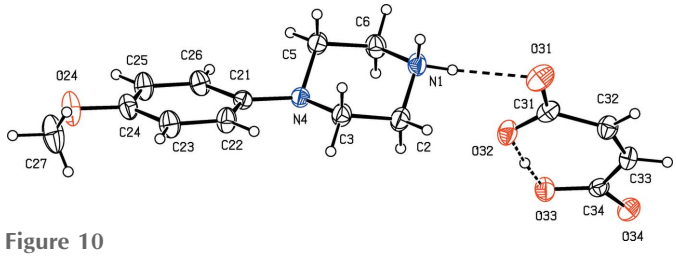


Figure 10
The independent components of compound (X), showing the atom-labelling scheme and the hydrogen bonds within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

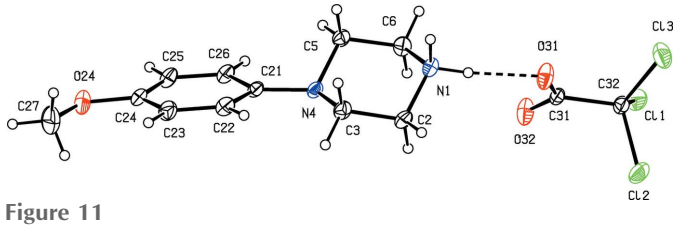


Figure 11
The independent components of compound (XI), showing the atom-labelling scheme and the hydrogen bond within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

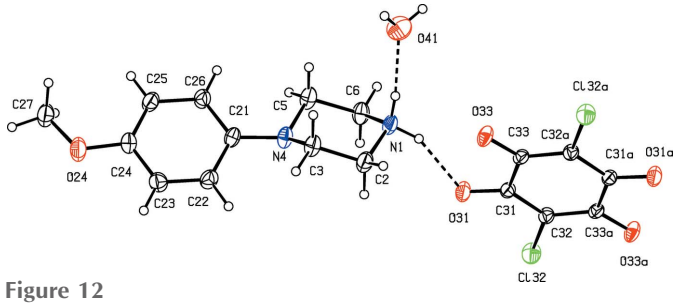


Figure 12
The independent components of compound (XII), showing the atom-labelling scheme and the hydrogen bonds within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level, and the atoms marked with the suffix 'a' are at the symmetry position ($1-x$, $1-y$, $-z$)

While compounds (I)–(IV) are isostructural, compounds (VIII) and (IX) are not, because of both the different configurations of their anions and the different degrees of disorder. Examples have been previously reported of compounds that are isomorphous but not strictly isostructural in terms of their intermolecular interactions (Acosta *et al.*, 2009).

In the anion of compound (VII), the carboxyl group is unionized, with C—O distances of 1.220 (3) and 1.309 (3) Å and it is the phenolic H atom which has been lost (Fig. 7). The C32—O33 distance, 1.280 (3) Å, is closer to that normally found in ketones than to that typical of phenols or phenolates (Allen *et al.*, 1987): in addition, the C31—C32 and C32—C33 distances, 1.437 (4) and 1.430 (4) Å, respectively, are significantly larger than the other C—C distances in this ring, which lie in the rather narrow range 1.370 (3)–1.385 (4) Å, but the C—N and N—O distances are all typical of their types (Allen *et al.*, 1987). These observations indicate that the negative charge in this anion is delocalized over the five atoms C31, C33, C34, C35 and C36, 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.*, 2017*a*,*b*).

The anion of compound (X) contains an almost linear and very short (Emsley, 1980; Herschlag & Pinney, 2018) O···H···O hydrogen bond, in which the H atom is almost, but not exactly, centred between the two O atoms (Table 1). In the centrosymmetric anion of compound (XII) (Fig. 12), the two

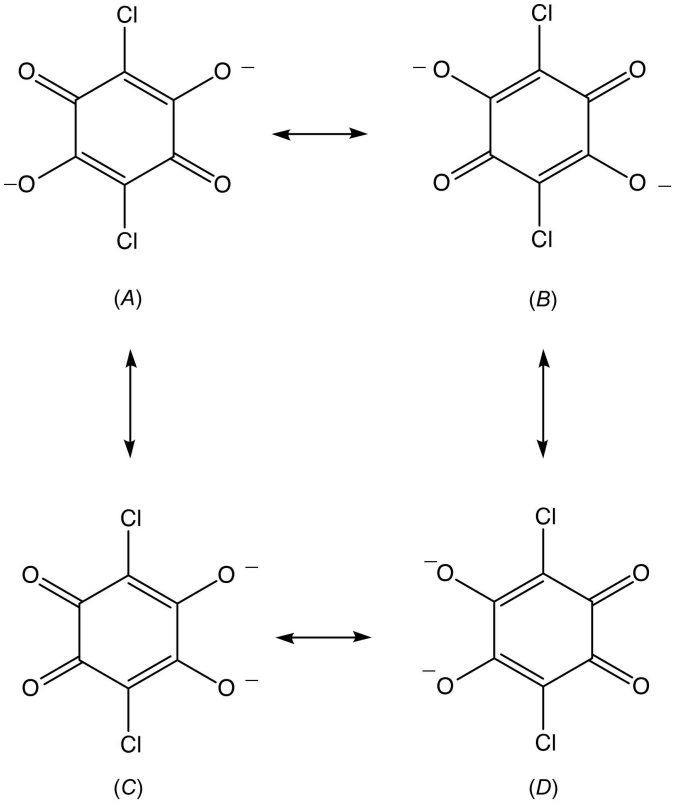


Figure 13
The canonical forms of the anion in compound (XII).

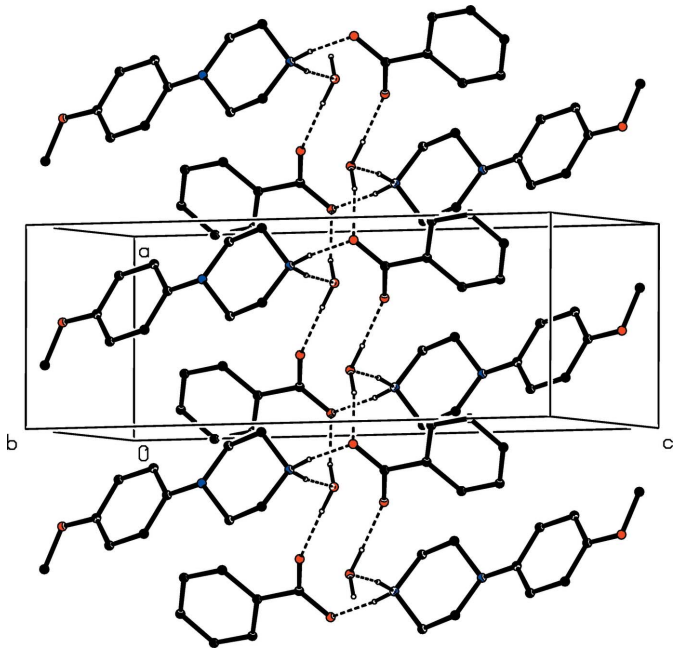


Figure 14
Part of the crystal structure of compound (I) showing the formation of a chain of rings parallel to the [100] direction. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the minor disorder component and the H atoms bonded to C atoms have been omitted.

independent C—O distances are identical within experimental uncertainty, 1.244 (2) and 1.246 (2) Å, as are the distances C31—C32 and C32—C33, 1.398 (3) and 1.392 (2) Å. However, the remaining C—C distance in this ring, 1.539 (3) Å is typical of a single C—C bond (Allen *et al.*, 1987). These observations indicates the delocalization of a negative charge across each of the O–C–C–C–O units, and that these two units are effectively isolated from each other electronically. Despite the apparent simplicity of this dianion, with its high intrinsic symmetry, it is not possible adequately to describe its electronic structure in a single diagrammatic form, and four forms (*A*)–(*D*) (Fig. 13) are required.

3. Supramolecular features

In each of the four isomorphous salts (I)–(IV), the ions are linked by a combination of N—H···O and O—H···O hydrogen bonds (Table 1) to form a chain of edge-fused centrosymmetric rings running parallel to the [100] direction, in which $R_6^4(12)$ (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995) rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ alternate with $R_6^6(16)$ rings centred at $(n+\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, where n represents an integer in each case (Fig. 14). In each of these four salts, a combination of C—H···O and C—H···π(arene) hydrogen bonds links the [100] chain into complex sheets lying parallel to (001).

There is an intermolecular O—H···O hydrogen bond in the anion of the unsolvated salt (V). The two anions in the selected asymmetric unit (Fig. 5) are linked by an asymmetric three-centre N—H···$(O)_2$ hydrogen bond, and the resulting ion pairs, which are related by 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{4})$, are

Table 1
Hydrogen-bond parameters and short intermolecular contacts (Å, °).

*Cg*1 and*Cg*2 are the centroids of the C31–C36 and C21–C26 rings, respectively.

Compound	*D*—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
(I)	N1—H11···O31	0.90 (2)	1.88 (2)	2.777 (3)	174.1 (19)
	N1—H12···O41	0.97 (2)	1.85 (2)	2.808 (3)	169.7 (18)
	O41—H41···O32^{i}	0.88 (3)	1.75 (3)	2.631 (3)	177 (3)
	O41—H42···O31^{ii}	0.91 (3)	1.87 (3)	2.763 (3)	169 (3)
	C2—H2*B*···O31^{iii}	0.97	2.54	3.485 (3)	165
	C22—H22···*Cg*1^{ii}	0.93	2.85	3.603 (3)	139
	C26—H26···*Cg*1^{iv}	0.93	2.90	3.62 (2)	135
	C56—H56···*Cg*1^{iv}	0.93	2.64	3.41 (5)	141
(II)	N1—H11···O31	1.09 (3)	1.67 (3)	2.758 (4)	174.1 (19)
	N1—H12···O41	0.86 (3)	1.96 (3)	2.818 (4)	170 (3)
	O41—H41···O32^{i}	0.86 (4)	1.75 (4)	2.627 (4)	174 (4)
	O41—H42···O31^{ii}	0.91 (4)	1.88 (4)	2.768 (3)	163 (3)
	C2—H2*B*···O31^{iii}	0.97	2.58	3.529 (4)	166
	C6—H6*B*···O41^{i}	0.97	2.57	3.386 (4)	142
	C26—H26···*Cg*1^{iv}	0.93	2.81	3.56 (2)	138
	C56—H56···*Cg*1^{iv}	0.93	2.96	3.55 (9)	123
(III)	N1—H11···O31	1.09 (3)	1.71 (3)	2.790 (4)	176 (3)
	N1—H12···O41	0.83 (3)	1.98 (3)	2.811 (4)	174 (3)
	O41—H41···O32^{i}	0.91 (4)	1.73 (4)	2.624 (4)	172 (4)
	O41—H42···O31^{ii}	0.94 (4)	1.84 (4)	2.775 (4)	170 (4)
	C2—H2*B*···O31^{iii}	0.97	2.52	3.467 (4)	165
	C6—H6*B*···O41^{i}	0.97	2.60	3.408 (4)	141
	C22—H22···*Cg*1^{iv}	0.93	2.89	3.631 (13)	137
	C26—H26···*Cg*1^{iv}	0.93	2.81	3.58 (2)	141
(IV)	N1—H11···O31	0.78 (4)	2.03 (4)	2.805 (5)	174 (5)
	N1—H12···O41	0.95 (5)	1.86 (5)	2.802 (5)	172 (4)
	O41—H41···O32^{i}	0.79 (6)	1.84 (6)	2.623 (6)	170 (6)
	O41—H42···O31^{ii}	0.79 (7)	2.00 (7)	2.772 (5)	169 (6)
	C2—H2*B*···O31^{iii}	0.97	2.52	3.471 (5)	166
	C22—H22···*Cg*1^{ii}	0.93	2.52	3.471 (5)	166
	C26—H26···*Cg*1^{iv}	0.93	2.84	3.58 (2)	137
(V)	N1—H11···O31	0.96 (3)	1.85 (3)	2.759 (3)	156 (3)
	N1—H11···O32	0.96 (3)	2.47 (3)	3.283 (3)	142 (2)
	N1—H12···O32^{v}	0.95 (3)	1.87 (3)	2.806 (3)	166 (2)
	O33—H33*A*···O31	0.97 (3)	1.60 (3)	2.516 (3)	156 (3)
	C6—H6*A*···O33^{vi}	0.97	2.58	3.444 (3)	148
	C2—H2*A*···*Cg*1^{vii}	0.97	2.88	3.711 (3)	144
	C26—H26···*Cg*1^{viii}	0.93	2.87	3.642 (3)	141
(VI)	N1—H11···O31	0.976 (19)	1.714 (19)	2.677 (2)	168.2 (18)
	N1—H12···O32^{ix}	0.94 (2)	1.82 (2)	2.749 (2)	168.3 (17)
	C2—H2*B*···N31^{iv}	0.97	2.56	3.518 (2)	169
	C36—H36···O24^{x}	0.93	2.51	3.432 (2)	172
	C3—H3*A*···*Cg*1^{xi}	0.97	2.97	3.775 (2)	156
(VII)	O32—H32···O33	1.04 (4)	1.47 (4)	2.472 (3)	158 (3)
	N1—H11···O33	0.93 (3)	1.98 (3)	2.020 (3)	150 (3)
	N1—H11···O34	0.93 (3)	2.27 (3)	2.910 (3)	126 (2)
	N1—H12···O31^{i}	0.93 (3)	2.04 (3)	2.931 (3)	160 (3)
	N1—H12···O32^{i}	0.93 (3)	2.58 (3)	3.250 (3)	129 (2)
	C34—H34···O36^{xii}	0.93	2.53	3.449 (3)	171
	C5—H5*B*···*Cg*2^{xiii}	0.97	2.84	3.639 (3)	140
(VIII)	N1—H11···O31	0.86 (3)	1.90 (3)	2.750 (15)	167 (4)
	N1—H12···O32^{xiv}	0.98 (3)	1.77 (4)	2.741 (19)	171 (3)
	O34—H34···O31^{xv}	0.82	1.79	2.60 (2)	168
	N1—H11···O41	0.86 (3)	2.18 (4)	3.03 (3)	165 (4)
	N1—H12···O42^{xiv}	0.98 (3)	1.82 (5)	2.77 (4)	163 (3)
	O44—H44···O41^{xv}	0.82	1.56	2.35 (2)	161
	C3—H3*A*···*Cg*2^{xvi}	0.97	2.76	3.652 (3)	154
(IX)	N1—H11···O31	0.81 (4)	2.18 (3)	2.940 (4)	155 (3)
	N1—H12···O32^{xiv}	0.96 (4)	1.77 (4)	2.714 (4)	169 (3)
	O34—H34···O31^{xv}	0.82	1.71	2.522 (5)	170
	O43—H34···O31^{xv}	0.82	1.62	2.44 (2)	175

Table 1 (continued)

Compound	D—H···A	D—H	H···A	D···A	D—H···A
	C3—H3A···$Cg2^{xvi}$	0.97	2.76	3.650 (3)	153
(*X*)	O33—H33A···O32	1.167 (18)	1.247 (18)	2.4121 (16)	175 (2)
	N1—H11···O31	0.915 (17)	2.126 (16)	2.9309 (19)	146.2 (15)
	N1—H11···O32	0.915 (17)	2.296 (17)	3.0798 (18)	143.5 (14)
	N1—H12···$O34^{xvii}$	0.919 (18)	1.881 (18)	2.7563 (17)	158.5 (17)
	C2—H2A···$O34^{ii}$	0.97	2.56	3.363 (2)	140
(XI)	N1—H11···O31	0.92 (4)	1.86 (4)	2.775 (4)	172 (3)
	N1—H11···$O32^{xviii}$	0.97 (3)	1.80 (3)	2.724 (3)	158 (3)
(XII)	N1—H11···O31	0.89 (3)	1.96 (3)	2.802 (3)	157 (2)
	N1—H11···O33	0.89 (3)	2.29 (2)	2.838 (3)	119 (2)
	N1—H12···O41	0.90 (2)	1.92 (2)	2.798 (3)	168 (3)
	O41—H41···$O33^{i}$	0.84 (4)	1.92 (4)	2.738 (3)	166 (3)
	O41—H42···$O24^{xix}$	0.82 (3)	2.49 (3)	3.269 (3)	160 (3)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $2-x, 1-y, 1-z$; (iii) $2-x, 2-y, 1-z$; (iv) $1-x, 2-y, 1-z$; (v) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vi) $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vii) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ix) $\frac{3}{2}-x, -\frac{1}{2}+y, z$; (x) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (xi) $-\frac{1}{2}+x, \frac{3}{2}-y, 1-z$; (xii) $3-x, 2-y, 1-z$; (xiii) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (xiv) $-\frac{1}{2}+x, \frac{3}{2}-y, z$; (xv) $-\frac{1}{2}+x, \frac{3}{2}-y, 1+z$; (xvi) $1-x, 1-y, \frac{1}{2}+z$; (xvii) $-1+x, y, z$; (xviii) $-\frac{1}{2}+x, 1-y, z$; (xix) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$.

linked by a two-centre N—H···O hydrogen bond to form chain of rings running parallel to the [010] direction (Fig. 15). Chains of this type are weakly linked into sheets lying parallel to (001) by a combination of C—H···O and C—H···π(arene) hydrogen bonds.

The component ions in compound (VI) (Fig. 6) are linked by a two-centre N—H···O hydrogen bond and the resulting ion pairs are further linked by a combination of N—H···O, C—H···O and C—H···N hydrogen bonds to form a three-dimensional framework structure, whose formation can readily be analysed in terms of three simple sub-structures (Ferguson *et al.*, 1998*a*,*b*; Gregson *et al.*, 2000). Ion pairs which are related by the *b*-glide plane at $x = \frac{3}{4}$ are linked by a second N—H···O hydrogen bond to form a $C_2^2(6)$ chain running

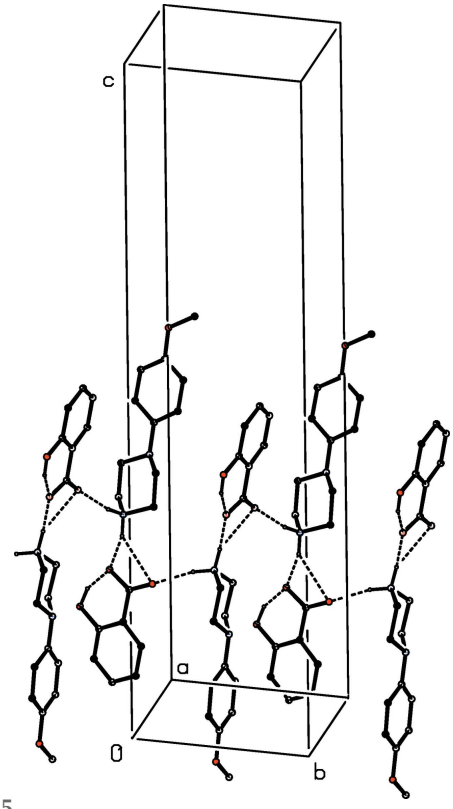


Figure 15
Part of the crystal structure of compound (V) showing the formation of a chain of rings parallel to the [010] direction. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have been omitted.

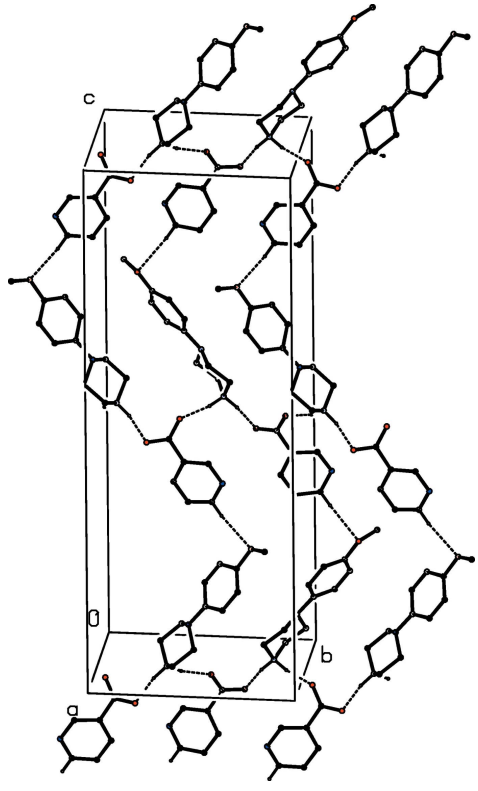


Figure 16
Part of the crystal structure of compound (VI) showing the formation of a sheet of $R_6^6(40)$ rings lying parallel to (100). Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms not involved in the motifs shown have been omitted.

parallel to the [010] direction, and in the second sub-structure, ion pairs which are related by the *c*-glide plane at $y = \frac{3}{4}$ are linked by a C—H···O hydrogen bond (Table 1) to form a $C_2^2(17)$ chain running parallel to the [001] direction. The combination of these two simple chain motifs generates a sheet of $R_6^6(40)$ rings lying parallel to (100) in the domain $\frac{1}{2} < x < 1.0$ (Fig. 16). A second sheet of this type, related to the first by inversion lies in the domain $0 < x < \frac{1}{2}$, and adjacent sheets are linked by the third sub-structure in which inversion-related ion pairs are linked by C—H···N hydrogen bonds into a centrosymmetric $R_4^4(18)$ ring (Fig. 17): the action of this interaction is to link all of the (100) sheets into a continuous three-dimensional array.

There is an intermolecular O—H···O hydrogen bond in the anion of compound (VII) (Fig. 7), but the carboxyl H atom plays no part in the supramolecular assembly. The ions are linked by a combination of N—H···O and C—H···O hydrogen bonds to form a chain of centrosymmetric rings

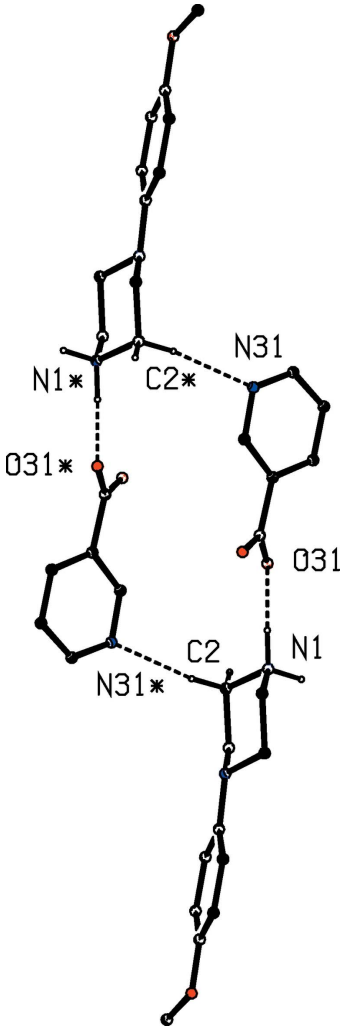


Figure 17
Part of the crystal structure of compound (VI) showing the formation of the $R_4^4(18)$ ring which links the (100) sheets. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the unit-cell outline and the H atoms which are bonded to the C atoms not involved in the motif shown have been omitted. The atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 2 - y, 1 - z)$.

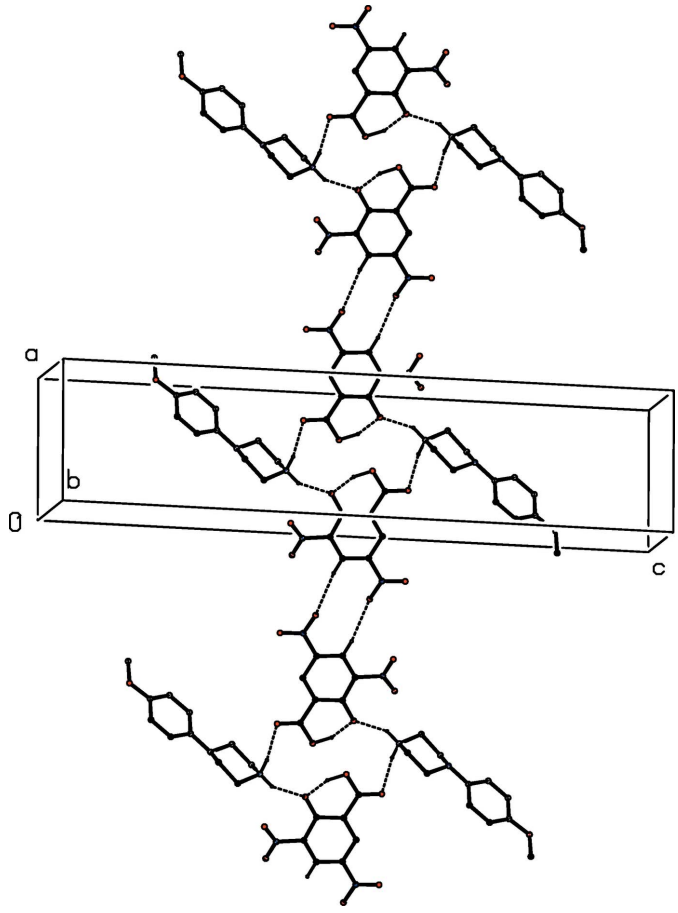


Figure 18
Part of the crystal structure of compound (VII) showing the formation of a chain of $R_2^2(10)$ and $R_6^4(16)$ rings parallel to the [210] direction. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms which are bonded to the C atoms not involved in the motif shown have been omitted.

running parallel to the [210] direction, in which $R_2^2(10)$ rings centred at $(2n - \frac{1}{2}, n, \frac{1}{2})$ alternate with $R_6^4(16)$ rings centred at $(2n + \frac{1}{2}, n + \frac{1}{2}, \frac{1}{2})$, where n represents an integer in each case (Fig. 18). Two chains of this type, related to one another by the translational symmetry operations, pass through each unit cell, and a weak C—H···π(arene) hydrogen bond links the chains into a three-dimensional framework structure.

For the disordered structure of compound (VIII), the hydrogen bonds formed by the major and minor disorder components are very similar (Table 1) so that only the major disorder form need be considered in detail. Within the selected asymmetric unit (Fig. 8), the component ions are linked by a two-centre N—H···O hydrogen bond: the ion pairs are linked by a combination of N—H···O and O—H···O hydrogen bonds to form sheets, whose formation can readily be analysed in terms of two simple sub-structures. In the simpler of these, anions which are related by the *a*-glide plane at $y = \frac{3}{4}$ are linked by O—H···O hydrogen bonds into $C(7)$ chains running parallel to the $[10\bar{2}]$ direction (Fig. 19); in the second sub-structure, ion pairs which are related by the same glide plane are linked by N—H···O hydrogen bonds to form a $C_2^2(6)$ chain running parallel to the [100] direction

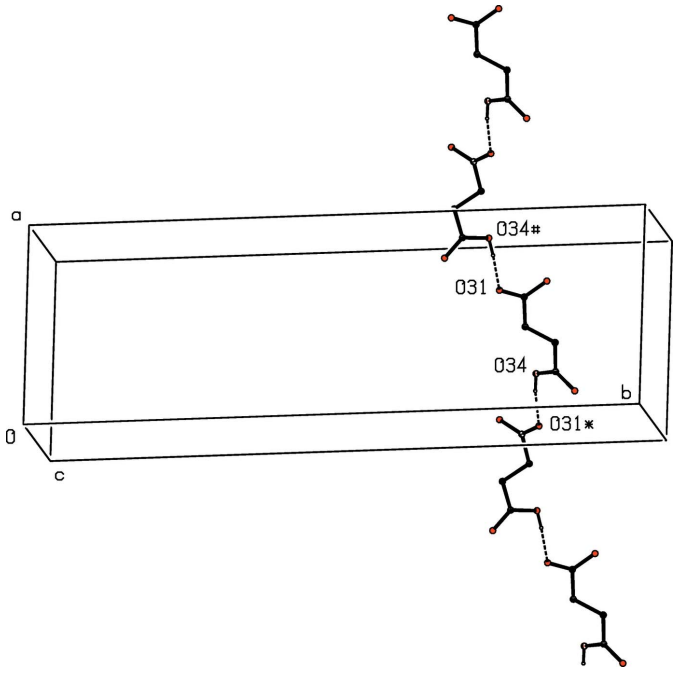


Figure 19
Part of the crystal structure of compound (VIII) showing the formation of a $C(7)$ chain of anions, parallel to $[10\bar{2}]$. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{3}{2} - y, -1 + z)$ and $(-\frac{1}{2} + x, \frac{3}{2} - y, 1 + z)$, respectively.

(Fig. 20). The combination of these two chain motifs generates a sheet lying parallel to (010), and a single C—H···π(arene) hydrogen bond links these sheets into a three-dimensional framework structure. The supramolecular aggregation in the isomorphous compound (IX) is similar to that in (VIII). As noted in Section 2 above, the anion in compound (X) contains

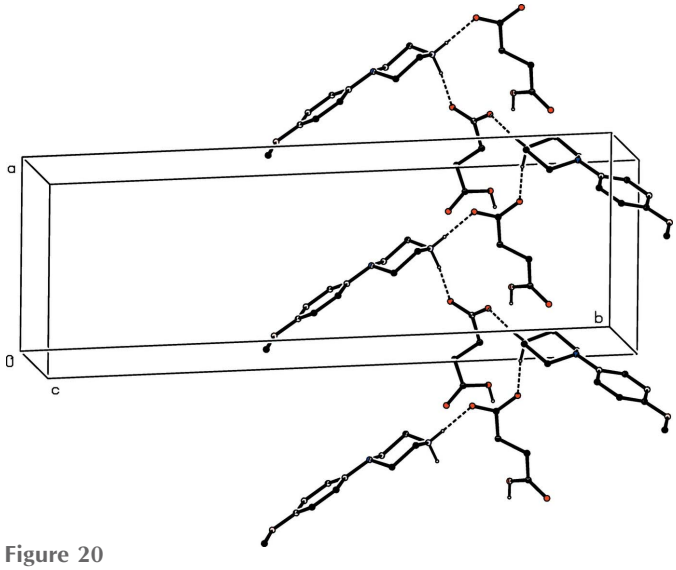


Figure 20
Part of the crystal structure of compound (VIII) showing the formation of a $C_2^2(6)$ chain parallel to [100]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have been omitted.

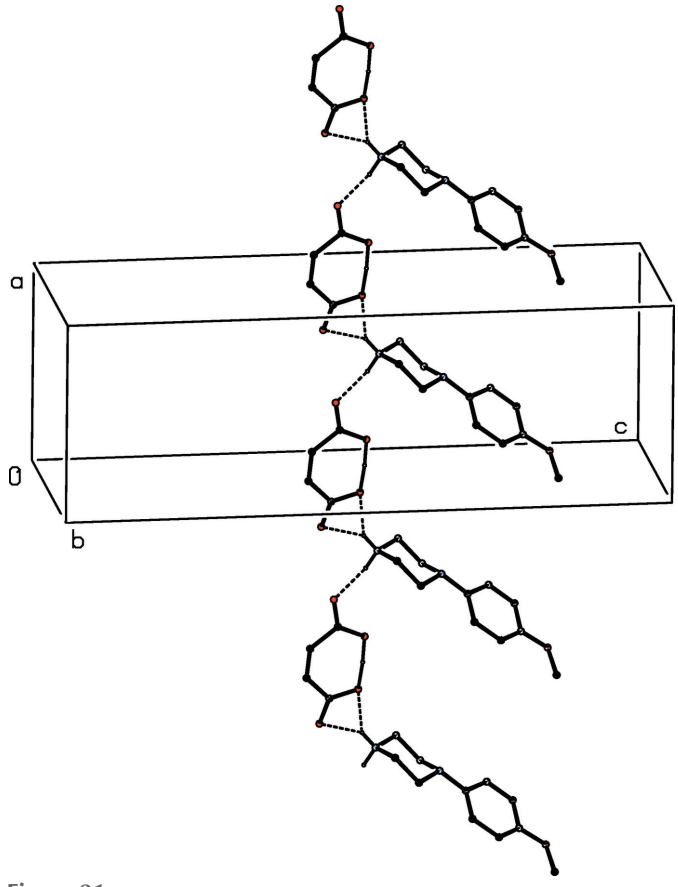


Figure 21
Part of the crystal structure of compound (X) showing the formation of a chain of rings parallel to [100]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have been omitted.

a very short and nearly symmetrical O···H···O hydrogen bond. Within the selected asymmetric unit, the component ions are linked by the three-centre N—H···$(O)_2$ hydrogen bond and ion pairs which are related by translation are linked by a two-centre N—H···O hydrogen bond to form a $C(9)C(9)[R_1^2(4)]$ chain of rings running parallel to the [100] direction (Fig. 21). The C—H···O contact is at the margin of significance (Wood *et al.*, 2009), but it involves chains related by inversion.

The supramolecular assembly of compound (XI) is extremely simple: two N—H···O hydrogen bonds link the ions into a $C_2^2(6)$ chain running parallel to the [100] direction (Fig. 22). In compound (XII), a combination of N—H···O and O—H···O hydrogen bonds links all three components into a chain of $R_6^6(18)$ rings running parallel to the [001] direction (Fig. 23), while a second O—H···O hydrogen bond links a combination of cations and water molecules into a simple $C_2^2(12)$ chain running parallel to the [101] direction (Fig. 24) and the combination of these two chain motifs generates a complex sheet lying parallel to (010).

Overall, therefore, the hydrogen-bonded assembly is one-dimensional in each of compounds (X) and (XI), two-dimensional in compounds (I)–(V) and (XII), and three-dimensional in compounds (VI)–(IX). Sub-structures in the

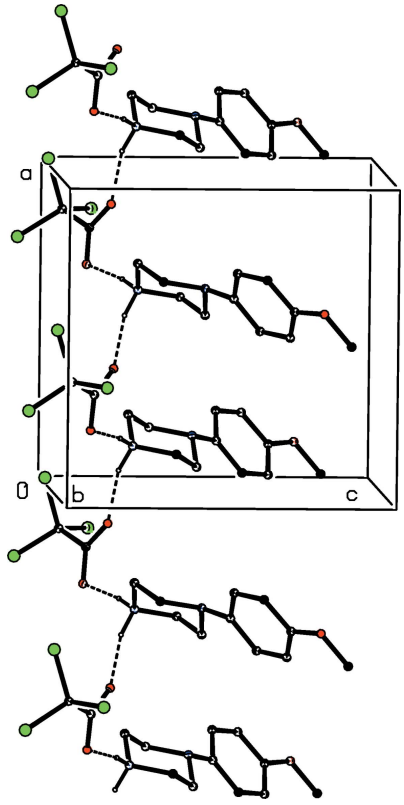


Figure 22
Part of the crystal structure of compound (XI) showing the formation of a $C_2^2(6)$ chain parallel to [100]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have been omitted.

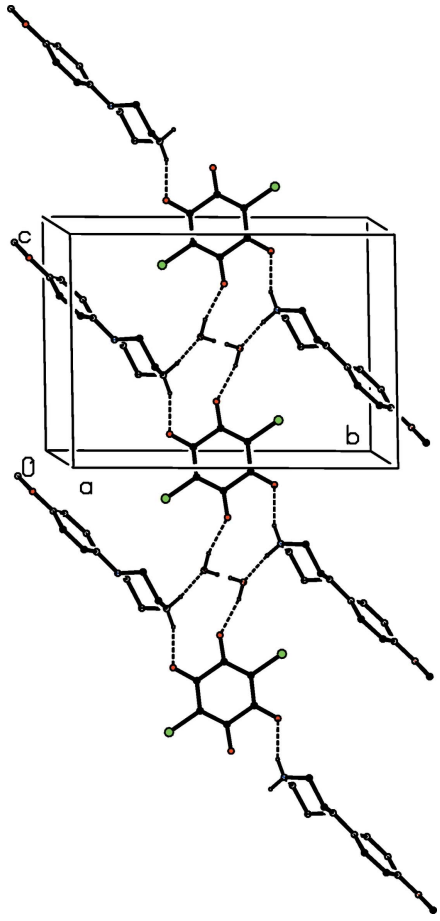


Figure 23
Part of the crystal structure of compound (XII) showing the formation of an $R_6^6(18)$ chain of rings parallel to [001]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have been omitted.

form of chains of rings can be identified in compounds (I)–(IV) and in (VII), although (I)–(IV) are all monohydrates, while (VII) is solvent free: within the chain of rings formed by (I)–(IV) it is possible to identify a $C_2^2(6)$ motif formed by water molecules and anions only (Fig. 14), and a $C_2^2(6)$ motif built from alternating cations and anions can, in fact, be identified in each of compounds (V), (VI), (VIII), (IX) and (XI) (Figs. 15, 16, 20, 22). By contrast, a $C_2^2(12)$ motif, built from water molecules and cations can be identified in the structure of compound (XII) (Fig. 24), but sub-structural motifs in the form of simple chains are uncommon in this series (Fig. 19).

4. Database survey

Compounds (I)–(IV), reported here, are isomorphous across the series of anions 4-XC$_6$H$_4$COO$^-$, where X = H, F, Cl or Br, despite the rather disparate sizes of the substituents X. A similar, but more extreme, series of isomorphous salts was found in the substituted anilinium 5-nitro(hydrogenphthalate) salts (4-XC$_6$H$_4$NH$_3$)$^+$·(C$_8$H$_4$NO$_6$)$^-$, which are isomorphous for X = H, Cl, Br and I (Glidewell *et al.*, 2005). The structures of a number of salts containing the chloranilate dianion have been reported (Ishida, 2004*a*,*b*,*c*,*d*; Sovago *et al.*, 2016), and the geometric features previously observed in this anion are fully consistent with the geometry found here in (XII): the

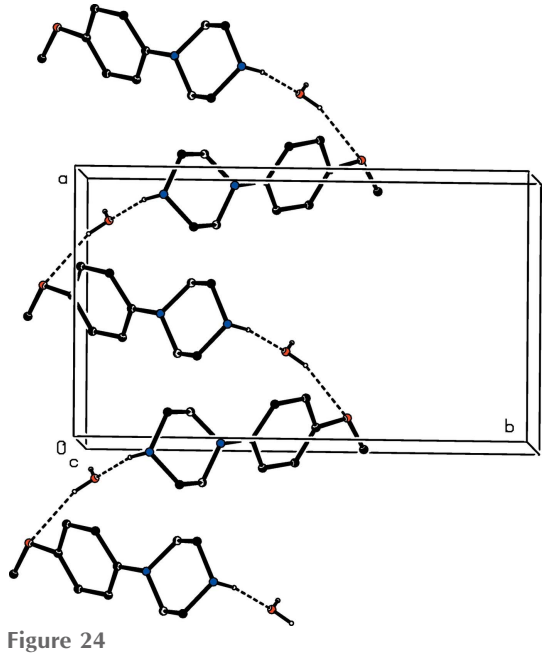


Figure 24
Part of the crystal structure of compound (XII) showing the formation of a $C_2^2(12)$ chain of cations and water molecules parallel to [101]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have been omitted.

nature of the electronic delocalization has been confirmed in several such salts using a combination of deformation density plots and net atomic charge calculations (Sovago *et al.*, 2016).

The structures of very few salts containing the 4-(methoxyphenyl)piperazin-1-ium cations have been reported. In 4-(4-methoxyphenyl)piperazin-1-ium chloride, two N—H···Cl hydrogen bonds link the ions into $C_2^1(4)$ chains (Zia-ur-Rehman *et al.*, 2009), and in the closely related 4-(4-nitrophenyl)piperazin-1-ium chloride monohydrate, a combination of N—H···O, O—H···Cl and N—H···Cl hydrogen bonds links the components into complex ribbons in which each anion accepts three hydrogen bonds (Lu, 2007). The structure of 4-(3-methoxyphenyl)piperazin-1-ium maleate has been reported (Verdonk *et al.*, 1997), as have those of the picrate (Verdonk *et al.*, 1997) and 6-chloro-5-isopropyl-2,4-dioxopyrimidin-1-ide (Al-Omary *et al.*, 2014) salts of the 4-(2-methoxyphenyl)piperazin-1-ium cation. Finally we note, in addition to the 1-aroyl-4-(4-methoxyphenyl)piperazines referred to in Section 1 above (Kiran Kumar *et al.*, 2019), the structure of 1-acetyl-(4-hydroxyphenyl)piperazine (Kavitha *et al.*, 2013), which is an *N*-acetylated derivative of 4-(4-hydroxyphenyl)piperazines, a metabolite of 4-(4-methoxyphenyl)-piperazine.

5. Synthesis and crystallization

All reagents were obtained commercially and were used as received. For the synthesis of each of compounds (I)–(XII), equimolar quantities (0.52 mmol of each component) of *N*-(4-methoxyphenyl)piperazine and the appropriate acid were separately dissolved in methanol (10 ml) and the two solutions were then mixed, stirred briefly, and then set aside to crystallize, giving the solid products (I)–(XII) after a few days. The products were all collected by filtration and then dried in air. Yields (I) 81%, (II) 83%, (III) 83%, (IV) 81%, (V) 83%, (VI) 78%, (VII) 80%, (VIII) 82%, (IX) 82%, (X) 84%, (XI) 79%, (XII) 82%: melting ranges (I) 513–515 K, (II) 405–407 K, (III) 449–451 K, (IV) 447–449 K, (V) 471–473 K, (VI) 441–443 K, (VII) 475–477 K, (VIII) 439–441 K, (IX) 483–485 K, (X) 429–431 K, (XI) 393–395 K, (XII) 575–577 K. Spectroscopic data (IR and ^{1}H NMR) are provided in the supporting information. Crystals of compounds (I), (II), and (VIII)–(XII) suitable for single-crystal X-ray diffraction analysis were selected directly from the prepared samples. Crystals of compounds (III)–(VII) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation, at ambient temperature and in the presence of air, of solutions in methanol–ethyl acetate (initial composition 1:1, *v*/*v*). A number of other acids were used in similar co-crystallization experiments but they did not provide crystal suitable for single-crystal X-ray diffraction, thus: 2- and 3-fluorobenzoic acids [*cf.* compound (II)], 2- and 3-chlorobenzoic acids [*cf.* compound (III)], 2- and 3-bromobenzoic acids [*cf.* compound (IV)], 2- and 3-iodobenzoic acids, phthalic acid, 3-methylbenzoic acid [*cf.* compound (I)], 2,4-dichlorobenzoic acid, crotonic and adipic acids [*cf.* compounds (VIII)–(X)], and ascorbic, aspartic and glutamic acids.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. In each of the isomorphous compounds (I)–(IV), the 4-methoxyphenyl group exhibits disorder over two sets of atomic sites, and in each of (VIII) and (IX), the anion exhibits disorder involving two sets of atomic sites having unequal occupancies. In each case, the bonded distances and the 1,3 non-bonded distances in the minor disorder component were restrained to be the same as the equivalent distances in the major disorder component, subject to s.u. values of 0.01 and 0.02 Å, respectively, and the anisotropic displacement parameters for pairs of partial-occupancy atoms occupying essentially the same physical space were constrained to be equal: in addition, it was found necessary to constrain the minor component of the carboxyl group in (IX) to be planar. The ratio of observed-to-unique data was only 39% for compounds (II) and (III): this is probably a consequence of the ambient temperature data collection allied to the disorder: in both (VII) and (IX), the average U_3/U_1 ratio was > 4.0: this may be consequence of the disorder. Apart from those in the minor disorder components of (I)–(IV), (VIII) and (IX), all H atoms were located in difference maps. The H atoms bonded to C atoms were then treated as riding atoms in geometrically idealized positions with C—H distances of 0.93 Å (alkenyl and aromatic), 0.96 Å (CH_3) or 0.97 Å (CH_2), and with $U_{iso}(H) = kU_{eq}(C)$, where k = 1.5 for the methyl groups which were permitted to rotate but not to tilt, and 1.2 for all other H atoms bonded to C atoms: the H atoms bonded to C atoms in the minor disorder components were included on the same basis. The H atoms bonded to O atoms in the disordered components of (VIII) and (IX) were treated as riding atoms with O—H = 0.82 Å and $U_{iso}(H) = 1.5U_{eq}(O)$, For the H atoms bonded to N atoms, and for the H atoms bonded to O atoms in (I)–(V), (VII), (X) and (XII), the atomic coordinates were refined with $U_{iso}(H) = 1.2U_{eq}(N)$ or $1.5U_{eq}(O)$, leading to the N—H and O—H distances shown in Table 1. The refined occupancies for the disorder components were 0.66 (2) and 0.34 (2) in (I), 0.81 (3) and 0.19 (3) in (II), 0.73 (2) and 0.27 (2) in (III), 0.80 (2) and 0.20 (2) in (IV), 0.660 (15) and 0.340 (15) in (VIII), and 0.906 (9) and 0.094 (9) in (IX). For compound (XI), the correct orientation of the structure relative to the polar axis direction was established using the Flack *x* parameter (Flack, 1983), *x* = 0.11 (7). However, for compounds (V), (VIII) and (IX), where there is very little resonant scattering the values of the Flack *x* parameter were indeterminate (Flack & Bernardinelli, 2000), with values −0.3 (5), −0.6 (7) and −0.3 (4), respectively: hence in these three cases, the correct orientation of the structure with respect to the polar axis direction cannot be established, although this has no chemical significance. The refinement of (XII) was treated as a non-merohedral twin, with twin matrix (−1, 0, 0/0, −1, 0/0.496, 0, 1) and with refined twin fractions 0.2467 (9) and 0.7533 (9).

Acknowledgements

HKK thanks University of Mysore for research facilities.

Table 2
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	$C_{11}H_{17}N_2O^+\cdot C_7H_5O_2^-\cdot H_2O$	$C_{11}H_{17}N_2O^+\cdot C_7H_4FO_2^-\cdot H_2O$	$C_{11}H_{17}N_2O^+\cdot C_7H_4ClO_2^-\cdot H_2O$	$C_{11}H_{17}N_2O^+\cdot C_7H_4BrO_2^-\cdot H_2O$
M_r	332.39	350.38	366.83	411.28
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	296	293	293	293
a, b, c (Å)	6.215 (1), 7.547 (1), 18.716 (4)	6.256 (1), 7.489 (1), 19.097 (2)	6.211 (1), 7.481 (1), 20.144 (4)	6.2004 (8), 7.4957 (9), 20.440 (2)
α, β, γ (°)	84.34 (2), 87.14 (2), 84.69 (2)	84.19 (1), 86.98 (2), 84.62 (2)	84.90 (2), 87.48 (2), 85.19 (2)	85.08 (1), 87.37 (1), 85.00 (1)
V (Å^3)	869.1 (3)	885.4 (2)	928.4 (3)	942.17 (19)
Z	2	2	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	0.10	0.23	2.21
Crystal size (mm)	0.40 × 0.24 × 0.04	0.40 × 0.24 × 0.04	0.20 × 0.16 × 0.02	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, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.834, 0.996	0.973, 0.996	0.951, 0.995	0.536, 0.719
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5751, 3442, 1839	5760, 3477, 1355	5883, 3454, 1343	6176, 3818, 2063
R_{int}	0.029	0.046	0.041	0.018
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618	0.618	0.607	0.629
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.134, 1.02	0.066, 0.128, 1.01	0.065, 0.135, 0.94	0.068, 0.197, 1.06
No. of reflections	3442	3477	3454	3818
No. of parameters	256	265	265	265
No. of restraints	17	17	17	17
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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.19	0.13, −0.14	0.24, −0.23	0.94, −0.64

	(V)	(VI)	(VII)	(VIII)
Crystal data				
Chemical formula	$C_{11}H_{17}N_2O^+\cdot C_7H_5O_3^-$	$C_{11}H_{17}N_2O^+\cdot C_6H_4NO_2^-$	$C_7H_3N_2O_7^+\cdot C_{11}H_{17}N_2O^-$	$C_{11}H_{17}N_2O^+\cdot C_4H_5O_4^-$
M_r	330.38	315.37	420.38	310.35
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $Pbca$	Monoclinic, $P2_1/c$	Orthorhombic, $Pna2_1$
Temperature (K)	296	296	296	296
a, b, c (Å)	6.5009 (8), 7.9735 (9), 32.155 (4)	9.2817 (7), 11.2905 (7), 30.309 (2)	7.5500 (9), 7.6489 (9), 32.719 (6)	9.3225 (9), 28.261 (3), 5.8228 (8)
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 91.30 (1), 90	90, 90, 90
V (Å^3)	1666.8 (3)	3176.2 (4)	1889.0 (5)	1534.1 (3)
Z	4	8	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	0.09	0.12	0.10
Crystal size (mm)	0.42 × 0.42 × 0.34	0.46 × 0.42 × 0.36	0.18 × 0.12 × 0.06	0.44 × 0.42 × 0.24
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, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.899, 0.969	0.879, 0.968	0.916, 0.993	0.816, 0.976
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6249, 3564, 2875	22154, 3593, 2616	8215, 4074, 2003	5828, 2419, 2053
R_{int}	0.014	0.028	0.038	0.018
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.656	0.658	0.660	0.649
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.089, 1.05	0.048, 0.119, 1.04	0.066, 0.128, 1.03	0.043, 0.104, 1.14
No. of reflections	3564	3593	4074	2419
No. of parameters	228	215	281	233
No. of restraints	0	0	0	16

Table 2 (continued)

	(V)	(VI)	(VII)	(VIII)
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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.14, −0.13	0.19, −0.16	0.22, −0.23	0.16, −0.24
Absolute structure	Flack *x* determined using 1011 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)	–	–	Flack *x* determined using 460 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	–	–	–	–

	(IX)	(X)	(XI)	(XII)
Crystal data				
Chemical formula	$C_{11}H_{17}N_2O^+\cdot C_4H_3O_4^-$	$C_{11}H_{17}N_2O^+\cdot C_4H_3O_4^-$	$C_{11}H_{17}N_2O^+\cdot C_2Cl_3O_2^-$	$C_{11}H_{17}N_2O^+\cdot 0.5C_6Cl_2O_4^{2-}\cdot H_2O$
M_r	308.33	308.33	355.64	314.76
Crystal system, space group	Orthorhombic, $Pna2_1$	Monoclinic, $P2_1/c$	Orthorhombic, $Pca2_1$	Monoclinic, $P2_1/n$
Temperature (K)	296	296	296	296
a, *b*, *c* (Å)	9.069 (1), 28.528 (3), 5.8375 (9)	9.063 (1), 6.4956 (9), 26.093 (3)	10.6117 (11), 13.808 (1), 10.9137 (8)	9.1597 (5), 15.1434 (8), 10.8742 (6)
α, β, γ (°)	90, 90, 90	90, 93.18 (1), 90	90, 90, 90	90, 102.067 (5), 90
V (Å^3)	1510.3 (3)	1533.7 (3)	1599.1 (2)	1475.02 (14)
Z	4	4	4	4
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.10	0.10	0.58	0.28
Crystal size (mm)	0.48 × 0.48 × 0.08	0.48 × 0.44 × 0.32	0.48 × 0.48 × 0.20	0.44 × 0.24 × 0.20
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, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.888, 0.992	0.871, 0.968	0.476, 0.892	0.892, 0.947
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	5834, 2827, 2316	6112, 3311, 2459	6173, 2428, 2278	9650, 9650, 7444
R_{int}	0.015	0.014	0.027	?
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650	0.651	0.654	0.651
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.101, 1.05	0.040, 0.111, 1.05	0.032, 0.086, 1.08	0.039, 0.105, 1.02
No. of reflections	2827	3311	2428	9650
No. of parameters	221	210	198	204
No. of restraints	11	0	1	0
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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.14	0.21, −0.13	0.25, −0.31	0.23, −0.32
Absolute structure	Flack *x* determined using 769 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)	–	Classical Flack method preferred over Parsons because s.u. lower	–
Absolute structure parameter	–	–	0.11 (7)	–

Computer programs: *CrysAlis CCD* (Oxford Diffraction, 2009), *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *PLATON* (Spek, 2009).

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References

Acosta, L. M., Bahsas, A., Palma, A., Cobo, J., Hursthouse, M. B. & Glidewell, C. (2009). *Acta Cryst.* C**65**, o92–o96.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.

Al-Omary, F. A. M., Ghabbour, H. A., El-Emam, A. A., Chidan Kumar, C. S. & Fun, H.-K. (2014). *Acta Cryst.* E**70**, o245–o246.

Arbo, M. D., Bastos, M. L. & Carmo, H. F. (2012). *Drug Alcohol Depend.* **122**, 174–185.

Asif, M. (2015). *Int. J. Adv. Sci. Res.* **1**, 5–11.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Brito, A., Moreira, L. K. S., Menegatti, R. & Costa, E. A. (2019). *Fundam. Clin. Pharmacol.* **33**, 13–24.

Emsley, J. (1980). *Chem. Soc. Rev.* **9**, 91–124.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998*a*). *Acta Cryst.* B**54**, 129–138.
Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998*b*). *Acta Cryst.* B**54**, 139–150.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flack, H. D. & Bernardinelli, G. (2000). *J. Appl. Cryst.* **33**, 1143–1148.
Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2005). *Acta Cryst.* C**61**, o276–o280.
Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (2000). *Acta Cryst.* B**56**, 39–57.
Herschlag, D. & Pinney, M. M. (2018). *Biochemistry*, **57**, 3338–3352.
Ishida, H. (2004*a*). *Acta Cryst.* E**60**, o974–o976.
Ishida, H. (2004*b*). *Acta Cryst.* E**60**, o1900–o1901.
Ishida, H. (2004*c*). *Acta Cryst.* E**60**, o2005–o2006.
Ishida, H. (2004*d*). *Acta Cryst.* E**60**, o2506–o2508.
Kaur, M., Jasinski, J. P., Yathirajan, H. S., Kavitha, C. N. & Glidewell, C. (2015). *Acta Cryst.* E**71**, 406–413.
Kavitha, C. N., Jasinski, J. P., Anderson, B. J., Yathirajan, H. S. & Kaur, M. (2013). *Acta Cryst.* E**69**, o1671.
Kavitha, C. N., Yathirajan, H. S., Kaur, M., Hosten, E. C., Betz, R. & Glidewell, C. (2014). *Acta Cryst.* C**70**, 805–811.
Kavitha, S. J., Panchanatheswaran, K., Low, J. N., Ferguson, G. & Glidewell, C. (2006). *Acta Cryst.* C**62**, o165–o169.
Kiran Kumar, H., Yathirajan, H. S., Sagar, B. K., Foro, S. & Glidewell, C. (2019). *Acta Cryst.* E**75**, 1253–1260.
Lu, Y.-X. (2007). *Acta Cryst.* E**63**, o3611.
Nagai, F., Nonaka, R. & Kamimura, K. S. H. (2007). *Eur. J. Pharmacol.* **559**, 132–137.
Oxford Diffraction (2009). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Sagar, B. K., Girisha, M., Yathirajan, H. S., Rathore, R. S. & Glidewell, C. (2017). *Acta Cryst.* E**73**, 1320–1325.
Shaibah, M. A. E., Sagar, B. K., Yathirajan, H. S., Kumar, S. M. & Glidewell, C. (2017*a*). *Acta Cryst.* E**73**, 1513–1516.
Shaibah, M. A. E., Yathirajan, H. S., Kumar, S. M., Byrappa, K. & Glidewell, C. (2017*b*). *Acta Cryst.* E**73**, 1488–1492.
Shaibah, M. A. E., Yathirajan, H. S., Rathore, R. S., Furuya, T., Haraguchi, T., Akitsu, T. & Glidewell, C. (2019). *Acta Cryst.* E**75**, 292–298.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Sovago, I., Thomas, L. H., Adam, M. S., Capelli, S. C., Wilson, C. C. & Farrugia, L. J. (2016). *CrystEngComm*, **18**, 5697–5709.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Staack, R. F. & Maurer, H. H. (2003). *J. Chromatogr. B*, **798**, 333–342.
Staack, R. F. & Maurer, H. H. (2005). *Curr. Drug Metab.* **6**, 259–274.
Staack, R. F., Theobald, D. S., Paul, D., Springer, D., Kraemer, T. & Maurer, H. H. (2004). *Xenobiotica*, **34**, 179–192.
Verdonk, M. L., Voogd, J. W., Kanters, J. A., Kroon, J., den Besten, R., Brandsma, L., Leysen, D. & Kelder, J. (1997). *Acta Cryst.* B**53**, 976–983.
Wohlfarth, A., Weinmann, W. & Dresen, S. (2010). *Anal. Bioanal. Chem.* **396**, 2403–2414.
Wood, P. A., Allen, F. H. & Pidcock, E. (2009). *CrystEngComm*, **11**, 1563–1571.
Zia-ur-Rehman, Tahir, M. N., Danish, M., Muhammad, N. & Ali, S. (2009). *Acta Cryst.* E**65**, o503.

supporting information

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Twelve 4-(4-methoxyphenyl)piperazin-1-ium salts containing organic anions: supramolecular assembly in one, two and three dimensions

Haruvegowda Kiran Kumar, Hemmige S. Yathirajan, Sabine Foro and Christopher Glidewell

Computing details

For all structures, data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b) and *PLATON* (Spek, 2009).

4-(4-Methoxyphenyl)piperazin-1-ium benzoate monohydrate (I)

Crystal data

$C_{11}H_{17}N_2O^+\cdot C_7H_5O_2^-\cdot H_2O$
M_r = 332.39
Triclinic, $P\overline{1}$
a = 6.215 (1) Å
b = 7.547 (1) Å
c = 18.716 (4) Å
α = 84.34 (2)°
β = 87.14 (2)°
γ = 84.69 (2)°
V = 869.1 (3) Å^3
Z = 2
$F(000)$ = 356
D_x = 1.270 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3742 reflections
θ = 2.8–28.0°
μ = 0.09 mm^{-1}
T = 296 K
Plate, colourless
0.40 × 0.24 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.834, T_{max} = 0.996
5751 measured reflections
3442 independent reflections
1839 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 26.1°, θ_{min} = 2.8°
h = −7→7
k = −9→9
l = −19→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.134
S = 1.02
3442 reflections
256 parameters
17 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Experimental. Compound (I). IR (KBr , cm^{-1}) 3328 (OH), 3002 (H_2) 2841 (OCH_3), 1591 (COO). NMR ($CDCl_3$) δ(^{1}H) 3.22 (m, 4H, piperazine), 3.29 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.86 (m, 4H, methoxyphenyl), 7.39 (m, 2H, phenyl), 7.46 (m, 1H, phenyl), 8.05 (m, 2H, phenyl).

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.7874 (3)	0.7435 (3)	0.44989 (10)	0.0482 (5)	
H11	0.834 (3)	0.766 (3)	0.4926 (13)	0.058*	
H12	0.748 (3)	0.621 (3)	0.4555 (11)	0.058*	
C2	0.9747 (3)	0.7530 (3)	0.39809 (12)	0.0519 (6)	
H2A	1.0940	0.6709	0.4157	0.062*	
H2B	1.0215	0.8729	0.3934	0.062*	
C3	0.9144 (3)	0.7056 (3)	0.32596 (12)	0.0497 (6)	
H3A	1.0363	0.7191	0.2921	0.060*	
H3B	0.8837	0.5812	0.3301	0.060*	
N4	0.7262 (2)	0.8168 (2)	0.29814 (9)	0.0394 (4)	
C5	0.5425 (3)	0.8133 (3)	0.35024 (11)	0.0463 (5)	
H5A	0.4932	0.6943	0.3561	0.056*	
H5B	0.4244	0.8957	0.3320	0.056*	
C6	0.6019 (3)	0.8640 (3)	0.42214 (12)	0.0513 (6)	
H6A	0.6397	0.9866	0.4173	0.062*	
H6B	0.4789	0.8557	0.4559	0.062*	
C21	0.677 (2)	0.782 (2)	0.2275 (6)	0.034 (2)	0.66 (2)
C22	0.8134 (13)	0.6810 (17)	0.1831 (5)	0.0450 (18)	0.66 (2)
H22	0.9414	0.6235	0.2007	0.054*	0.66 (2)
C23	0.7627 (13)	0.6649 (18)	0.1132 (5)	0.053 (2)	0.66 (2)
H23	0.8602	0.6005	0.0841	0.064*	0.66 (2)
C24	0.5725 (14)	0.7413 (16)	0.0858 (5)	0.0438 (17)	0.66 (2)
C25	0.438 (2)	0.846 (3)	0.1278 (8)	0.0599 (10)	0.66 (2)
H25	0.3145	0.9097	0.1088	0.072*	0.66 (2)
C26	0.486 (3)	0.858 (3)	0.1984 (8)	0.054 (2)	0.66 (2)
H26	0.3857	0.9191	0.2276	0.064*	0.66 (2)
O24	0.541 (3)	0.720 (3)	0.0149 (7)	0.078 (3)	0.66 (2)
C27	0.335 (3)	0.773 (4)	−0.0122 (11)	0.090 (2)	0.66 (2)
H27A	0.2297	0.7017	0.0128	0.135*	0.66 (2)
H27B	0.3373	0.7580	−0.0626	0.135*	0.66 (2)
H27C	0.2962	0.8970	−0.0053	0.135*	0.66 (2)
C51	0.669 (5)	0.815 (5)	0.2258 (12)	0.034 (2)	0.34 (2)
C52	0.817 (3)	0.735 (2)	0.1784 (11)	0.0450 (18)	0.34 (2)

H52	0.9535	0.6917	0.1937	0.054*	0.34 (2)
C53	0.764 (3)	0.718 (3)	0.1087 (10)	0.053 (2)	0.34 (2)
H53	0.8615	0.6555	0.0790	0.064*	0.34 (2)
C54	0.571 (3)	0.792 (2)	0.0828 (10)	0.0438 (17)	0.34 (2)
C55	0.414 (4)	0.854 (7)	0.1309 (15)	0.0599 (10)	0.34 (2)
H55	0.2702	0.8738	0.1184	0.072*	0.34 (2)
C56	0.474 (5)	0.886 (7)	0.1983 (15)	0.054 (2)	0.34 (2)
H56	0.3803	0.9570	0.2260	0.064*	0.34 (2)
O54	0.528 (6)	0.756 (7)	0.0142 (14)	0.078 (3)	0.34 (2)
C57	0.310 (6)	0.780 (9)	−0.006 (2)	0.090 (2)	0.34 (2)
H57A	0.2919	0.7103	−0.0451	0.135*	0.34 (2)
H57B	0.2718	0.9042	−0.0207	0.135*	0.34 (2)
H57C	0.2171	0.7422	0.0342	0.135*	0.34 (2)
C31	0.8112 (3)	0.7289 (3)	0.70824 (12)	0.0441 (5)	
C32	0.6694 (4)	0.6501 (3)	0.75905 (17)	0.0642 (7)	
H32	0.5518	0.5977	0.7441	0.077*	
C33	0.7024 (5)	0.6491 (3)	0.83138 (17)	0.0777 (9)	
H33	0.6070	0.5956	0.8649	0.093*	
C34	0.8735 (5)	0.7259 (3)	0.85422 (15)	0.0741 (8)	
H34	0.8935	0.7264	0.9031	0.089*	
C35	1.0147 (4)	0.8017 (3)	0.80535 (14)	0.0631 (7)	
H35	1.1322	0.8530	0.8209	0.076*	
C36	0.9850 (3)	0.8032 (3)	0.73275 (13)	0.0483 (6)	
H36	1.0835	0.8550	0.6999	0.058*	
C37	0.7750 (4)	0.7325 (3)	0.62925 (15)	0.0563 (6)	
O31	0.9017 (3)	0.8122 (2)	0.58536 (9)	0.0664 (5)	
O32	0.6242 (3)	0.6520 (3)	0.61161 (12)	0.1072 (8)	
O41	0.7231 (3)	0.3783 (2)	0.45956 (10)	0.0657 (5)	
H41	0.607 (5)	0.372 (4)	0.4354 (16)	0.099*	
H42	0.839 (5)	0.318 (4)	0.4391 (16)	0.099*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0614 (13)	0.0460 (11)	0.0394 (12)	−0.0089 (9)	−0.0119 (10)	−0.0069 (9)
C2	0.0452 (14)	0.0584 (14)	0.0529 (16)	−0.0018 (11)	−0.0116 (11)	−0.0075 (12)
C3	0.0424 (13)	0.0583 (14)	0.0483 (15)	0.0016 (10)	−0.0047 (10)	−0.0084 (11)
N4	0.0391 (10)	0.0403 (10)	0.0386 (11)	0.0002 (7)	−0.0018 (8)	−0.0064 (8)
C5	0.0414 (12)	0.0553 (13)	0.0413 (14)	0.0022 (10)	−0.0001 (10)	−0.0072 (10)
C6	0.0561 (14)	0.0529 (14)	0.0438 (15)	0.0044 (11)	−0.0012 (11)	−0.0083 (11)
C21	0.0428 (15)	0.022 (6)	0.0377 (14)	−0.001 (3)	−0.0009 (10)	−0.002 (2)
C22	0.0449 (14)	0.041 (5)	0.048 (2)	0.005 (3)	−0.0021 (13)	−0.007 (3)
C23	0.0575 (16)	0.053 (6)	0.048 (2)	0.008 (3)	0.0060 (13)	−0.015 (3)
C24	0.0628 (16)	0.031 (5)	0.0378 (17)	−0.004 (3)	−0.0012 (13)	−0.002 (3)
C25	0.057 (3)	0.072 (2)	0.047 (2)	0.020 (3)	−0.013 (2)	−0.0097 (16)
C26	0.057 (2)	0.054 (7)	0.0477 (16)	0.022 (2)	−0.0054 (14)	−0.014 (3)
O24	0.083 (2)	0.110 (10)	0.0410 (12)	0.009 (3)	−0.0107 (11)	−0.023 (3)
C27	0.081 (5)	0.140 (3)	0.052 (3)	−0.008 (4)	−0.018 (4)	−0.020 (4)

C51	0.0428 (15)	0.022 (6)	0.0377 (14)	−0.001 (3)	−0.0009 (10)	−0.002 (2)
C52	0.0449 (14)	0.041 (5)	0.048 (2)	0.005 (3)	−0.0021 (13)	−0.007 (3)
C53	0.0575 (16)	0.053 (6)	0.048 (2)	0.008 (3)	0.0060 (13)	−0.015 (3)
C54	0.0628 (16)	0.031 (5)	0.0378 (17)	−0.004 (3)	−0.0012 (13)	−0.002 (3)
C55	0.057 (3)	0.072 (2)	0.047 (2)	0.020 (3)	−0.013 (2)	−0.0097 (16)
C56	0.057 (2)	0.054 (7)	0.0477 (16)	0.022 (2)	−0.0054 (14)	−0.014 (3)
O54	0.083 (2)	0.110 (10)	0.0410 (12)	0.009 (3)	−0.0107 (11)	−0.023 (3)
C57	0.081 (5)	0.140 (3)	0.052 (3)	−0.008 (4)	−0.018 (4)	−0.020 (4)
C31	0.0428 (12)	0.0353 (11)	0.0550 (15)	0.0023 (10)	−0.0041 (11)	−0.0117 (10)
C32	0.0510 (15)	0.0506 (15)	0.092 (2)	−0.0061 (11)	0.0098 (14)	−0.0174 (14)
C33	0.091 (2)	0.0614 (17)	0.073 (2)	0.0018 (15)	0.0343 (17)	0.0038 (15)
C34	0.099 (2)	0.0639 (17)	0.0554 (19)	0.0101 (16)	−0.0013 (17)	−0.0025 (14)
C35	0.0746 (18)	0.0624 (16)	0.0530 (18)	−0.0031 (13)	−0.0179 (14)	−0.0044 (13)
C36	0.0509 (13)	0.0454 (13)	0.0492 (16)	−0.0057 (10)	−0.0079 (11)	−0.0023 (10)
C37	0.0540 (15)	0.0504 (15)	0.0680 (19)	0.0062 (12)	−0.0207 (13)	−0.0233 (13)
O31	0.0856 (13)	0.0687 (11)	0.0468 (11)	−0.0072 (10)	−0.0138 (9)	−0.0092 (9)
O32	0.0869 (14)	0.1422 (19)	0.1065 (18)	−0.0380 (13)	−0.0368 (12)	−0.0380 (15)
O41	0.0653 (12)	0.0631 (11)	0.0715 (14)	−0.0142 (9)	−0.0198 (9)	−0.0044 (9)

Geometric parameters (Å, º)

N1—C2	1.480 (3)	C27—H27C	0.9600
N1—C6	1.483 (3)	C51—C56	1.381 (7)
N1—H11	0.90 (2)	C51—C52	1.385 (7)
N1—H12	0.97 (2)	C52—C53	1.380 (7)
C2—C3	1.504 (3)	C52—H52	0.9300
C2—H2A	0.9700	C53—C54	1.368 (7)
C2—H2B	0.9700	C53—H53	0.9300
C3—N4	1.461 (2)	C54—C55	1.374 (9)
C3—H3A	0.9700	C54—O54	1.380 (7)
C3—H3B	0.9700	C55—C56	1.383 (9)
N4—C51	1.42 (2)	C55—H55	0.9300
N4—C21	1.428 (10)	C56—H56	0.9300
N4—C5	1.464 (2)	O54—C57	1.415 (9)
C5—C6	1.507 (3)	C57—H57A	0.9600
C5—H5A	0.9700	C57—H57B	0.9600
C5—H5B	0.9700	C57—H57C	0.9600
C6—H6A	0.9700	C31—C36	1.380 (3)
C6—H6B	0.9700	C31—C32	1.391 (3)
C21—C26	1.382 (4)	C31—C37	1.504 (3)
C21—C22	1.386 (4)	C32—C33	1.378 (4)
C22—C23	1.380 (4)	C32—H32	0.9300
C22—H22	0.9300	C33—C34	1.363 (4)
C23—C24	1.367 (4)	C33—H33	0.9300
C23—H23	0.9300	C34—C35	1.358 (3)
C24—C25	1.372 (7)	C34—H34	0.9300
C24—O24	1.378 (4)	C35—C36	1.379 (3)
C25—C26	1.382 (5)	C35—H35	0.9300

C25—H25	0.9300	C36—H36	0.9300
C26—H26	0.9300	C37—O32	1.238 (3)
O24—C27	1.413 (6)	C37—O31	1.258 (3)
C27—H27A	0.9600	O41—H41	0.88 (3)
C27—H27B	0.9600	O41—H42	0.91 (3)

C2—N1—C6	109.95 (18)	O24—C27—H27A	109.5
C2—N1—H11	106.8 (14)	O24—C27—H27B	109.5
C6—N1—H11	115.6 (14)	H27A—C27—H27B	109.5
C2—N1—H12	108.2 (12)	O24—C27—H27C	109.5
C6—N1—H12	109.2 (12)	H27A—C27—H27C	109.5
H11—N1—H12	106.8 (18)	H27B—C27—H27C	109.5
N1—C2—C3	110.23 (17)	C56—C51—C52	116.4 (9)
N1—C2—H2A	109.6	C56—C51—N4	125.0 (16)
C3—C2—H2A	109.6	C52—C51—N4	118.6 (16)
N1—C2—H2B	109.6	C53—C52—C51	121.0 (9)
C3—C2—H2B	109.6	C53—C52—H52	119.5
H2A—C2—H2B	108.1	C51—C52—H52	119.5
N4—C3—C2	112.64 (17)	C54—C53—C52	121.0 (9)
N4—C3—H3A	109.1	C54—C53—H53	119.5
C2—C3—H3A	109.1	C52—C53—H53	119.5
N4—C3—H3B	109.1	C53—C54—C55	118.1 (9)
C2—C3—H3B	109.1	C53—C54—O54	116.3 (10)
H3A—C3—H3B	107.8	C55—C54—O54	123.3 (12)
C51—N4—C3	120.7 (9)	C54—C55—C56	118.8 (13)
C21—N4—C3	113.1 (5)	C54—C55—H55	120.6
C51—N4—C5	114.2 (13)	C56—C55—H55	120.6
C21—N4—C5	114.4 (6)	C51—C56—C55	122.1 (10)
C3—N4—C5	111.20 (16)	C51—C56—H56	119.0
N4—C5—C6	111.63 (17)	C55—C56—H56	119.0
N4—C5—H5A	109.3	C54—O54—C57	117.7 (12)
C6—C5—H5A	109.3	O54—C57—H57A	109.5
N4—C5—H5B	109.3	O54—C57—H57B	109.5
C6—C5—H5B	109.3	H57A—C57—H57B	109.5
H5A—C5—H5B	108.0	O54—C57—H57C	109.5
N1—C6—C5	110.23 (17)	H57A—C57—H57C	109.5
N1—C6—H6A	109.6	H57B—C57—H57C	109.5
C5—C6—H6A	109.6	C36—C31—C32	117.9 (2)
N1—C6—H6B	109.6	C36—C31—C37	121.4 (2)
C5—C6—H6B	109.6	C32—C31—C37	120.8 (2)
H6A—C6—H6B	108.1	C33—C32—C31	120.4 (2)
C26—C21—C22	116.0 (4)	C33—C32—H32	119.8
C26—C21—N4	119.5 (8)	C31—C32—H32	119.8
C22—C21—N4	124.4 (8)	C34—C33—C32	120.6 (3)
C23—C22—C21	121.2 (4)	C34—C33—H33	119.7
C23—C22—H22	119.4	C32—C33—H33	119.7
C21—C22—H22	119.4	C35—C34—C33	119.8 (3)
C24—C23—C22	121.5 (4)	C35—C34—H34	120.1

C24—C23—H23	119.3	C33—C34—H34	120.1
C22—C23—H23	119.3	C34—C35—C36	120.5 (2)
C23—C24—C25	118.5 (4)	C34—C35—H35	119.7
C23—C24—O24	116.6 (5)	C36—C35—H35	119.7
C25—C24—O24	124.6 (6)	C35—C36—C31	120.9 (2)
C24—C25—C26	119.5 (7)	C35—C36—H36	119.6
C24—C25—H25	120.3	C31—C36—H36	119.6
C26—C25—H25	120.3	O32—C37—O31	124.1 (3)
C21—C26—C25	122.9 (5)	O32—C37—C31	117.3 (3)
C21—C26—H26	118.5	O31—C37—C31	118.6 (2)
C25—C26—H26	118.5	H41—O41—H42	111 (3)
C24—O24—C27	118.1 (6)		

C6—N1—C2—C3	−57.3 (2)	C3—N4—C51—C56	166 (4)
N1—C2—C3—N4	55.6 (2)	C5—N4—C51—C56	30 (5)
C2—C3—N4—C51	168.3 (19)	C21—N4—C51—C52	−56 (9)
C2—C3—N4—C21	175.8 (8)	C3—N4—C51—C52	−13 (4)
C2—C3—N4—C5	−53.8 (2)	C5—N4—C51—C52	−149 (2)
C51—N4—C5—C6	−164.9 (15)	C56—C51—C52—C53	−4 (5)
C21—N4—C5—C6	−176.0 (7)	N4—C51—C52—C53	175 (2)
C3—N4—C5—C6	54.3 (2)	C51—C52—C53—C54	5 (3)
C2—N1—C6—C5	58.3 (2)	C52—C53—C54—C55	−12 (4)
N4—C5—C6—N1	−57.0 (2)	C52—C53—C54—O54	−176 (3)
C51—N4—C21—C26	−49 (10)	C53—C54—C55—C56	18 (6)
C3—N4—C21—C26	170.7 (16)	O54—C54—C55—C56	−180 (5)
C5—N4—C21—C26	42 (2)	C52—C51—C56—C55	10 (7)
C51—N4—C21—C22	128 (12)	N4—C51—C56—C55	−169 (4)
C3—N4—C21—C22	−12.5 (17)	C54—C55—C56—C51	−17 (8)
C5—N4—C21—C22	−141.2 (12)	C53—C54—O54—C57	161 (4)
C26—C21—C22—C23	2 (2)	C55—C54—O54—C57	−2 (7)
N4—C21—C22—C23	−174.5 (11)	C36—C31—C32—C33	0.7 (3)
C21—C22—C23—C24	−2.6 (14)	C37—C31—C32—C33	−179.3 (2)
C22—C23—C24—C25	4.6 (17)	C31—C32—C33—C34	0.3 (4)
C22—C23—C24—O24	178.6 (15)	C32—C33—C34—C35	−1.0 (4)
C23—C24—C25—C26	−6 (3)	C33—C34—C35—C36	0.7 (4)
O24—C24—C25—C26	−180 (2)	C34—C35—C36—C31	0.4 (3)
C22—C21—C26—C25	−4 (3)	C32—C31—C36—C35	−1.0 (3)
N4—C21—C26—C25	173 (2)	C37—C31—C36—C35	178.9 (2)
C24—C25—C26—C21	7 (4)	C36—C31—C37—O32	175.1 (2)
C23—C24—O24—C27	171 (2)	C32—C31—C37—O32	−5.0 (3)
C25—C24—O24—C27	−16 (3)	C36—C31—C37—O31	−3.1 (3)
C21—N4—C51—C56	123 (14)	C32—C31—C37—O31	176.9 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O31	0.90 (2)	1.88 (2)	2.777 (3)	174.1 (19)
N1—H12···O41	0.97 (2)	1.85 (2)	2.808 (3)	169.7 (18)

O41—H41···O32^{i}	0.88 (3)	1.75 (3)	2.631 (3)	177 (3)
O41—H42···O31^{ii}	0.91 (3)	1.87 (3)	2.763 (3)	169 (3)
C2—H2*B*···O31^{iii}	0.97	2.54	3.485 (3)	165
C22—H22···*Cg*1^{ii}	0.93	2.85	3.603 (3)	139
C26—H26···*Cg*1^{iv}	0.93	2.90	3.62 (2)	135
C56—H56···*Cg*1^{iv}	0.93	2.64	3.41 (5)	141

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

4-(4-Methoxyphenyl)piperazin-1-ium 4-fluorobenzoate monohydrate (II)

Crystal data

$C_{11}H_{17}N_2O^+·C_7H_4FO_2^-·H_2O$
M_r = 350.38
Triclinic, $P\overline{1}$
a = 6.256 (1) Å
b = 7.489 (1) Å
c = 19.097 (2) Å
α = 84.19 (1)°
β = 86.98 (2)°
γ = 84.62 (2)°
V = 885.4 (2) Å^3
Z = 2
F(000) = 372
D_x = 1.314 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3771 reflections
θ = 2.9–27.9°
μ = 0.10 mm^{-1}
T = 293 K
Plate, colourless
0.40 × 0.24 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.973, T_{max} = 0.996
5760 measured reflections
3477 independent reflections
1355 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 26.1°, θ_{min} = 2.9°
h = −7→6
k = −9→9
l = −23→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.128
S = 1.01
3477 reflections
265 parameters
17 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Special details

Experimental. Compound (II). IR (KBr , cm^{-1}) 3317 (OH), 3011 (NH_2), 2838 (OCH_3), 1588 (COO), 1365 (CF) NMR ($CDCl_3$) δ(^{1}H) 3.23 (m, 4H, piperazine), 3.29 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.86 (m, 4H, methoxyphenyl), 7.05 (m, 2H, fluorophenyl), 8.05 (m, 2H, fluorophenyl).

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)
N1	0.7813 (5)	0.7442 (3)	0.45140 (15)	0.0536 (8)	
H11	0.823 (4)	0.778 (3)	0.5031 (15)	0.064*	
H12	0.749 (4)	0.634 (4)	0.4565 (14)	0.064*	
C2	0.9661 (5)	0.7540 (4)	0.39966 (16)	0.0599 (9)	
H2A	1.0848	0.6706	0.4164	0.072*	
H2B	1.0131	0.8746	0.3952	0.072*	
C3	0.9056 (5)	0.7083 (4)	0.32889 (15)	0.0574 (9)	
H3A	1.0264	0.7229	0.2955	0.069*	
H3B	0.8755	0.5829	0.3326	0.069*	
N4	0.7185 (4)	0.8206 (3)	0.30227 (12)	0.0444 (6)	
C5	0.5377 (5)	0.8151 (4)	0.35391 (14)	0.0527 (8)	
H5A	0.4900	0.6947	0.3596	0.063*	
H5B	0.4192	0.8977	0.3365	0.063*	
C6	0.5960 (5)	0.8649 (4)	0.42410 (14)	0.0567 (9)	
H6A	0.6324	0.9887	0.4194	0.068*	
H6B	0.4736	0.8556	0.4572	0.068*	
C21	0.670 (3)	0.795 (6)	0.2319 (6)	0.0442 (18)	0.81 (3)
C22	0.8062 (12)	0.6932 (18)	0.1883 (4)	0.064 (2)	0.81 (3)
H22	0.9351	0.6378	0.2053	0.077*	0.81 (3)
C23	0.7544 (9)	0.673 (2)	0.1207 (3)	0.069 (3)	0.81 (3)
H23	0.8520	0.6083	0.0923	0.083*	0.81 (3)
C24	0.5644 (10)	0.7455 (18)	0.0942 (3)	0.058 (2)	0.81 (3)
C25	0.4255 (15)	0.846 (3)	0.1357 (5)	0.0680 (18)	0.81 (3)
H25	0.2967	0.9002	0.1182	0.082*	0.81 (3)
C26	0.4782 (18)	0.866 (3)	0.2037 (5)	0.062 (2)	0.81 (3)
H26	0.3798	0.9313	0.2317	0.074*	0.81 (3)
O24	0.5299 (13)	0.7159 (19)	0.0261 (3)	0.095 (2)	0.81 (3)
C27	0.3282 (18)	0.772 (3)	−0.0015 (6)	0.107 (4)	0.81 (3)
H27A	0.2181	0.7178	0.0279	0.160*	0.81 (3)
H27B	0.3249	0.7366	−0.0483	0.160*	0.81 (3)
H27C	0.3035	0.9011	−0.0029	0.160*	0.81 (3)
C51	0.655 (11)	0.79 (3)	0.236 (2)	0.0442 (18)	0.19 (3)
C52	0.810 (6)	0.754 (6)	0.1833 (17)	0.064 (2)	0.19 (3)
H52	0.9531	0.7290	0.1949	0.077*	0.19 (3)
C53	0.756 (4)	0.752 (6)	0.1146 (15)	0.069 (3)	0.19 (3)
H53	0.8593	0.7106	0.0818	0.083*	0.19 (3)
C54	0.554 (4)	0.808 (5)	0.0936 (13)	0.058 (2)	0.19 (3)
C55	0.396 (6)	0.842 (13)	0.144 (2)	0.0680 (18)	0.19 (3)
H55	0.2524	0.8581	0.1327	0.082*	0.19 (3)
C56	0.453 (7)	0.851 (13)	0.213 (2)	0.062 (2)	0.19 (3)
H56	0.3509	0.8987	0.2444	0.074*	0.19 (3)
O54	0.512 (5)	0.786 (6)	0.0251 (14)	0.095 (2)	0.19 (3)
C57	0.300 (7)	0.827 (12)	0.004 (3)	0.107 (4)	0.19 (3)
H57A	0.2472	0.9444	0.0166	0.160*	0.19 (3)
H57B	0.2101	0.7391	0.0266	0.160*	0.19 (3)

H57C	0.2965	0.8256	−0.0463	0.160*	0.19 (3)
C31	0.8132 (5)	0.7284 (4)	0.70495 (17)	0.0485 (8)	
C32	0.6742 (5)	0.6533 (4)	0.7564 (2)	0.0676 (10)	
H32	0.5542	0.6028	0.7431	0.081*	
C33	0.7114 (6)	0.6527 (5)	0.8267 (2)	0.0798 (11)	
H33	0.6181	0.6022	0.8611	0.096*	
C34	0.8883 (7)	0.7278 (5)	0.8448 (2)	0.0752 (11)	
F34	0.9236 (3)	0.7291 (3)	0.91437 (11)	0.1208 (9)	
C35	1.0294 (5)	0.8010 (4)	0.7961 (2)	0.0658 (10)	
H35	1.1495	0.8505	0.8100	0.079*	
C36	0.9911 (5)	0.8003 (4)	0.72606 (17)	0.0542 (9)	
H36	1.0870	0.8494	0.6922	0.065*	
C37	0.7690 (6)	0.7297 (5)	0.6289 (2)	0.0614 (10)	
O31	0.8943 (4)	0.8069 (3)	0.58380 (12)	0.0715 (7)	
O32	0.6112 (4)	0.6566 (4)	0.61332 (13)	0.1091 (10)	
O41	0.7239 (4)	0.3737 (3)	0.46049 (12)	0.0700 (8)	
H41	0.615 (6)	0.356 (5)	0.4356 (17)	0.105*	
H42	0.835 (6)	0.312 (5)	0.4379 (18)	0.105*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.065 (2)	0.0429 (18)	0.0550 (18)	−0.0089 (16)	−0.0145 (16)	−0.0061 (15)
C2	0.050 (2)	0.060 (3)	0.070 (2)	−0.0047 (18)	−0.0107 (19)	−0.0069 (18)
C3	0.049 (2)	0.065 (2)	0.059 (2)	−0.0019 (18)	−0.0035 (17)	−0.0091 (18)
N4	0.0405 (16)	0.0437 (17)	0.0483 (16)	0.0016 (13)	−0.0044 (13)	−0.0054 (12)
C5	0.049 (2)	0.057 (2)	0.052 (2)	−0.0005 (16)	−0.0015 (17)	−0.0083 (16)
C6	0.059 (2)	0.057 (2)	0.053 (2)	0.0029 (18)	−0.0011 (17)	−0.0049 (17)
C21	0.044 (3)	0.042 (3)	0.047 (2)	−0.004 (4)	0.001 (2)	−0.008 (3)
C22	0.055 (2)	0.070 (7)	0.068 (3)	0.009 (3)	−0.005 (2)	−0.020 (3)
C23	0.063 (3)	0.080 (8)	0.067 (3)	0.009 (3)	0.004 (2)	−0.030 (4)
C24	0.066 (3)	0.058 (6)	0.053 (3)	−0.007 (3)	−0.003 (2)	−0.017 (3)
C25	0.061 (3)	0.087 (3)	0.054 (4)	0.012 (4)	−0.009 (3)	−0.009 (4)
C26	0.056 (3)	0.070 (5)	0.056 (3)	0.016 (4)	−0.001 (2)	−0.013 (4)
O24	0.094 (3)	0.129 (7)	0.0660 (19)	0.008 (4)	−0.0132 (16)	−0.039 (3)
C27	0.102 (5)	0.156 (14)	0.067 (4)	−0.004 (5)	−0.027 (4)	−0.023 (4)
C51	0.044 (3)	0.042 (3)	0.047 (2)	−0.004 (4)	0.001 (2)	−0.008 (3)
C52	0.055 (2)	0.070 (7)	0.068 (3)	0.009 (3)	−0.005 (2)	−0.020 (3)
C53	0.063 (3)	0.080 (8)	0.067 (3)	0.009 (3)	0.004 (2)	−0.030 (4)
C54	0.066 (3)	0.058 (6)	0.053 (3)	−0.007 (3)	−0.003 (2)	−0.017 (3)
C55	0.061 (3)	0.087 (3)	0.054 (4)	0.012 (4)	−0.009 (3)	−0.009 (4)
C56	0.056 (3)	0.070 (5)	0.056 (3)	0.016 (4)	−0.001 (2)	−0.013 (4)
O54	0.094 (3)	0.129 (7)	0.0660 (19)	0.008 (4)	−0.0132 (16)	−0.039 (3)
C57	0.102 (5)	0.156 (14)	0.067 (4)	−0.004 (5)	−0.027 (4)	−0.023 (4)
C31	0.045 (2)	0.039 (2)	0.063 (2)	0.0008 (16)	−0.0084 (18)	−0.0119 (16)
C32	0.051 (2)	0.055 (3)	0.099 (3)	−0.0062 (18)	−0.002 (2)	−0.017 (2)
C33	0.072 (3)	0.073 (3)	0.089 (3)	−0.004 (2)	0.020 (2)	−0.001 (2)
C34	0.083 (3)	0.084 (3)	0.057 (3)	0.003 (2)	−0.009 (2)	−0.004 (2)

F34	0.131 (2)	0.164 (2)	0.0633 (15)	0.0008 (17)	−0.0068 (13)	−0.0036 (14)
C35	0.059 (2)	0.068 (3)	0.072 (3)	−0.0106 (19)	−0.011 (2)	−0.006 (2)
C36	0.056 (2)	0.052 (2)	0.056 (2)	−0.0059 (18)	−0.0122 (17)	−0.0070 (16)
C37	0.057 (3)	0.042 (2)	0.087 (3)	0.0070 (19)	−0.022 (2)	−0.019 (2)
O31	0.0848 (18)	0.0686 (18)	0.0638 (17)	−0.0057 (15)	−0.0208 (14)	−0.0123 (13)
O32	0.0871 (19)	0.129 (3)	0.124 (2)	−0.0362 (18)	−0.0427 (16)	−0.0343 (17)
O41	0.0693 (17)	0.0628 (18)	0.0816 (18)	−0.0137 (14)	−0.0227 (13)	−0.0073 (13)

Geometric parameters (Å, º)

N1—C2	1.483 (4)	C27—H27C	0.9600
N1—C6	1.485 (4)	C51—C56	1.380 (9)
N1—H11	1.09 (3)	C51—C52	1.390 (19)
N1—H12	0.87 (3)	C52—C53	1.374 (9)
C2—C3	1.503 (3)	C52—H52	0.9300
C2—H2A	0.9700	C53—C54	1.362 (9)
C2—H2B	0.9700	C53—H53	0.9300
C3—N4	1.458 (3)	C54—C55	1.370 (13)
C3—H3A	0.9700	C54—O54	1.377 (9)
C3—H3B	0.9700	C55—C56	1.383 (9)
N4—C51	1.39 (5)	C55—H55	0.9300
N4—C21	1.429 (10)	C56—H56	0.9300
N4—C5	1.462 (3)	O54—C57	1.408 (10)
C5—C6	1.499 (3)	C57—H57A	0.9600
C5—H5A	0.9700	C57—H57B	0.9600
C5—H5B	0.9700	C57—H57C	0.9600
C6—H6A	0.9700	C31—C36	1.377 (3)
C6—H6B	0.9700	C31—C32	1.388 (4)
C21—C26	1.379 (6)	C31—C37	1.491 (4)
C21—C22	1.389 (15)	C32—C33	1.374 (4)
C22—C23	1.374 (4)	C32—H32	0.9300
C22—H22	0.9300	C33—C34	1.363 (4)
C23—C24	1.361 (5)	C33—H33	0.9300
C23—H23	0.9300	C34—C35	1.358 (4)
C24—C25	1.369 (9)	C34—F34	1.360 (4)
C24—O24	1.373 (4)	C35—C36	1.373 (4)
C25—C26	1.383 (5)	C35—H35	0.9300
C25—H25	0.9300	C36—H36	0.9300
C26—H26	0.9300	C37—O32	1.236 (3)
O24—C27	1.405 (4)	C37—O31	1.266 (4)
C27—H27A	0.9600	O41—H41	0.88 (3)
C27—H27B	0.9600	O41—H42	0.91 (4)
C2—N1—C6	109.5 (2)	O24—C27—H27A	109.5
C2—N1—H11	111.6 (13)	O24—C27—H27B	109.5
C6—N1—H11	111.1 (13)	H27A—C27—H27B	109.5
C2—N1—H12	107 (2)	O24—C27—H27C	109.5
C6—N1—H12	110.0 (19)	H27A—C27—H27C	109.5

H11—N1—H12	107 (2)	H27B—C27—H27C	109.5
N1—C2—C3	110.9 (2)	C56—C51—C52	115.3 (18)
N1—C2—H2A	109.5	C56—C51—N4	122 (4)
C3—C2—H2A	109.5	C52—C51—N4	120 (5)
N1—C2—H2B	109.5	C53—C52—C51	121.2 (14)
C3—C2—H2B	109.5	C53—C52—H52	119.4
H2A—C2—H2B	108.1	C51—C52—H52	119.4
N4—C3—C2	112.7 (2)	C54—C53—C52	121.5 (11)
N4—C3—H3A	109.0	C54—C53—H53	119.3
C2—C3—H3A	109.0	C52—C53—H53	119.3
N4—C3—H3B	109.0	C53—C54—C55	118.3 (12)
C2—C3—H3B	109.0	C53—C54—O54	116.6 (13)
H3A—C3—H3B	107.8	C55—C54—O54	123.2 (15)
C51—N4—C3	117 (4)	C54—C55—C56	119.0 (16)
C21—N4—C3	114.4 (9)	C54—C55—H55	120.5
C51—N4—C5	111 (4)	C56—C55—H55	120.5
C21—N4—C5	115.5 (10)	C51—C56—C55	122.8 (13)
C3—N4—C5	110.9 (2)	C51—C56—H56	118.6
N4—C5—C6	112.1 (2)	C55—C56—H56	118.6
N4—C5—H5A	109.2	C54—O54—C57	117.8 (15)
C6—C5—H5A	109.2	O54—C57—H57A	109.5
N4—C5—H5B	109.2	O54—C57—H57B	109.5
C6—C5—H5B	109.2	H57A—C57—H57B	109.5
H5A—C5—H5B	107.9	O54—C57—H57C	109.5
N1—C6—C5	110.6 (2)	H57A—C57—H57C	109.5
N1—C6—H6A	109.5	H57B—C57—H57C	109.5
C5—C6—H6A	109.5	C36—C31—C32	118.3 (3)
N1—C6—H6B	109.5	C36—C31—C37	121.4 (3)
C5—C6—H6B	109.5	C32—C31—C37	120.2 (3)
H6A—C6—H6B	108.1	C33—C32—C31	121.0 (3)
C26—C21—C22	115.6 (7)	C33—C32—H32	119.5
C26—C21—N4	121.3 (11)	C31—C32—H32	119.5
C22—C21—N4	123.1 (9)	C34—C33—C32	118.3 (4)
C23—C22—C21	121.3 (4)	C34—C33—H33	120.8
C23—C22—H22	119.4	C32—C33—H33	120.8
C21—C22—H22	119.4	C35—C34—F34	119.1 (4)
C24—C23—C22	121.8 (4)	C35—C34—C33	122.6 (4)
C24—C23—H23	119.1	F34—C34—C33	118.3 (4)
C22—C23—H23	119.1	C34—C35—C36	118.6 (3)
C23—C24—C25	118.5 (4)	C34—C35—H35	120.7
C23—C24—O24	116.6 (4)	C36—C35—H35	120.7
C25—C24—O24	124.8 (4)	C35—C36—C31	121.2 (3)
C24—C25—C26	119.5 (6)	C35—C36—H36	119.4
C24—C25—H25	120.2	C31—C36—H36	119.4
C26—C25—H25	120.2	O32—C37—O31	123.5 (4)
C21—C26—C25	123.2 (6)	O32—C37—C31	118.3 (4)
C21—C26—H26	118.4	O31—C37—C31	118.2 (3)
C25—C26—H26	118.4	H41—O41—H42	101 (3)

C24—O24—C27	118.8 (4)		
C6—N1—C2—C3	−56.3 (3)	C3—N4—C51—C52	−38 (19)
N1—C2—C3—N4	55.3 (3)	C5—N4—C51—C52	−166 (12)
C2—C3—N4—C51	178 (9)	C56—C51—C52—C53	−9 (19)
C2—C3—N4—C21	174 (2)	N4—C51—C52—C53	−170 (10)
C2—C3—N4—C5	−53.7 (3)	C51—C52—C53—C54	8 (11)
C51—N4—C5—C6	−174 (8)	C52—C53—C54—C55	−10 (7)
C21—N4—C5—C6	−173 (2)	C52—C53—C54—O54	−175 (4)
C3—N4—C5—C6	54.6 (3)	C53—C54—C55—C56	12 (11)
C2—N1—C6—C5	57.4 (3)	O54—C54—C55—C56	176 (7)
N4—C5—C6—N1	−57.2 (3)	N4—C51—C56—C55	172 (13)
C3—N4—C21—C26	169 (3)	C54—C55—C56—C51	−14 (15)
C5—N4—C21—C26	38 (4)	C53—C54—O54—C57	174 (5)
C3—N4—C21—C22	−10 (5)	C55—C54—O54—C57	10 (8)
C5—N4—C21—C22	−140 (3)	C36—C31—C32—C33	0.8 (4)
C26—C21—C22—C23	2 (4)	C37—C31—C32—C33	−179.3 (3)
N4—C21—C22—C23	−179 (2)	C31—C32—C33—C34	0.1 (5)
C21—C22—C23—C24	−3 (2)	C32—C33—C34—C35	−0.7 (5)
C22—C23—C24—C25	2.3 (13)	C32—C33—C34—F34	179.2 (3)
C22—C23—C24—O24	−179.7 (6)	F34—C34—C35—C36	−179.4 (3)
C23—C24—C25—C26	−2 (2)	C33—C34—C35—C36	0.5 (5)
O24—C24—C25—C26	−179.9 (14)	C34—C35—C36—C31	0.4 (5)
C22—C21—C26—C25	−2 (4)	C32—C31—C36—C35	−1.0 (4)
N4—C21—C26—C25	179 (3)	C37—C31—C36—C35	179.1 (3)
C24—C25—C26—C21	2 (3)	C36—C31—C37—O32	177.2 (3)
C23—C24—O24—C27	173.8 (10)	C32—C31—C37—O32	−2.7 (4)
C25—C24—O24—C27	−8.4 (16)	C36—C31—C37—O31	−3.3 (4)
C3—N4—C51—C56	162 (12)	C32—C31—C37—O31	176.8 (3)
C5—N4—C51—C56	34 (18)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O31	1.09 (3)	1.67 (3)	2.758 (4)	174.1 (19)
N1—H12···O41	0.86 (3)	1.96 (3)	2.818 (4)	170 (3)
O41—H41···O32^{i}	0.86 (4)	1.75 (4)	2.627 (4)	174 (4)
O41—H42···O31^{ii}	0.91 (4)	1.88 (4)	2.768 (3)	163 (3)
C2—H2*B*···O31^{iii}	0.97	2.58	3.529 (4)	166
C6—H6*B*···O41^{i}	0.97	2.57	3.386 (4)	142
C22—H22···*Cg*1^{ii}	0.93	2.93	3.664 (12)	137
C26—H26···*Cg*1^{iv}	0.93	2.81	3.56 (2)	138
C56—H56···*Cg*1^{iv}	0.93	2.96	3.55 (9)	123

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

4-(4-Methoxyphenyl)piperazin-1-ium 4-chlorobenzoate monohydrate (III)

Crystal data

$C_{11}H_{17}N_2O^+ \cdot C_7H_4ClO_2^- \cdot H_2O$
$M_r = 366.83$
Triclinic, $P\overline{1}$
$a = 6.211$ (1) Å
$b = 7.481$ (1) Å
$c = 20.144$ (4) Å
$\alpha = 84.90$ (2)°
$\beta = 87.48$ (2)°
$\gamma = 85.19$ (2)°
$V = 928.4$ (3) Å^3
$Z = 2$
$F(000) = 388$
$D_x = 1.312$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3962 reflections
$\theta = 2.8$–$28.8°$
$\mu = 0.23$ mm^{-1}
$T = 293$ K
Plate, colourless
0.20 × 0.16 × 0.02 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
$T_{min} = 0.951$, $T_{max} = 0.995$
5883 measured reflections
3454 independent reflections
1343 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.8°$
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 8$
$l = -24 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.135$
$S = 0.94$
3454 reflections
265 parameters
17 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Experimental. Compound (III). IR (KBr , cm^{-1}) 3320 (OH), 3003 (NH_2), 2837 (OCH_3), 1582 (COO), 772(CCl). NMR ($CDCl_3$) δ(^{1}H) 3.23 (m, 4H, piperazine), 3.28 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.86 (m, 4H, methoxyphenyl), 7.36 (d, J = 8.4 Hz, 2H, chlorophenyl), 7.98 (d, J = 8.4 Hz,2H, chlorophenyl).

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.7833 (5)	0.7442 (4)	0.45388 (15)	0.0536 (9)	
H11	0.827 (5)	0.777 (4)	0.5028 (16)	0.064*	
H12	0.760 (5)	0.636 (4)	0.4593 (16)	0.064*	
C2	0.9718 (6)	0.7498 (5)	0.40636 (16)	0.0570 (10)	
H2A	1.0888	0.6667	0.4234	0.068*	

H2B	1.0216	0.8699	0.4020	0.068*	
C3	0.9136 (6)	0.6998 (4)	0.33895 (16)	0.0545 (10)	
H3A	1.0371	0.7116	0.3082	0.065*	
H3B	0.8803	0.5749	0.3427	0.065*	
N4	0.7287 (4)	0.8126 (3)	0.31215 (12)	0.0433 (7)	
C5	0.5425 (5)	0.8110 (4)	0.35968 (15)	0.0516 (9)	
H5A	0.4918	0.6912	0.3650	0.062*	
H5B	0.4260	0.8935	0.3420	0.062*	
C6	0.5992 (6)	0.8644 (4)	0.42667 (15)	0.0551 (10)	
H6A	0.6377	0.9880	0.4222	0.066*	
H6B	0.4747	0.8569	0.4573	0.066*	
C21	0.685 (4)	0.783 (9)	0.2449 (9)	0.0446 (14)	0.73 (2)
C22	0.8261 (13)	0.6777 (19)	0.2052 (4)	0.060 (3)	0.73 (2)
H22	0.9523	0.6211	0.2230	0.072*	0.73 (2)
C23	0.7808 (13)	0.657 (2)	0.1401 (4)	0.074 (3)	0.73 (2)
H23	0.8807	0.5916	0.1141	0.088*	0.73 (2)
C24	0.5923 (18)	0.730 (3)	0.1130 (5)	0.065 (4)	0.73 (2)
C25	0.450 (2)	0.828 (5)	0.1516 (8)	0.075 (3)	0.73 (2)
H25	0.3196	0.8781	0.1341	0.089*	0.73 (2)
C26	0.496 (2)	0.854 (3)	0.2162 (6)	0.060 (3)	0.73 (2)
H26	0.3958	0.9221	0.2413	0.072*	0.73 (2)
O24	0.564 (2)	0.697 (2)	0.0482 (6)	0.104 (4)	0.73 (2)
C27	0.362 (3)	0.743 (2)	0.0203 (7)	0.101 (4)	0.73 (2)
H27A	0.2517	0.6892	0.0485	0.152*	0.73 (2)
H27B	0.3623	0.6989	−0.0231	0.152*	0.73 (2)
H27C	0.3331	0.8713	0.0164	0.152*	0.73 (2)
C51	0.668 (10)	0.79 (3)	0.247 (2)	0.0446 (14)	0.27 (2)
C52	0.833 (4)	0.755 (4)	0.1991 (13)	0.060 (3)	0.27 (2)
H52	0.9761	0.7413	0.2112	0.072*	0.27 (2)
C53	0.783 (4)	0.739 (4)	0.1340 (12)	0.074 (3)	0.27 (2)
H53	0.8924	0.7021	0.1039	0.088*	0.27 (2)
C54	0.577 (5)	0.775 (9)	0.1126 (15)	0.065 (4)	0.27 (2)
C55	0.418 (6)	0.825 (15)	0.158 (2)	0.075 (3)	0.27 (2)
H55	0.2775	0.8534	0.1437	0.089*	0.27 (2)
C56	0.464 (5)	0.834 (8)	0.2235 (18)	0.060 (3)	0.27 (2)
H56	0.3532	0.8701	0.2531	0.072*	0.27 (2)
O54	0.548 (7)	0.751 (7)	0.0468 (16)	0.104 (4)	0.27 (2)
C57	0.351 (8)	0.814 (6)	0.018 (2)	0.101 (4)	0.27 (2)
H57A	0.2346	0.7622	0.0438	0.152*	0.27 (2)
H57B	0.3518	0.7814	−0.0267	0.152*	0.27 (2)
H57C	0.3326	0.9432	0.0182	0.152*	0.27 (2)
C31	0.8074 (6)	0.7372 (4)	0.69495 (18)	0.0470 (9)	
C32	0.6605 (7)	0.6665 (5)	0.7412 (2)	0.0704 (11)	
H32	0.5407	0.6164	0.7267	0.084*	
C33	0.6886 (8)	0.6688 (5)	0.8091 (2)	0.0834 (13)	
H33	0.5883	0.6212	0.8400	0.100*	
C34	0.8662 (9)	0.7424 (6)	0.8301 (2)	0.0770 (13)	
Cl34	0.8970 (3)	0.74735 (19)	0.91487 (5)	0.1383 (7)	

C35	1.0144 (7)	0.8114 (5)	0.7851 (2)	0.0695 (11)
H35	1.1350	0.8601	0.7997	0.083*
C36	0.9845 (6)	0.8084 (4)	0.71778 (17)	0.0543 (10)
H36	1.0861	0.8555	0.6872	0.065*
C37	0.7721 (7)	0.7351 (5)	0.6222 (2)	0.0581 (11)
O31	0.9006 (5)	0.8125 (3)	0.58079 (12)	0.0697 (8)
O32	0.6183 (5)	0.6568 (4)	0.60573 (15)	0.1085 (11)
O41	0.7230 (5)	0.3744 (3)	0.46334 (13)	0.0683 (8)
H41	0.614 (7)	0.363 (5)	0.4360 (19)	0.102*
H42	0.846 (7)	0.315 (5)	0.4434 (19)	0.102*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.065 (2)	0.0467 (18)	0.0505 (19)	−0.0043 (19)	−0.0122 (18)	−0.0079 (17)
C2	0.044 (2)	0.069 (3)	0.057 (2)	−0.003 (2)	−0.008 (2)	−0.0023 (19)
C3	0.043 (2)	0.065 (2)	0.053 (2)	0.007 (2)	−0.0072 (19)	−0.0050 (18)
N4	0.0390 (19)	0.0473 (17)	0.0432 (17)	0.0009 (15)	−0.0023 (15)	−0.0044 (13)
C5	0.049 (2)	0.055 (2)	0.049 (2)	0.0054 (19)	0.0007 (19)	−0.0041 (18)
C6	0.057 (3)	0.056 (2)	0.051 (2)	0.006 (2)	−0.0009 (19)	−0.0052 (18)
C21	0.038 (4)	0.046 (7)	0.049 (3)	0.001 (5)	0.001 (3)	−0.005 (2)
C22	0.054 (3)	0.064 (8)	0.059 (3)	0.021 (4)	−0.007 (2)	−0.011 (4)
C23	0.073 (4)	0.084 (9)	0.059 (3)	0.035 (5)	−0.002 (3)	−0.020 (5)
C24	0.074 (4)	0.077 (12)	0.043 (2)	0.008 (3)	−0.004 (2)	−0.016 (4)
C25	0.064 (5)	0.104 (4)	0.053 (4)	0.021 (7)	−0.013 (4)	−0.013 (5)
C26	0.048 (4)	0.081 (6)	0.049 (4)	0.012 (5)	0.003 (3)	−0.012 (4)
O24	0.104 (3)	0.148 (12)	0.059 (2)	0.039 (5)	−0.0194 (19)	−0.038 (4)
C27	0.109 (5)	0.125 (13)	0.070 (3)	0.022 (7)	−0.034 (3)	−0.025 (7)
C51	0.038 (4)	0.046 (7)	0.049 (3)	0.001 (5)	0.001 (3)	−0.005 (2)
C52	0.054 (3)	0.064 (8)	0.059 (3)	0.021 (4)	−0.007 (2)	−0.011 (4)
C53	0.073 (4)	0.084 (9)	0.059 (3)	0.035 (5)	−0.002 (3)	−0.020 (5)
C54	0.074 (4)	0.077 (12)	0.043 (2)	0.008 (3)	−0.004 (2)	−0.016 (4)
C55	0.064 (5)	0.104 (4)	0.053 (4)	0.021 (7)	−0.013 (4)	−0.013 (5)
C56	0.048 (4)	0.081 (6)	0.049 (4)	0.012 (5)	0.003 (3)	−0.012 (4)
O54	0.104 (3)	0.148 (12)	0.059 (2)	0.039 (5)	−0.0194 (19)	−0.038 (4)
C57	0.109 (5)	0.125 (13)	0.070 (3)	0.022 (7)	−0.034 (3)	−0.025 (7)
C31	0.042 (2)	0.040 (2)	0.059 (2)	0.0033 (19)	−0.006 (2)	−0.0082 (18)
C32	0.061 (3)	0.061 (3)	0.090 (3)	−0.008 (2)	0.005 (3)	−0.012 (2)
C33	0.080 (4)	0.085 (3)	0.080 (4)	−0.001 (3)	0.029 (3)	0.002 (3)
C34	0.089 (4)	0.078 (3)	0.060 (3)	0.017 (3)	−0.007 (3)	−0.005 (2)
Cl34	0.1856 (16)	0.1630 (13)	0.0572 (8)	0.0402 (11)	−0.0065 (8)	−0.0083 (8)
C35	0.070 (3)	0.077 (3)	0.062 (3)	−0.002 (2)	−0.015 (3)	−0.010 (2)
C36	0.054 (3)	0.054 (2)	0.055 (3)	−0.007 (2)	−0.007 (2)	−0.0026 (18)
C37	0.056 (3)	0.044 (2)	0.075 (3)	0.007 (2)	−0.017 (3)	−0.017 (2)
O31	0.087 (2)	0.0683 (18)	0.0553 (17)	−0.0048 (16)	−0.0119 (16)	−0.0086 (14)
O32	0.095 (2)	0.132 (3)	0.110 (2)	−0.033 (2)	−0.040 (2)	−0.0309 (19)
O41	0.068 (2)	0.0661 (17)	0.0737 (19)	−0.0116 (16)	−0.0191 (15)	−0.0057 (14)

Geometric parameters (Å, º)

N1—C2	1.481 (4)	C27—H27C	0.9600
N1—C6	1.487 (4)	C51—C56	1.376 (12)
N1—H11	1.09 (3)	C51—C52	1.40 (2)
N1—H12	0.83 (3)	C52—C53	1.378 (9)
C2—C3	1.507 (4)	C52—H52	0.9300
C2—H2A	0.9700	C53—C54	1.366 (9)
C2—H2B	0.9700	C53—H53	0.9300
C3—N4	1.461 (4)	C54—C55	1.363 (14)
C3—H3A	0.9700	C54—O54	1.373 (8)
C3—H3B	0.9700	C55—C56	1.380 (9)
N4—C51	1.40 (3)	C55—H55	0.9300
N4—C21	1.434 (12)	C56—H56	0.9300
N4—C5	1.468 (4)	O54—C57	1.401 (9)
C5—C6	1.505 (4)	C57—H57A	0.9600
C5—H5A	0.9700	C57—H57B	0.9600
C5—H5B	0.9700	C57—H57C	0.9600
C6—H6A	0.9700	C31—C36	1.376 (4)
C6—H6B	0.9700	C31—C32	1.378 (5)
C21—C26	1.376 (12)	C31—C37	1.494 (5)
C21—C22	1.40 (2)	C32—C33	1.389 (5)
C22—C23	1.378 (5)	C32—H32	0.9300
C22—H22	0.9300	C33—C34	1.372 (5)
C23—C24	1.366 (6)	C33—H33	0.9300
C23—H23	0.9300	C34—C35	1.363 (5)
C24—C25	1.363 (12)	C34—Cl34	1.731 (4)
C24—O24	1.373 (5)	C35—C36	1.379 (4)
C25—C26	1.380 (6)	C35—H35	0.9300
C25—H25	0.9300	C36—H36	0.9300
C26—H26	0.9300	C37—O32	1.233 (4)
O24—C27	1.400 (6)	C37—O31	1.265 (4)
C27—H27A	0.9600	O41—H41	0.91 (4)
C27—H27B	0.9600	O41—H42	0.94 (4)
C2—N1—C6	110.0 (3)	O24—C27—H27A	109.5
C2—N1—H11	110.7 (16)	O24—C27—H27B	109.5
C6—N1—H11	112.6 (15)	H27A—C27—H27B	109.5
C2—N1—H12	105 (2)	O24—C27—H27C	109.5
C6—N1—H12	114 (2)	H27A—C27—H27C	109.5
H11—N1—H12	105 (3)	H27B—C27—H27C	109.5
N1—C2—C3	110.9 (3)	C56—C51—C52	116.1 (16)
N1—C2—H2A	109.5	C56—C51—N4	125 (2)
C3—C2—H2A	109.5	C52—C51—N4	118 (4)
N1—C2—H2B	109.5	C53—C52—C51	120.5 (14)
C3—C2—H2B	109.5	C53—C52—H52	119.7
H2A—C2—H2B	108.1	C51—C52—H52	119.7
N4—C3—C2	112.4 (3)	C54—C53—C52	121.5 (11)

N4—C3—H3A	109.1	C54—C53—H53	119.2
C2—C3—H3A	109.1	C52—C53—H53	119.2
N4—C3—H3B	109.1	C55—C54—C53	118.5 (10)
C2—C3—H3B	109.1	C55—C54—O54	125.5 (13)
H3A—C3—H3B	107.9	C53—C54—O54	116.0 (12)
C51—N4—C3	118 (4)	C54—C55—C56	120.5 (12)
C21—N4—C3	113.7 (13)	C54—C55—H55	119.8
C51—N4—C5	112 (4)	C56—C55—H55	119.8
C21—N4—C5	115.8 (14)	C51—C56—C55	122.4 (12)
C3—N4—C5	111.1 (2)	C51—C56—H56	118.8
N4—C5—C6	111.8 (3)	C55—C56—H56	118.8
N4—C5—H5A	109.3	C54—O54—C57	119.2 (14)
C6—C5—H5A	109.3	O54—C57—H57A	109.5
N4—C5—H5B	109.3	O54—C57—H57B	109.5
C6—C5—H5B	109.3	H57A—C57—H57B	109.5
H5A—C5—H5B	107.9	O54—C57—H57C	109.5
N1—C6—C5	110.5 (3)	H57A—C57—H57C	109.5
N1—C6—H6A	109.6	H57B—C57—H57C	109.5
C5—C6—H6A	109.6	C36—C31—C32	118.3 (3)
N1—C6—H6B	109.6	C36—C31—C37	121.7 (4)
C5—C6—H6B	109.6	C32—C31—C37	120.0 (4)
H6A—C6—H6B	108.1	C31—C32—C33	121.0 (4)
C26—C21—C22	116.2 (8)	C31—C32—H32	119.5
C26—C21—N4	121.0 (15)	C33—C32—H32	119.5
C22—C21—N4	122.8 (12)	C34—C33—C32	119.1 (4)
C23—C22—C21	120.9 (6)	C34—C33—H33	120.4
C23—C22—H22	119.5	C32—C33—H33	120.4
C21—C22—H22	119.5	C35—C34—C33	120.7 (4)
C24—C23—C22	121.4 (5)	C35—C34—Cl34	120.7 (4)
C24—C23—H23	119.3	C33—C34—Cl34	118.6 (4)
C22—C23—H23	119.3	C34—C35—C36	119.6 (4)
C25—C24—C23	118.5 (5)	C34—C35—H35	120.2
C25—C24—O24	125.6 (6)	C36—C35—H35	120.2
C23—C24—O24	115.9 (6)	C31—C36—C35	121.3 (4)
C24—C25—C26	120.7 (8)	C31—C36—H36	119.4
C24—C25—H25	119.7	C35—C36—H36	119.4
C26—C25—H25	119.7	O32—C37—O31	123.5 (4)
C21—C26—C25	122.3 (10)	O32—C37—C31	117.7 (4)
C21—C26—H26	118.8	O31—C37—C31	118.7 (4)
C25—C26—H26	118.8	H41—O41—H42	105 (3)
C24—O24—C27	119.3 (6)		

C6—N1—C2—C3	−56.4 (3)	C3—N4—C51—C52	−37 (18)
N1—C2—C3—N4	55.4 (4)	C5—N4—C51—C52	−168 (11)
C2—C3—N4—C51	175 (9)	C56—C51—C52—C53	−9 (19)
C2—C3—N4—C21	173 (3)	N4—C51—C52—C53	−178 (9)
C2—C3—N4—C5	−54.1 (3)	C51—C52—C53—C54	7 (11)
C51—N4—C5—C6	−171 (8)	C52—C53—C54—C55	−1 (10)

C21—N4—C5—C6	−173 (3)	C52—C53—C54—O54	−179 (5)
C3—N4—C5—C6	54.8 (3)	C53—C54—C55—C56	−2 (14)
C2—N1—C6—C5	57.2 (3)	O54—C54—C55—C56	176 (8)
N4—C5—C6—N1	−56.8 (4)	C52—C51—C56—C55	6 (20)
C3—N4—C21—C26	169 (4)	N4—C51—C56—C55	174 (13)
C5—N4—C21—C26	38 (7)	C54—C55—C56—C51	−1 (17)
C3—N4—C21—C22	−10 (7)	C55—C54—O54—C57	13 (13)
C5—N4—C21—C22	−140 (4)	C53—C54—O54—C57	−169 (5)
C26—C21—C22—C23	3 (7)	C36—C31—C32—C33	0.8 (5)
N4—C21—C22—C23	−178 (4)	C37—C31—C32—C33	−179.2 (3)
C21—C22—C23—C24	−3 (4)	C31—C32—C33—C34	−0.3 (6)
C22—C23—C24—C25	1 (3)	C32—C33—C34—C35	−0.4 (6)
C22—C23—C24—O24	−178.6 (14)	C32—C33—C34—Cl34	179.1 (3)
C23—C24—C25—C26	1 (5)	C33—C34—C35—C36	0.5 (6)
O24—C24—C25—C26	−180 (3)	Cl34—C34—C35—C36	−179.0 (3)
C22—C21—C26—C25	−2 (7)	C32—C31—C36—C35	−0.7 (5)
N4—C21—C26—C25	180 (4)	C37—C31—C36—C35	179.3 (3)
C24—C25—C26—C21	0 (6)	C34—C35—C36—C31	0.1 (5)
C25—C24—O24—C27	−10 (4)	C36—C31—C37—O32	174.6 (3)
C23—C24—O24—C27	169.9 (15)	C32—C31—C37—O32	−5.3 (5)
C3—N4—C51—C56	155 (12)	C36—C31—C37—O31	−5.1 (5)
C5—N4—C51—C56	24 (19)	C32—C31—C37—O31	174.9 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O31	1.09 (3)	1.71 (3)	2.790 (4)	176 (3)
N1—H12···O41	0.83 (3)	1.98 (3)	2.811 (4)	174 (3)
O41—H41···O32^{i}	0.91 (4)	1.73 (4)	2.624 (4)	172 (4)
O41—H42···O31^{ii}	0.94 (4)	1.84 (4)	2.775 (4)	170 (4)
C2—H2*B*···O31^{iii}	0.97	2.52	3.467 (4)	165
C6—H6*B*···O41^{i}	0.97	2.60	3.408 (4)	141
C22—H22···*Cg*1^{iv}	0.93	2.89	3.631 (13)	137
C26—H26···*Cg*1^{iv}	0.93	2.81	3.58 (2)	141

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

4-(4-Methoxyphenyl)piperazin-1-ium 4-bromobenzoate monohydrate (IV)

Crystal data

$C_{11}H_{17}N_2O^+·C_7H_4BrO_2^-·H_2O$
M_r = 411.28
Triclinic, $P\overline{1}$
a = 6.2004 (8) Å
b = 7.4957 (9) Å
c = 20.440 (2) Å
α = 85.08 (1)°
β = 87.37 (1)°
γ = 85.00 (1)°
V = 942.17 (19) Å^3

Z = 2
F(000) = 424
D_x = 1.450 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3927 reflections
θ = 2.8–27.9°
μ = 2.21 mm^{-1}
T = 293 K
Plate, colourless
0.48 × 0.44 × 0.16 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.536, T_{max} = 0.719
6176 measured reflections
3818 independent reflections
2063 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 26.6°, θ_{min} = 2.8°
h = −7→7
k = −8→9
l = −23→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.197
S = 1.06
3818 reflections
265 parameters
17 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0819P)^2 + 0.9249P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.94 e Å^{-3}
$\Delta\rho_{min}$ = −0.64 e Å^{-3}

Special details

Experimental. Compound (IV). IR (KBr , cm^{-1}) 3319 (OH), 3001 (NH_2), 2836 (OCH_3), 1580 (COO), 600(CBr). . NMR ($CDCl_3$) δ(^{1}H)) 3.23 (m, 4H, piperazine), 3.30 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.85 (m, 4H, methoxyphenyl), 7.51 (d, J = 8.4 Hz, 2H, bromophenyl), 7.90 (d, J = 8.4 Hz,2H, bromophenyl).

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.7803 (6)	0.7425 (5)	0.45428 (17)	0.0475 (9)	
H11	0.813 (7)	0.770 (6)	0.488 (2)	0.057*	
H12	0.753 (7)	0.620 (7)	0.461 (2)	0.057*	
C2	0.9709 (7)	0.7508 (6)	0.4079 (2)	0.0530 (11)	
H2A	1.0899	0.6702	0.4250	0.064*	
H2B	1.0169	0.8718	0.4034	0.064*	
C3	0.9143 (6)	0.6978 (6)	0.3414 (2)	0.0502 (10)	
H3A	1.0382	0.7086	0.3110	0.060*	
H3B	0.8808	0.5732	0.3454	0.060*	
N4	0.7286 (5)	0.8112 (4)	0.31535 (14)	0.0389 (7)	
C5	0.5420 (6)	0.8089 (6)	0.36137 (18)	0.0454 (10)	
H5A	0.4924	0.6891	0.3665	0.055*	
H5B	0.4249	0.8909	0.3438	0.055*	
C6	0.5976 (7)	0.8631 (6)	0.42775 (19)	0.0485 (10)	
H6A	0.6368	0.9862	0.4234	0.058*	
H6B	0.4723	0.8565	0.4578	0.058*	
C21	0.6845 (19)	0.784 (6)	0.2485 (4)	0.0421 (11)	0.80 (2)

C22	0.8313 (11)	0.6853 (18)	0.2086 (3)	0.066 (3)	0.80 (2)
H22	0.9604	0.6325	0.2256	0.079*	0.80 (2)
C23	0.7862 (12)	0.666 (2)	0.1442 (3)	0.084 (4)	0.80 (2)
H23	0.8895	0.6040	0.1183	0.101*	0.80 (2)
C24	0.5980 (13)	0.7331 (16)	0.1174 (4)	0.062 (3)	0.80 (2)
C25	0.4512 (15)	0.826 (5)	0.1561 (6)	0.080 (4)	0.80 (2)
H25	0.3201	0.8733	0.1390	0.096*	0.80 (2)
C26	0.4941 (16)	0.850 (3)	0.2209 (4)	0.064 (4)	0.80 (2)
H26	0.3899	0.9127	0.2462	0.077*	0.80 (2)
O24	0.5730 (16)	0.7011 (17)	0.0530 (3)	0.101 (3)	0.80 (2)
C27	0.373 (2)	0.743 (3)	0.0258 (6)	0.114 (6)	0.80 (2)
H27A	0.2623	0.6966	0.0551	0.171*	0.80 (2)
H27B	0.3717	0.6905	−0.0154	0.171*	0.80 (2)
H27C	0.3464	0.8712	0.0186	0.171*	0.80 (2)
C51	0.672 (7)	0.79 (2)	0.2512 (15)	0.0421 (11)	0.20 (2)
C52	0.838 (5)	0.786 (6)	0.2026 (13)	0.066 (3)	0.20 (2)
H52	0.9785	0.8027	0.2134	0.079*	0.20 (2)
C53	0.795 (5)	0.760 (7)	0.1384 (13)	0.084 (4)	0.20 (2)
H53	0.9078	0.7242	0.1096	0.101*	0.20 (2)
C54	0.590 (5)	0.787 (9)	0.1169 (14)	0.062 (3)	0.20 (2)
C55	0.426 (6)	0.81 (2)	0.163 (2)	0.080 (4)	0.20 (2)
H55	0.2833	0.8234	0.1492	0.096*	0.20 (2)
C56	0.466 (6)	0.818 (13)	0.2286 (19)	0.064 (4)	0.20 (2)
H56	0.3515	0.8441	0.2581	0.077*	0.20 (2)
O54	0.565 (7)	0.773 (7)	0.0512 (15)	0.101 (3)	0.20 (2)
C57	0.364 (9)	0.817 (13)	0.025 (3)	0.114 (6)	0.20 (2)
H57A	0.2541	0.7740	0.0554	0.171*	0.20 (2)
H57B	0.3582	0.7635	−0.0157	0.171*	0.20 (2)
H57C	0.3404	0.9457	0.0173	0.171*	0.20 (2)
C31	0.8064 (6)	0.7392 (5)	0.6932 (2)	0.0436 (9)	
C32	0.6590 (8)	0.6690 (7)	0.7386 (3)	0.0661 (13)	
H32	0.5388	0.6192	0.7245	0.079*	
C33	0.6890 (10)	0.6724 (8)	0.8053 (3)	0.0832 (17)	
H33	0.5888	0.6259	0.8360	0.100*	
C34	0.8682 (10)	0.7450 (8)	0.8256 (2)	0.0802 (16)	
Br34	0.90280 (17)	0.75220 (15)	0.91705 (3)	0.1491 (5)	
C35	1.0170 (9)	0.8124 (7)	0.7814 (2)	0.0683 (14)	
H35	1.1383	0.8599	0.7959	0.082*	
C36	0.9870 (7)	0.8100 (6)	0.7146 (2)	0.0500 (10)	
H36	1.0884	0.8561	0.6843	0.060*	
C37	0.7721 (7)	0.7357 (6)	0.6201 (2)	0.0528 (11)	
O31	0.8989 (6)	0.8126 (4)	0.57976 (15)	0.0631 (9)	
O32	0.6180 (7)	0.6578 (6)	0.6044 (2)	0.0999 (14)	
O41	0.7233 (6)	0.3743 (5)	0.46351 (17)	0.0633 (9)	
H41	0.620 (10)	0.353 (8)	0.445 (3)	0.095*	
H42	0.820 (11)	0.313 (9)	0.449 (3)	0.095*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.062 (2)	0.048 (2)	0.0349 (17)	−0.0089 (18)	−0.0128 (16)	−0.0048 (16)
C2	0.044 (2)	0.067 (3)	0.049 (2)	−0.004 (2)	−0.0092 (19)	−0.004 (2)
C3	0.037 (2)	0.067 (3)	0.046 (2)	0.002 (2)	−0.0018 (18)	−0.003 (2)
N4	0.0365 (17)	0.047 (2)	0.0333 (15)	−0.0045 (14)	0.0000 (13)	−0.0017 (14)
C5	0.039 (2)	0.059 (3)	0.038 (2)	0.0005 (19)	−0.0004 (17)	−0.0020 (19)
C6	0.055 (3)	0.052 (3)	0.037 (2)	0.003 (2)	0.0016 (18)	−0.0034 (18)
C21	0.044 (3)	0.048 (3)	0.034 (2)	−0.006 (3)	0.0000 (19)	−0.002 (3)
C22	0.053 (3)	0.093 (9)	0.048 (3)	0.025 (4)	−0.009 (2)	−0.017 (4)
C23	0.076 (4)	0.122 (10)	0.049 (3)	0.036 (5)	0.001 (3)	−0.031 (5)
C24	0.072 (3)	0.079 (9)	0.036 (2)	0.009 (4)	−0.007 (2)	−0.018 (3)
C25	0.058 (4)	0.133 (10)	0.046 (4)	0.015 (7)	−0.015 (3)	−0.008 (6)
C26	0.055 (4)	0.099 (10)	0.036 (3)	0.015 (5)	−0.001 (2)	−0.015 (5)
O24	0.108 (3)	0.148 (10)	0.046 (2)	0.033 (5)	−0.019 (2)	−0.037 (4)
C27	0.108 (5)	0.181 (19)	0.058 (4)	0.008 (7)	−0.030 (4)	−0.038 (7)
C51	0.044 (3)	0.048 (3)	0.034 (2)	−0.006 (3)	0.0000 (19)	−0.002 (3)
C52	0.053 (3)	0.093 (9)	0.048 (3)	0.025 (4)	−0.009 (2)	−0.017 (4)
C53	0.076 (4)	0.122 (10)	0.049 (3)	0.036 (5)	0.001 (3)	−0.031 (5)
C54	0.072 (3)	0.079 (9)	0.036 (2)	0.009 (4)	−0.007 (2)	−0.018 (3)
C55	0.058 (4)	0.133 (10)	0.046 (4)	0.015 (7)	−0.015 (3)	−0.008 (6)
C56	0.055 (4)	0.099 (10)	0.036 (3)	0.015 (5)	−0.001 (2)	−0.015 (5)
O54	0.108 (3)	0.148 (10)	0.046 (2)	0.033 (5)	−0.019 (2)	−0.037 (4)
C57	0.108 (5)	0.181 (19)	0.058 (4)	0.008 (7)	−0.030 (4)	−0.038 (7)
C31	0.041 (2)	0.040 (2)	0.049 (2)	0.0019 (18)	−0.0051 (18)	−0.0056 (18)
C32	0.052 (3)	0.070 (3)	0.076 (3)	−0.009 (2)	0.001 (2)	−0.005 (3)
C33	0.082 (4)	0.098 (4)	0.063 (3)	−0.002 (3)	0.023 (3)	0.011 (3)
C34	0.089 (4)	0.100 (4)	0.048 (3)	0.001 (3)	−0.006 (3)	0.004 (3)
Br34	0.1950 (10)	0.2001 (11)	0.0444 (4)	0.0349 (8)	−0.0150 (4)	−0.0114 (4)
C35	0.073 (3)	0.082 (4)	0.053 (3)	−0.006 (3)	−0.021 (3)	−0.010 (3)
C36	0.049 (2)	0.056 (3)	0.046 (2)	−0.010 (2)	−0.0083 (19)	0.000 (2)
C37	0.051 (3)	0.045 (3)	0.063 (3)	0.006 (2)	−0.020 (2)	−0.012 (2)
O31	0.083 (2)	0.063 (2)	0.0446 (17)	−0.0054 (18)	−0.0124 (17)	−0.0053 (15)
O32	0.087 (3)	0.130 (4)	0.094 (3)	−0.037 (3)	−0.038 (2)	−0.024 (3)
O41	0.064 (2)	0.065 (2)	0.064 (2)	−0.0133 (17)	−0.0210 (17)	−0.0029 (17)

Geometric parameters (Å, º)

N1—C6	1.479 (5)	C27—H27C	0.9600
N1—C2	1.483 (6)	C51—C56	1.369 (11)
N1—H11	0.78 (5)	C51—C52	1.40 (2)
N1—H12	0.95 (5)	C52—C53	1.383 (11)
C2—C3	1.513 (6)	C52—H52	0.9300
C2—H2A	0.9700	C53—C54	1.353 (11)
C2—H2B	0.9700	C53—H53	0.9300
C3—N4	1.463 (5)	C54—C55	1.362 (19)
C3—H3A	0.9700	C54—O54	1.374 (10)

C3—H3B	0.9700	C55—C56	1.392 (11)
N4—C51	1.40 (4)	C55—H55	0.9300
N4—C21	1.441 (10)	C56—H56	0.9300
N4—C5	1.458 (5)	O54—C57	1.383 (12)
C5—C6	1.512 (5)	C57—H57A	0.9600
C5—H5A	0.9700	C57—H57B	0.9600
C5—H5B	0.9700	C57—H57C	0.9600
C6—H6A	0.9700	C31—C32	1.377 (6)
C6—H6B	0.9700	C31—C36	1.385 (5)
C21—C26	1.367 (10)	C31—C37	1.521 (6)
C21—C22	1.399 (19)	C32—C33	1.387 (7)
C22—C23	1.380 (7)	C32—H32	0.9300
C22—H22	0.9300	C33—C34	1.375 (8)
C23—C24	1.351 (8)	C33—H33	0.9300
C23—H23	0.9300	C34—C35	1.360 (8)
C24—C25	1.362 (16)	C34—Br34	1.897 (5)
C24—O24	1.374 (6)	C35—C36	1.388 (6)
C25—C26	1.392 (8)	C35—H35	0.9300
C25—H25	0.9300	C36—H36	0.9300
C26—H26	0.9300	C37—O32	1.231 (5)
O24—C27	1.383 (8)	C37—O31	1.252 (6)
C27—H27A	0.9600	O41—H41	0.79 (6)
C27—H27B	0.9600	O41—H42	0.79 (7)

C6—N1—C2	109.7 (3)	O24—C27—H27A	109.5
C6—N1—H11	111 (3)	O24—C27—H27B	109.5
C2—N1—H11	108 (3)	H27A—C27—H27B	109.5
C6—N1—H12	115 (3)	O24—C27—H27C	109.5
C2—N1—H12	106 (3)	H27A—C27—H27C	109.5
H11—N1—H12	106 (4)	H27B—C27—H27C	109.5
N1—C2—C3	110.1 (3)	C56—C51—C52	115 (2)
N1—C2—H2A	109.6	C56—C51—N4	125 (3)
C3—C2—H2A	109.6	C52—C51—N4	117 (4)
N1—C2—H2B	109.6	C53—C52—C51	120.4 (19)
C3—C2—H2B	109.6	C53—C52—H52	119.8
H2A—C2—H2B	108.1	C51—C52—H52	119.8
N4—C3—C2	111.3 (3)	C54—C53—C52	120.8 (13)
N4—C3—H3A	109.4	C54—C53—H53	119.6
C2—C3—H3A	109.4	C52—C53—H53	119.6
N4—C3—H3B	109.4	C53—C54—C55	117.8 (11)
C2—C3—H3B	109.4	C53—C54—O54	116.7 (13)
H3A—C3—H3B	108.0	C55—C54—O54	125.2 (15)
C51—N4—C5	112 (2)	C54—C55—C56	121.2 (16)
C21—N4—C5	115.3 (7)	C54—C55—H55	119.4
C51—N4—C3	117 (4)	C56—C55—H55	119.4
C21—N4—C3	114.0 (11)	C51—C56—C55	121.4 (12)
C5—N4—C3	111.5 (3)	C51—C56—H56	119.3
N4—C5—C6	111.4 (3)	C55—C56—H56	119.3

N4—C5—H5A	109.4	C54—O54—C57	119.3 (17)
C6—C5—H5A	109.4	O54—C57—H57A	109.5
N4—C5—H5B	109.4	O54—C57—H57B	109.5
C6—C5—H5B	109.4	H57A—C57—H57B	109.5
H5A—C5—H5B	108.0	O54—C57—H57C	109.5
N1—C6—C5	110.0 (3)	H57A—C57—H57C	109.5
N1—C6—H6A	109.7	H57B—C57—H57C	109.5
C5—C6—H6A	109.7	C32—C31—C36	119.5 (4)
N1—C6—H6B	109.7	C32—C31—C37	120.0 (4)
C5—C6—H6B	109.7	C36—C31—C37	120.5 (4)
H6A—C6—H6B	108.2	C31—C32—C33	120.3 (5)
C26—C21—C22	116.1 (7)	C31—C32—H32	119.9
C26—C21—N4	121.7 (13)	C33—C32—H32	119.9
C22—C21—N4	122.2 (10)	C34—C33—C32	119.4 (5)
C23—C22—C21	120.6 (6)	C34—C33—H33	120.3
C23—C22—H22	119.7	C32—C33—H33	120.3
C21—C22—H22	119.7	C35—C34—C33	121.1 (5)
C24—C23—C22	122.6 (5)	C35—C34—Br34	120.3 (5)
C24—C23—H23	118.7	C33—C34—Br34	118.6 (4)
C22—C23—H23	118.7	C34—C35—C36	119.7 (5)
C23—C24—C25	117.4 (5)	C34—C35—H35	120.2
C23—C24—O24	116.5 (5)	C36—C35—H35	120.2
C25—C24—O24	126.1 (6)	C31—C36—C35	120.1 (4)
C24—C25—C26	121.1 (10)	C31—C36—H36	119.9
C24—C25—H25	119.5	C35—C36—H36	119.9
C26—C25—H25	119.5	O32—C37—O31	124.0 (5)
C21—C26—C25	122.1 (10)	O32—C37—C31	117.1 (5)
C21—C26—H26	119.0	O31—C37—C31	118.9 (4)
C25—C26—H26	119.0	H41—O41—H42	105 (6)
C24—O24—C27	119.2 (5)		

C6—N1—C2—C3	−58.3 (5)	C5—N4—C51—C52	−180 (9)
N1—C2—C3—N4	56.7 (5)	C3—N4—C51—C52	−49 (14)
C2—C3—N4—C51	174 (7)	C56—C51—C52—C53	−20 (15)
C2—C3—N4—C21	172.1 (16)	N4—C51—C52—C53	179 (8)
C2—C3—N4—C5	−55.2 (4)	C51—C52—C53—C54	19 (9)
C51—N4—C5—C6	−171 (8)	C52—C53—C54—C55	−10 (12)
C21—N4—C5—C6	−172.5 (19)	C52—C53—C54—O54	175 (5)
C3—N4—C5—C6	55.6 (4)	C53—C54—C55—C56	3 (19)
C2—N1—C6—C5	58.6 (4)	O54—C54—C55—C56	178 (10)
N4—C5—C6—N1	−57.4 (4)	C52—C51—C56—C55	13 (18)
C5—N4—C21—C26	36 (4)	N4—C51—C56—C55	173 (14)
C3—N4—C21—C26	166 (2)	C54—C55—C56—C51	−5 (21)
C5—N4—C21—C22	−143 (2)	C53—C54—O54—C57	−173 (6)
C3—N4—C21—C22	−12 (4)	C55—C54—O54—C57	12 (14)
C26—C21—C22—C23	3 (4)	C36—C31—C32—C33	1.2 (7)
N4—C21—C22—C23	−178 (2)	C37—C31—C32—C33	−179.8 (5)
C21—C22—C23—C24	−3 (2)	C31—C32—C33—C34	−0.5 (8)

C22—C23—C24—C25	1 (2)	C32—C33—C34—C35	−0.4 (9)
C22—C23—C24—O24	−178.9 (9)	C32—C33—C34—Br34	178.8 (4)
C23—C24—C25—C26	0 (4)	C33—C34—C35—C36	0.7 (9)
O24—C24—C25—C26	180 (2)	Br34—C34—C35—C36	−178.5 (4)
C22—C21—C26—C25	−2 (4)	C32—C31—C36—C35	−0.9 (6)
N4—C21—C26—C25	179 (3)	C37—C31—C36—C35	−179.9 (4)
C24—C25—C26—C21	1 (4)	C34—C35—C36—C31	0.0 (7)
C23—C24—O24—C27	170.6 (12)	C32—C31—C37—O32	−4.8 (6)
C25—C24—O24—C27	−9 (3)	C36—C31—C37—O32	174.2 (4)
C5—N4—C51—C56	21 (16)	C32—C31—C37—O31	174.5 (4)
C3—N4—C51—C56	151 (11)	C36—C31—C37—O31	−6.5 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O31	0.78 (4)	2.03 (4)	2.805 (5)	174 (5)
N1—H12···O41	0.95 (5)	1.86 (5)	2.802 (5)	172 (4)
O41—H41···O32^{i}	0.79 (6)	1.84 (6)	2.623 (6)	170 (6)
O41—H42···O31^{ii}	0.79 (7)	2.00 (7)	2.772 (5)	169 (6)
C2—H2*B*···O31^{iii}	0.97	2.52	3.471 (5)	166
C22—H22···*Cg*1^{ii}	0.93	2.52	3.471 (5)	166
C26—H26···*Cg*1^{iv}	0.93	2.84	3.58 (2)	137

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

4-(4-Methoxyphenyl)piperazin-1-ium 2-hydroxybenzoate (V)

Crystal data

$C_{11}H_{17}N_2O^+·C_7H_5O_3^-$
M_r = 330.38
Orthorhombic, $P2_12_12_1$
a = 6.5009 (8) Å
b = 7.9735 (9) Å
c = 32.155 (4) Å
V = 1666.8 (3) Å^3
Z = 4
F(000) = 704
D_x = 1.317 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 3564 reflections
θ = 2.5–27.8°
μ = 0.09 mm^{-1}
T = 296 K
Block, colourless
0.42 × 0.42 × 0.34 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.899, T_{max} = 0.969
6249 measured reflections
3564 independent reflections
2875 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 27.8°, θ_{min} = 2.5°
h = −6→8
k = −10→6
l = −38→41

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.089$
$S = 1.05$
3564 reflections
228 parameters
0 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 0.3737P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ e Å^{-3}
Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0244 (17)
Absolute structure: Flack *x* determined using 1011 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Special details

Experimental. Compound (V). IR (KBr , cm^{-1}) 3650 (OH), 3040 (NH_2), 2835 (OCH_3), 1571 (COO). NMR ($CDCl_3$) δ(^{1}H) 3.31 (m, 8H, piperazine), 3.77 (s, 3H, OCH_3), 6.85 (m, 5H, hydroxyphenyl and methoxyphenyl), 6.92 (m, 1H, hydroxyphenyl), 7.35 (t, 1H, hydroxyphenyl), 7.87 (m, 1H, hydroxyphenyl).

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}
N1	0.5261 (3)	0.3567 (3)	0.21309 (7)	0.0468 (5)
H11	0.616 (4)	0.369 (4)	0.2367 (9)	0.056*
H12	0.452 (4)	0.254 (4)	0.2144 (8)	0.056*
C2	0.6568 (4)	0.3607 (4)	0.17563 (8)	0.0488 (6)
H2A	0.7532	0.2680	0.1765	0.059*
H2B	0.7353	0.4642	0.1753	0.059*
C3	0.5299 (4)	0.3490 (3)	0.13672 (8)	0.0443 (6)
H3A	0.6189	0.3643	0.1128	0.053*
H3B	0.4705	0.2377	0.1349	0.053*
N4	0.3654 (3)	0.4727 (3)	0.13512 (6)	0.0381 (5)
C5	0.2422 (4)	0.4788 (3)	0.17339 (7)	0.0426 (6)
H5A	0.1606	0.3773	0.1755	0.051*
H5B	0.1485	0.5733	0.1720	0.051*
C6	0.3752 (4)	0.4953 (3)	0.21130 (8)	0.0460 (6)
H6A	0.4472	0.6018	0.2106	0.055*
H6B	0.2898	0.4933	0.2360	0.055*
C21	0.2490 (4)	0.4737 (3)	0.09771 (7)	0.0373 (5)
C22	0.3077 (4)	0.3820 (4)	0.06280 (8)	0.0515 (7)
H22	0.4232	0.3134	0.0642	0.062*
C23	0.1976 (5)	0.3911 (4)	0.02617 (8)	0.0544 (7)
H23	0.2412	0.3295	0.0033	0.065*
C24	0.0260 (4)	0.4886 (3)	0.02292 (8)	0.0460 (6)
C25	−0.0385 (4)	0.5770 (4)	0.05738 (8)	0.0529 (7)

H25	−0.1573	0.6418	0.0560	0.063*
C26	0.0728 (4)	0.5697 (4)	0.09394 (8)	0.0503 (7)
H26	0.0277	0.6312	0.1168	0.060*
O24	−0.0704 (3)	0.4899 (3)	−0.01523 (5)	0.0638 (6)
C27	−0.2374 (6)	0.6009 (5)	−0.02052 (10)	0.0833 (11)
H27A	−0.2851	0.5953	−0.0487	0.125*
H27B	−0.1938	0.7133	−0.0144	0.125*
H27C	−0.3469	0.5697	−0.0020	0.125*
C31	0.9904 (4)	0.4542 (3)	0.32938 (7)	0.0370 (5)
C32	1.1705 (4)	0.3584 (3)	0.32627 (7)	0.0394 (5)
C33	1.3127 (4)	0.3600 (4)	0.35834 (8)	0.0501 (7)
H33	1.4324	0.2967	0.3561	0.060*
C34	1.2782 (5)	0.4544 (4)	0.39334 (8)	0.0557 (7)
H34	1.3746	0.4546	0.4147	0.067*
C35	1.1023 (5)	0.5484 (4)	0.39698 (8)	0.0584 (8)
H35	1.0790	0.6119	0.4208	0.070*
C36	0.9613 (4)	0.5480 (3)	0.36539 (8)	0.0501 (7)
H36	0.8427	0.6123	0.3681	0.060*
O33	1.2074 (3)	0.2609 (2)	0.29254 (6)	0.0548 (5)
H33A	1.082 (5)	0.275 (4)	0.2766 (10)	0.082*
C37	0.8348 (4)	0.4561 (3)	0.29516 (8)	0.0453 (6)
O31	0.8614 (3)	0.3519 (3)	0.26569 (6)	0.0601 (6)
O32	0.6867 (3)	0.5531 (3)	0.29674 (7)	0.0682 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0464 (13)	0.0489 (12)	0.0452 (12)	−0.0102 (11)	−0.0143 (11)	0.0037 (11)
C2	0.0363 (13)	0.0520 (15)	0.0581 (15)	−0.0003 (12)	−0.0058 (13)	−0.0004 (14)
C3	0.0364 (13)	0.0475 (14)	0.0489 (14)	0.0030 (12)	0.0007 (11)	−0.0024 (12)
N4	0.0353 (10)	0.0416 (11)	0.0374 (10)	0.0037 (9)	−0.0007 (8)	−0.0024 (9)
C5	0.0388 (12)	0.0494 (14)	0.0395 (12)	0.0027 (12)	0.0008 (11)	−0.0041 (11)
C6	0.0484 (14)	0.0492 (15)	0.0404 (13)	−0.0030 (13)	0.0000 (12)	−0.0022 (12)
C21	0.0396 (12)	0.0350 (12)	0.0374 (12)	−0.0018 (11)	0.0015 (10)	−0.0011 (10)
C22	0.0559 (16)	0.0543 (16)	0.0444 (14)	0.0172 (14)	0.0005 (13)	−0.0062 (13)
C23	0.0699 (19)	0.0551 (17)	0.0381 (13)	0.0109 (15)	0.0013 (14)	−0.0102 (12)
C24	0.0555 (15)	0.0431 (14)	0.0393 (13)	−0.0032 (13)	−0.0070 (12)	0.0005 (11)
C25	0.0501 (15)	0.0582 (17)	0.0503 (16)	0.0139 (14)	−0.0088 (13)	−0.0047 (13)
C26	0.0523 (15)	0.0567 (17)	0.0418 (14)	0.0153 (14)	−0.0030 (12)	−0.0121 (12)
O24	0.0793 (14)	0.0684 (14)	0.0435 (10)	0.0051 (12)	−0.0190 (10)	−0.0036 (9)
C27	0.080 (2)	0.102 (3)	0.068 (2)	0.014 (2)	−0.0331 (19)	0.000 (2)
C31	0.0382 (12)	0.0331 (12)	0.0396 (13)	−0.0030 (10)	−0.0004 (10)	0.0076 (10)
C32	0.0416 (12)	0.0353 (12)	0.0413 (13)	−0.0017 (11)	−0.0006 (12)	0.0047 (11)
C33	0.0398 (14)	0.0552 (16)	0.0554 (16)	0.0006 (13)	−0.0092 (13)	0.0093 (14)
C34	0.0586 (17)	0.0642 (18)	0.0442 (15)	−0.0139 (16)	−0.0139 (14)	0.0084 (14)
C35	0.076 (2)	0.0595 (18)	0.0401 (15)	−0.0090 (17)	0.0015 (14)	−0.0046 (13)
C36	0.0524 (15)	0.0472 (15)	0.0506 (15)	0.0064 (14)	0.0064 (13)	0.0028 (12)
O33	0.0547 (12)	0.0555 (12)	0.0542 (11)	0.0139 (10)	−0.0054 (10)	−0.0087 (9)

C37	0.0431 (14)	0.0409 (14)	0.0517 (15)	−0.0037 (13)	−0.0069 (12)	0.0127 (12)
O31	0.0639 (13)	0.0586 (12)	0.0580 (12)	0.0036 (11)	−0.0245 (10)	−0.0057 (10)
O32	0.0524 (11)	0.0730 (14)	0.0793 (14)	0.0200 (11)	−0.0115 (11)	0.0136 (11)

Geometric parameters (Å, º)

N1—C2	1.474 (3)	C24—C25	1.379 (4)
N1—C6	1.479 (3)	C25—C26	1.382 (4)
N1—H11	0.96 (3)	C25—H25	0.9300
N1—H12	0.95 (3)	C26—H26	0.9300
C2—C3	1.502 (3)	O24—C27	1.411 (4)
C2—H2A	0.9700	C27—H27A	0.9600
C2—H2B	0.9700	C27—H27B	0.9600
C3—N4	1.456 (3)	C27—H27C	0.9600
C3—H3A	0.9700	C31—C36	1.391 (3)
C3—H3B	0.9700	C31—C32	1.401 (3)
N4—C21	1.421 (3)	C31—C37	1.495 (3)
N4—C5	1.469 (3)	C32—O33	1.356 (3)
C5—C6	1.500 (3)	C32—C33	1.385 (3)
C5—H5A	0.9700	C33—C34	1.372 (4)
C5—H5B	0.9700	C33—H33	0.9300
C6—H6A	0.9700	C34—C35	1.372 (4)
C6—H6B	0.9700	C34—H34	0.9300
C21—C26	1.383 (3)	C35—C36	1.368 (4)
C21—C22	1.393 (3)	C35—H35	0.9300
C22—C23	1.380 (4)	C36—H36	0.9300
C22—H22	0.9300	O33—H33A	0.97 (3)
C23—C24	1.364 (4)	C37—O32	1.236 (3)
C23—H23	0.9300	C37—O31	1.272 (3)
C24—O24	1.378 (3)		
C2—N1—C6	109.5 (2)	C24—C23—H23	119.3
C2—N1—H11	107.1 (16)	C22—C23—H23	119.3
C6—N1—H11	110.9 (17)	C23—C24—O24	116.4 (2)
C2—N1—H12	110.3 (16)	C23—C24—C25	118.6 (2)
C6—N1—H12	108.2 (16)	O24—C24—C25	125.0 (2)
H11—N1—H12	111 (2)	C24—C25—C26	120.2 (2)
N1—C2—C3	111.3 (2)	C24—C25—H25	119.9
N1—C2—H2A	109.4	C26—C25—H25	119.9
C3—C2—H2A	109.4	C25—C26—C21	122.1 (2)
N1—C2—H2B	109.4	C25—C26—H26	118.9
C3—C2—H2B	109.4	C21—C26—H26	118.9
H2A—C2—H2B	108.0	C24—O24—C27	117.5 (2)
N4—C3—C2	113.0 (2)	O24—C27—H27A	109.5
N4—C3—H3A	109.0	O24—C27—H27B	109.5
C2—C3—H3A	109.0	H27A—C27—H27B	109.5
N4—C3—H3B	109.0	O24—C27—H27C	109.5
C2—C3—H3B	109.0	H27A—C27—H27C	109.5

H3A—C3—H3B	107.8	H27B—C27—H27C	109.5
C21—N4—C3	115.14 (18)	C36—C31—C32	117.8 (2)
C21—N4—C5	114.77 (18)	C36—C31—C37	121.0 (2)
C3—N4—C5	113.17 (19)	C32—C31—C37	121.2 (2)
N4—C5—C6	111.69 (19)	O33—C32—C33	118.8 (2)
N4—C5—H5A	109.3	O33—C32—C31	121.2 (2)
C6—C5—H5A	109.3	C33—C32—C31	120.0 (2)
N4—C5—H5B	109.3	C34—C33—C32	120.4 (3)
C6—C5—H5B	109.3	C34—C33—H33	119.8
H5A—C5—H5B	107.9	C32—C33—H33	119.8
N1—C6—C5	110.4 (2)	C35—C34—C33	120.4 (3)
N1—C6—H6A	109.6	C35—C34—H34	119.8
C5—C6—H6A	109.6	C33—C34—H34	119.8
N1—C6—H6B	109.6	C36—C35—C34	119.6 (3)
C5—C6—H6B	109.6	C36—C35—H35	120.2
H6A—C6—H6B	108.1	C34—C35—H35	120.2
C26—C21—C22	116.5 (2)	C35—C36—C31	121.9 (3)
C26—C21—N4	121.2 (2)	C35—C36—H36	119.1
C22—C21—N4	122.2 (2)	C31—C36—H36	119.1
C23—C22—C21	121.2 (3)	C32—O33—H33A	102 (2)
C23—C22—H22	119.4	O32—C37—O31	123.0 (2)
C21—C22—H22	119.4	O32—C37—C31	120.2 (3)
C24—C23—C22	121.3 (2)	O31—C37—C31	116.7 (2)

C6—N1—C2—C3	−57.5 (3)	C22—C21—C26—C25	−1.0 (4)
N1—C2—C3—N4	52.5 (3)	N4—C21—C26—C25	177.7 (3)
C2—C3—N4—C21	176.2 (2)	C23—C24—O24—C27	−174.6 (3)
C2—C3—N4—C5	−49.1 (3)	C25—C24—O24—C27	5.7 (4)
C21—N4—C5—C6	−174.1 (2)	C36—C31—C32—O33	178.5 (2)
C3—N4—C5—C6	51.0 (3)	C37—C31—C32—O33	−1.6 (3)
C2—N1—C6—C5	59.7 (3)	C36—C31—C32—C33	−0.3 (3)
N4—C5—C6—N1	−56.4 (3)	C37—C31—C32—C33	179.5 (2)
C3—N4—C21—C26	171.8 (2)	O33—C32—C33—C34	−178.6 (2)
C5—N4—C21—C26	37.8 (3)	C31—C32—C33—C34	0.3 (4)
C3—N4—C21—C22	−9.6 (3)	C32—C33—C34—C35	0.0 (4)
C5—N4—C21—C22	−143.6 (2)	C33—C34—C35—C36	−0.2 (4)
C26—C21—C22—C23	1.7 (4)	C34—C35—C36—C31	0.2 (4)
N4—C21—C22—C23	−176.9 (3)	C32—C31—C36—C35	0.1 (4)
C21—C22—C23—C24	−0.8 (4)	C37—C31—C36—C35	−179.8 (2)
C22—C23—C24—O24	179.2 (3)	C36—C31—C37—O32	6.6 (4)
C22—C23—C24—C25	−1.0 (4)	C32—C31—C37—O32	−173.2 (2)
C23—C24—C25—C26	1.8 (4)	C36—C31—C37—O31	−171.9 (2)
O24—C24—C25—C26	−178.5 (3)	C32—C31—C37—O31	8.3 (3)
C24—C25—C26—C21	−0.7 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O31	0.96 (3)	1.85 (3)	2.759 (3)	156 (3)
N1—H11···O32	0.96 (3)	2.47 (3)	3.283 (3)	142 (2)
N1—H12···O32^{i}	0.95 (3)	1.87 (3)	2.806 (3)	166 (2)
O33—H33*A*···O31	0.97 (3)	1.60 (3)	2.516 (3)	156 (3)
C6—H6*A*···O33^{ii}	0.97	2.58	3.444 (3)	148
C2—H2*A*···*Cg*1^{iii}	0.97	2.88	3.711 (3)	144
C26—H26···*Cg*1^{iv}	0.93	2.87	3.642 (3)	141

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

4-(4-Methoxyphenyl)piperazin-1-ium pyridine-3-carboxylate (VI)

Crystal data

$C_{11}H_{17}N_2O^+·C_6H_4NO_2^-$
M_r = 315.37
Orthorhombic, *Pbca*
a = 9.2817 (7) Å
b = 11.2905 (7) Å
c = 30.309 (2) Å
V = 3176.2 (4) Å^3
Z = 8
F(000) = 1344
D_x = 1.319 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3593 reflections
θ = 2.6–27.9°
μ = 0.09 mm^{-1}
T = 296 K
Block, colourless
0.46 × 0.42 × 0.36 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.879, T_{max} = 0.968
22154 measured reflections
3593 independent reflections
2616 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 27.9°, θ_{min} = 2.6°
h = −11→11
k = −14→13
l = −38→35

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.119
S = 1.03
3593 reflections
215 parameters
0 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 1.5726P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0074 (6)

Special details

Experimental. Compound (VI). IR (KBr , cm^{-1}) 3040 (NH_2), 2829 (OCH_3), 1584 (COO). NMR ($CDCl_3$) δ(^{1}H) 3.27 (m, 4H, piperazine), 3.34 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.90 (m, 4H, methoxyphenyl), 7.33 (m, 1H, nicotinate), 8.67 (m, 2H, nicotinate), 9.24 (m, 1H, nicotinate).

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}
N1	0.66467 (17)	0.63416 (13)	0.53807 (5)	0.0405 (4)
H12	0.711 (2)	0.5701 (18)	0.5241 (6)	0.049*
H11	0.650 (2)	0.6962 (17)	0.5161 (6)	0.049*
C2	0.52299 (18)	0.59306 (15)	0.55418 (6)	0.0401 (4)
H2A	0.4642	0.5684	0.5294	0.048*
H2B	0.4739	0.6577	0.5690	0.048*
C3	0.54099 (18)	0.49095 (14)	0.58566 (5)	0.0368 (4)
H3A	0.4473	0.4669	0.5967	0.044*
H3B	0.5831	0.4242	0.5702	0.044*
N4	0.63342 (14)	0.52403 (11)	0.62269 (4)	0.0337 (3)
C5	0.77180 (19)	0.57192 (16)	0.60810 (6)	0.0440 (4)
H5A	0.8273	0.5094	0.5942	0.053*
H5B	0.8255	0.5995	0.6336	0.053*
C6	0.7534 (2)	0.67296 (16)	0.57600 (6)	0.0479 (5)
H6A	0.7070	0.7391	0.5907	0.058*
H6B	0.8470	0.6990	0.5656	0.058*
C21	0.63956 (17)	0.44215 (13)	0.65799 (5)	0.0317 (3)
C22	0.5429 (2)	0.35039 (16)	0.66255 (6)	0.0449 (4)
H22	0.4750	0.3379	0.6405	0.054*
C23	0.5436 (2)	0.27603 (15)	0.69898 (6)	0.0464 (5)
H23	0.4759	0.2155	0.7010	0.056*
C24	0.64245 (19)	0.29057 (14)	0.73195 (5)	0.0391 (4)
C25	0.7405 (2)	0.38118 (18)	0.72806 (6)	0.0558 (5)
H25	0.8087	0.3926	0.7501	0.067*
C26	0.7395 (2)	0.45523 (17)	0.69203 (6)	0.0523 (5)
H26	0.8073	0.5157	0.6903	0.063*
O24	0.65388 (16)	0.22083 (12)	0.76910 (4)	0.0551 (4)
C27	0.5378 (3)	0.14351 (19)	0.77845 (7)	0.0632 (6)
H27A	0.5581	0.0999	0.8049	0.095*
H27B	0.4512	0.1888	0.7824	0.095*
H27C	0.5252	0.0893	0.7544	0.095*
N31	0.6143 (2)	1.14730 (14)	0.39733 (6)	0.0587 (5)
C32	0.6210 (2)	1.07950 (15)	0.43309 (6)	0.0439 (4)
H32	0.6092	1.1158	0.4604	0.053*
C33	0.64434 (17)	0.95882 (13)	0.43243 (5)	0.0332 (4)
C34	0.66384 (19)	0.90618 (16)	0.39174 (6)	0.0419 (4)
H34	0.6786	0.8249	0.3896	0.050*
C35	0.6611 (2)	0.97549 (19)	0.35436 (6)	0.0517 (5)
H35	0.6767	0.9422	0.3267	0.062*
C36	0.6353 (2)	1.09376 (19)	0.35863 (7)	0.0588 (6)

H36	0.6321	1.1397	0.3332	0.071*
C37	0.64844 (18)	0.88736 (15)	0.47434 (6)	0.0378 (4)
O31	0.60454 (17)	0.78319 (11)	0.47188 (4)	0.0589 (4)
O32	0.69492 (15)	0.93503 (12)	0.50849 (4)	0.0543 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0484 (9)	0.0353 (7)	0.0379 (8)	0.0052 (7)	0.0025 (7)	0.0083 (6)
C2	0.0387 (9)	0.0413 (9)	0.0403 (9)	0.0052 (7)	−0.0030 (7)	0.0026 (8)
C3	0.0337 (9)	0.0384 (9)	0.0383 (9)	−0.0016 (7)	−0.0021 (7)	0.0027 (7)
N4	0.0313 (7)	0.0354 (7)	0.0344 (7)	−0.0020 (6)	0.0001 (6)	0.0032 (6)
C5	0.0382 (9)	0.0509 (10)	0.0428 (9)	−0.0112 (8)	−0.0039 (8)	0.0099 (8)
C6	0.0515 (11)	0.0435 (10)	0.0488 (11)	−0.0119 (8)	−0.0021 (9)	0.0082 (8)
C21	0.0315 (8)	0.0321 (8)	0.0314 (8)	0.0024 (6)	0.0031 (6)	−0.0009 (6)
C22	0.0483 (11)	0.0452 (10)	0.0413 (10)	−0.0135 (8)	−0.0089 (8)	0.0042 (8)
C23	0.0536 (11)	0.0405 (9)	0.0452 (10)	−0.0153 (8)	0.0004 (8)	0.0044 (8)
C24	0.0465 (10)	0.0363 (8)	0.0345 (8)	0.0008 (8)	0.0049 (7)	0.0038 (7)
C25	0.0547 (12)	0.0632 (12)	0.0495 (11)	−0.0151 (10)	−0.0169 (9)	0.0159 (10)
C26	0.0487 (11)	0.0556 (11)	0.0526 (11)	−0.0201 (9)	−0.0122 (9)	0.0165 (9)
O24	0.0657 (9)	0.0559 (8)	0.0436 (7)	−0.0092 (7)	−0.0005 (6)	0.0169 (6)
C27	0.0701 (14)	0.0575 (12)	0.0620 (13)	−0.0050 (11)	0.0117 (11)	0.0232 (10)
N31	0.0794 (13)	0.0393 (8)	0.0573 (10)	−0.0007 (9)	−0.0084 (9)	0.0127 (8)
C32	0.0537 (11)	0.0356 (9)	0.0425 (10)	0.0018 (8)	−0.0021 (8)	0.0007 (8)
C33	0.0283 (8)	0.0318 (8)	0.0396 (9)	−0.0024 (6)	−0.0031 (7)	0.0036 (6)
C34	0.0434 (10)	0.0364 (9)	0.0458 (10)	0.0001 (8)	−0.0040 (8)	−0.0040 (8)
C35	0.0523 (12)	0.0664 (13)	0.0363 (10)	−0.0086 (10)	−0.0004 (8)	−0.0028 (9)
C36	0.0712 (14)	0.0595 (13)	0.0458 (11)	−0.0115 (11)	−0.0079 (10)	0.0195 (10)
C37	0.0343 (9)	0.0377 (9)	0.0415 (9)	−0.0008 (7)	−0.0032 (7)	0.0065 (7)
O31	0.0833 (11)	0.0368 (7)	0.0566 (8)	−0.0120 (7)	−0.0157 (7)	0.0144 (6)
O32	0.0670 (9)	0.0575 (8)	0.0385 (7)	−0.0166 (7)	−0.0106 (6)	0.0060 (6)

Geometric parameters (Å, º)

N1—C2	1.477 (2)	C24—C25	1.375 (3)
N1—C6	1.480 (2)	C24—O24	1.3781 (19)
N1—H12	0.94 (2)	C25—C26	1.375 (2)
N1—H11	0.97 (2)	C25—H25	0.9300
C2—C3	1.506 (2)	C26—H26	0.9300
C2—H2A	0.9700	O24—C27	1.416 (2)
C2—H2B	0.9700	C27—H27A	0.9600
C3—N4	1.461 (2)	C27—H27B	0.9600
C3—H3A	0.9700	C27—H27C	0.9600
C3—H3B	0.9700	N31—C32	1.328 (2)
N4—C21	1.4152 (19)	N31—C36	1.334 (3)
N4—C5	1.462 (2)	C32—C33	1.380 (2)
C5—C6	1.509 (2)	C32—H32	0.9300
C5—H5A	0.9700	C33—C34	1.381 (2)

C5—H5B	0.9700	C33—C37	1.505 (2)
C6—H6A	0.9700	C34—C35	1.377 (3)
C6—H6B	0.9700	C34—H34	0.9300
C21—C22	1.377 (2)	C35—C36	1.363 (3)
C21—C26	1.395 (2)	C35—H35	0.9300
C22—C23	1.387 (2)	C36—H36	0.9300
C22—H22	0.9300	C37—O32	1.244 (2)
C23—C24	1.366 (3)	C37—O31	1.247 (2)
C23—H23	0.9300		

C2—N1—C6	109.37 (13)	C24—C23—C22	120.82 (16)
C2—N1—H12	108.5 (12)	C24—C23—H23	119.6
C6—N1—H12	108.6 (12)	C22—C23—H23	119.6
C2—N1—H11	109.1 (11)	C23—C24—C25	118.14 (16)
C6—N1—H11	113.2 (11)	C23—C24—O24	125.48 (16)
H12—N1—H11	107.9 (15)	C25—C24—O24	116.38 (16)
N1—C2—C3	110.55 (13)	C24—C25—C26	121.05 (17)
N1—C2—H2A	109.5	C24—C25—H25	119.5
C3—C2—H2A	109.5	C26—C25—H25	119.5
N1—C2—H2B	109.5	C25—C26—C21	121.82 (17)
C3—C2—H2B	109.5	C25—C26—H26	119.1
H2A—C2—H2B	108.1	C21—C26—H26	119.1
N4—C3—C2	110.87 (13)	C24—O24—C27	117.22 (15)
N4—C3—H3A	109.5	O24—C27—H27A	109.5
C2—C3—H3A	109.5	O24—C27—H27B	109.5
N4—C3—H3B	109.5	H27A—C27—H27B	109.5
C2—C3—H3B	109.5	O24—C27—H27C	109.5
H3A—C3—H3B	108.1	H27A—C27—H27C	109.5
C21—N4—C3	115.94 (13)	H27B—C27—H27C	109.5
C21—N4—C5	115.77 (13)	C32—N31—C36	116.71 (16)
C3—N4—C5	112.21 (13)	N31—C32—C33	124.38 (17)
N4—C5—C6	112.02 (15)	N31—C32—H32	117.8
N4—C5—H5A	109.2	C33—C32—H32	117.8
C6—C5—H5A	109.2	C32—C33—C34	117.29 (16)
N4—C5—H5B	109.2	C32—C33—C37	121.41 (15)
C6—C5—H5B	109.2	C34—C33—C37	121.31 (14)
H5A—C5—H5B	107.9	C35—C34—C33	119.20 (17)
N1—C6—C5	109.88 (14)	C35—C34—H34	120.4
N1—C6—H6A	109.7	C33—C34—H34	120.4
C5—C6—H6A	109.7	C36—C35—C34	118.80 (18)
N1—C6—H6B	109.7	C36—C35—H35	120.6
C5—C6—H6B	109.7	C34—C35—H35	120.6
H6A—C6—H6B	108.2	N31—C36—C35	123.59 (18)
C22—C21—C26	116.02 (15)	N31—C36—H36	118.2
C22—C21—N4	122.74 (15)	C35—C36—H36	118.2
C26—C21—N4	121.11 (14)	O32—C37—O31	124.84 (16)
C21—C22—C23	122.14 (16)	O32—C37—C33	118.62 (15)
C21—C22—H22	118.9	O31—C37—C33	116.54 (15)

C23—C22—H22	118.9		
C6—N1—C2—C3	−59.85 (18)	O24—C24—C25—C26	179.32 (18)
N1—C2—C3—N4	57.18 (18)	C24—C25—C26—C21	0.1 (3)
C2—C3—N4—C21	170.15 (13)	C22—C21—C26—C25	−0.4 (3)
C2—C3—N4—C5	−53.72 (18)	N4—C21—C26—C25	175.52 (18)
C21—N4—C5—C6	−170.28 (14)	C23—C24—O24—C27	−13.4 (3)
C3—N4—C5—C6	53.52 (19)	C25—C24—O24—C27	167.31 (18)
C2—N1—C6—C5	58.59 (19)	C36—N31—C32—C33	−1.7 (3)
N4—C5—C6—N1	−55.7 (2)	N31—C32—C33—C34	0.9 (3)
C3—N4—C21—C22	−13.9 (2)	N31—C32—C33—C37	−179.08 (17)
C5—N4—C21—C22	−148.45 (17)	C32—C33—C34—C35	0.9 (3)
C3—N4—C21—C26	170.48 (16)	C37—C33—C34—C35	−179.12 (16)
C5—N4—C21—C26	35.9 (2)	C33—C34—C35—C36	−1.8 (3)
C26—C21—C22—C23	0.7 (3)	C32—N31—C36—C35	0.7 (3)
N4—C21—C22—C23	−175.17 (16)	C34—C35—C36—N31	1.0 (3)
C21—C22—C23—C24	−0.6 (3)	C32—C33—C37—O32	−32.1 (2)
C22—C23—C24—C25	0.3 (3)	C34—C33—C37—O32	147.86 (17)
C22—C23—C24—O24	−178.99 (17)	C32—C33—C37—O31	148.09 (18)
C23—C24—C25—C26	0.0 (3)	C34—C33—C37—O31	−31.9 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O31	0.976 (19)	1.714 (19)	2.677 (2)	168.2 (18)
N1—H12···O32^{i}	0.94 (2)	1.82 (2)	2.749 (2)	168.3 (17)
C2—H2*B*···N31^{ii}	0.97	2.56	3.518 (2)	169
C36—H36···O24^{iii}	0.93	2.51	3.432 (2)	172
C3—H3*A*···*Cg*1^{iv}	0.97	2.97	3.775 (2)	156

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

4-(4-Methoxyphenyl)piperazin-1-ium 2-hydroxy-3,5-dinitrobenzoate (VII)

Crystal data

$C_7H_3N_2O_7^+·C_{11}H_{17}N_2O^-$
M_r = 420.38
Monoclinic, $P2_1/c$
a = 7.5500 (9) Å
b = 7.6489 (9) Å
c = 32.719 (6) Å
β = 91.30 (1)°
V = 1889.0 (5) Å^3
Z = 4
F(000) = 880
D_x = 1.478 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 4078 reflections
θ = 2.7–28.0°
μ = 0.12 mm^{-1}
T = 296 K
Block, colourless
0.18 × 0.12 × 0.06 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.916, T_{max} = 0.993
8215 measured reflections
4074 independent reflections

2003 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.7°$

$h = -9 \rightarrow 5$
$k = -9 \rightarrow 9$
$l = -42 \rightarrow 41$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.128$
$S = 1.03$
4074 reflections
281 parameters
0 restraints

Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.4471P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Experimental. Compound (VII). IR (KBr , cm^{-1}) 3084 (NH_2), 2834 (OCH_3), 1568 (COO), 1499 (NO_2). NMR ($CDCl_3$) δ(^{1}H) 3.05 (m, 4H, piperazine), 3.37 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.85 (m, 4H, methoxyphenyl), 7.52 (s, 1H, 3,5-dinitrosalicylate), 8.09 (s, 1H, 3,5-dinitrosalicylate), 8.99 (s, 1H, 3,5-dinitrosalicylate).

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.6215 (3)	0.5723 (4)	0.61103 (8)	0.0465 (7)
H11	0.703 (4)	0.587 (4)	0.5906 (9)	0.056*
H12	0.533 (4)	0.494 (4)	0.6028 (9)	0.056*
C2	0.5349 (4)	0.7433 (4)	0.61776 (9)	0.0531 (9)
H2A	0.4783	0.7826	0.5925	0.064*
H2B	0.6235	0.8292	0.6258	0.064*
C3	0.3982 (4)	0.7294 (4)	0.65055 (9)	0.0489 (8)
H3A	0.3504	0.8446	0.6559	0.059*
H3B	0.3016	0.6558	0.6407	0.059*
N4	0.4712 (3)	0.6567 (3)	0.68854 (7)	0.0399 (6)
C5	0.5669 (4)	0.4924 (4)	0.68187 (9)	0.0483 (8)
H5A	0.4832	0.4024	0.6734	0.058*
H5B	0.6233	0.4554	0.7074	0.058*
C6	0.7057 (4)	0.5118 (4)	0.64972 (8)	0.0505 (8)
H6A	0.7947	0.5955	0.6588	0.061*
H6B	0.7637	0.4003	0.6454	0.061*
C21	0.3501 (4)	0.6515 (4)	0.72152 (9)	0.0382 (7)
C22	0.1878 (4)	0.7370 (4)	0.72002 (10)	0.0510 (8)
H22	0.1538	0.7966	0.6963	0.061*
C23	0.0745 (4)	0.7358 (4)	0.75303 (10)	0.0522 (8)
H23	−0.0327	0.7954	0.7512	0.063*
C24	0.1201 (4)	0.6473 (4)	0.78814 (9)	0.0455 (8)
C25	0.2807 (4)	0.5624 (4)	0.79002 (9)	0.0547 (9)

H25	0.3138	0.5028	0.8138	0.066*
C26	0.3934 (4)	0.5636 (4)	0.75758 (9)	0.0499 (8)
H26	0.5008	0.5044	0.7598	0.060*
O24	0.0184 (3)	0.6354 (3)	0.82246 (6)	0.0640 (7)
C27	−0.1485 (4)	0.7203 (5)	0.82152 (11)	0.0745 (11)
H27A	−0.2061	0.7017	0.8470	0.112*
H27B	−0.2206	0.6733	0.7996	0.112*
H27C	−0.1318	0.8433	0.8173	0.112*
C31	0.8836 (3)	0.6893 (4)	0.46865 (8)	0.0355 (7)
C32	0.8864 (3)	0.7026 (4)	0.51247 (9)	0.0374 (7)
C33	1.0424 (3)	0.7812 (4)	0.52995 (8)	0.0352 (7)
C34	1.1812 (3)	0.8371 (4)	0.50706 (8)	0.0372 (7)
H34	1.2797	0.8892	0.5195	0.045*
C35	1.1728 (3)	0.8150 (4)	0.46526 (9)	0.0368 (7)
C36	1.0252 (3)	0.7425 (4)	0.44590 (9)	0.0383 (7)
H36	1.0217	0.7298	0.4176	0.046*
C37	0.7243 (4)	0.6189 (4)	0.44690 (10)	0.0446 (8)
O31	0.7120 (3)	0.6063 (3)	0.40978 (6)	0.0609 (7)
O32	0.5931 (2)	0.5689 (3)	0.46961 (7)	0.0626 (7)
H32	0.638 (4)	0.590 (5)	0.4996 (12)	0.094*
O33	0.7553 (2)	0.6499 (3)	0.53332 (6)	0.0530 (6)
N33	1.0576 (3)	0.8102 (4)	0.57403 (8)	0.0481 (7)
O34	0.9695 (3)	0.7215 (4)	0.59704 (7)	0.0868 (9)
O35	1.1628 (3)	0.9203 (3)	0.58660 (6)	0.0627 (7)
N35	1.3207 (3)	0.8725 (3)	0.44092 (9)	0.0492 (7)
O36	1.4399 (3)	0.9552 (3)	0.45754 (7)	0.0715 (7)
O37	1.3199 (3)	0.8357 (3)	0.40434 (7)	0.0687 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0429 (15)	0.061 (2)	0.0360 (15)	−0.0125 (14)	0.0016 (11)	−0.0055 (14)
C2	0.064 (2)	0.053 (2)	0.0417 (19)	−0.0007 (17)	0.0004 (16)	0.0075 (17)
C3	0.0565 (19)	0.053 (2)	0.0371 (18)	0.0086 (16)	0.0021 (15)	0.0053 (16)
N4	0.0438 (13)	0.0416 (16)	0.0342 (14)	0.0040 (11)	−0.0003 (11)	0.0033 (12)
C5	0.0505 (18)	0.055 (2)	0.0397 (19)	0.0108 (16)	0.0033 (14)	0.0063 (16)
C6	0.0477 (18)	0.066 (2)	0.0374 (18)	0.0033 (16)	−0.0019 (14)	−0.0007 (17)
C21	0.0430 (16)	0.0340 (18)	0.0375 (17)	−0.0001 (13)	−0.0035 (13)	−0.0012 (14)
C22	0.0511 (19)	0.057 (2)	0.045 (2)	0.0118 (16)	0.0001 (15)	0.0135 (17)
C23	0.0480 (18)	0.053 (2)	0.056 (2)	0.0132 (15)	0.0034 (16)	0.0039 (18)
C24	0.0482 (18)	0.045 (2)	0.044 (2)	0.0021 (15)	0.0057 (15)	−0.0026 (16)
C25	0.062 (2)	0.064 (2)	0.0382 (19)	0.0154 (18)	−0.0005 (15)	0.0126 (18)
C26	0.0490 (18)	0.059 (2)	0.0417 (19)	0.0167 (16)	−0.0010 (15)	0.0055 (17)
O24	0.0614 (15)	0.0814 (18)	0.0497 (14)	0.0129 (12)	0.0142 (11)	0.0028 (13)
C27	0.057 (2)	0.096 (3)	0.071 (3)	0.014 (2)	0.0207 (19)	−0.007 (2)
C31	0.0344 (15)	0.0352 (17)	0.0366 (17)	−0.0028 (13)	−0.0008 (13)	−0.0002 (14)
C32	0.0318 (15)	0.0367 (18)	0.0437 (18)	0.0004 (13)	0.0011 (13)	0.0046 (15)
C33	0.0367 (16)	0.0371 (18)	0.0315 (16)	0.0003 (13)	−0.0022 (13)	0.0003 (14)

C34	0.0352 (15)	0.0340 (18)	0.0422 (18)	−0.0016 (13)	−0.0053 (13)	−0.0020 (15)
C35	0.0316 (15)	0.0345 (17)	0.0443 (19)	−0.0064 (13)	0.0036 (13)	0.0017 (15)
C36	0.0405 (16)	0.0355 (17)	0.0388 (17)	−0.0019 (13)	0.0018 (13)	−0.0015 (14)
C37	0.0397 (17)	0.048 (2)	0.046 (2)	−0.0086 (14)	−0.0020 (15)	0.0005 (16)
O31	0.0570 (13)	0.0868 (19)	0.0389 (14)	−0.0254 (12)	−0.0012 (10)	−0.0093 (13)
O32	0.0429 (13)	0.099 (2)	0.0455 (13)	−0.0297 (12)	−0.0024 (10)	0.0073 (14)
O33	0.0396 (12)	0.0793 (17)	0.0404 (13)	−0.0153 (11)	0.0032 (10)	0.0039 (12)
N33	0.0381 (14)	0.063 (2)	0.0424 (17)	0.0001 (13)	−0.0041 (12)	0.0013 (15)
O34	0.0712 (16)	0.146 (3)	0.0427 (15)	−0.0443 (16)	0.0011 (12)	0.0102 (16)
O35	0.0688 (15)	0.0690 (17)	0.0495 (14)	−0.0132 (13)	−0.0138 (11)	−0.0063 (13)
N35	0.0460 (16)	0.0512 (18)	0.0505 (18)	−0.0110 (13)	0.0022 (13)	0.0012 (15)
O36	0.0604 (14)	0.092 (2)	0.0616 (16)	−0.0425 (13)	0.0006 (12)	−0.0031 (14)
O37	0.0643 (15)	0.095 (2)	0.0474 (15)	−0.0258 (13)	0.0132 (11)	−0.0123 (15)

Geometric parameters (Å, º)

N1—C6	1.478 (4)	C25—H25	0.9300
N1—C2	1.481 (4)	C26—H26	0.9300
N1—H11	0.93 (3)	O24—C27	1.417 (3)
N1—H12	0.93 (3)	C27—H27A	0.9600
C2—C3	1.509 (4)	C27—H27B	0.9600
C2—H2A	0.9700	C27—H27C	0.9600
C2—H2B	0.9700	C31—C36	1.378 (4)
C3—N4	1.458 (3)	C31—C32	1.437 (4)
C3—H3A	0.9700	C31—C37	1.485 (4)
C3—H3B	0.9700	C32—O33	1.280 (3)
N4—C21	1.431 (3)	C32—C33	1.430 (4)
N4—C5	1.469 (3)	C33—C34	1.370 (3)
C5—C6	1.509 (4)	C33—N33	1.461 (3)
C5—H5A	0.9700	C34—C35	1.378 (4)
C5—H5B	0.9700	C34—H34	0.9300
C6—H6A	0.9700	C35—C36	1.385 (4)
C6—H6B	0.9700	C35—N35	1.455 (3)
C21—C22	1.389 (4)	C36—H36	0.9300
C21—C26	1.391 (4)	C37—O31	1.220 (3)
C22—C23	1.393 (4)	C37—O32	1.309 (3)
C22—H22	0.9300	O32—H32	1.04 (4)
C23—C24	1.371 (4)	N33—O34	1.222 (3)
C23—H23	0.9300	N33—O35	1.223 (3)
C24—C25	1.376 (4)	N35—O36	1.218 (3)
C24—O24	1.378 (3)	N35—O37	1.229 (3)
C25—C26	1.375 (4)		

C6—N1—C2	109.4 (2)	C25—C24—O24	116.1 (3)
C6—N1—H11	112.1 (18)	C26—C25—C24	121.5 (3)
C2—N1—H11	107.5 (18)	C26—C25—H25	119.2
C6—N1—H12	109.6 (18)	C24—C25—H25	119.2
C2—N1—H12	107.2 (18)	C25—C26—C21	121.3 (3)

H11—N1—H12	111 (3)	C25—C26—H26	119.3
N1—C2—C3	110.8 (2)	C21—C26—H26	119.3
N1—C2—H2A	109.5	C24—O24—C27	117.6 (3)
C3—C2—H2A	109.5	O24—C27—H27A	109.5
N1—C2—H2B	109.5	O24—C27—H27B	109.5
C3—C2—H2B	109.5	H27A—C27—H27B	109.5
H2A—C2—H2B	108.1	O24—C27—H27C	109.5
N4—C3—C2	112.4 (2)	H27A—C27—H27C	109.5
N4—C3—H3A	109.1	H27B—C27—H27C	109.5
C2—C3—H3A	109.1	C36—C31—C32	121.6 (2)
N4—C3—H3B	109.1	C36—C31—C37	118.6 (3)
C2—C3—H3B	109.1	C32—C31—C37	119.8 (2)
H3A—C3—H3B	107.8	O33—C32—C33	124.0 (3)
C21—N4—C3	114.7 (2)	O33—C32—C31	121.0 (2)
C21—N4—C5	114.4 (2)	C33—C32—C31	115.0 (2)
C3—N4—C5	112.2 (2)	C34—C33—C32	123.1 (3)
N4—C5—C6	111.8 (3)	C34—C33—N33	116.7 (2)
N4—C5—H5A	109.3	C32—C33—N33	120.3 (2)
C6—C5—H5A	109.3	C33—C34—C35	119.0 (2)
N4—C5—H5B	109.3	C33—C34—H34	120.5
C6—C5—H5B	109.3	C35—C34—H34	120.5
H5A—C5—H5B	107.9	C34—C35—C36	121.5 (2)
N1—C6—C5	109.6 (2)	C34—C35—N35	119.2 (2)
N1—C6—H6A	109.7	C36—C35—N35	119.4 (3)
C5—C6—H6A	109.7	C31—C36—C35	119.8 (3)
N1—C6—H6B	109.7	C31—C36—H36	120.1
C5—C6—H6B	109.7	C35—C36—H36	120.1
H6A—C6—H6B	108.2	O31—C37—O32	120.1 (3)
C22—C21—C26	116.6 (3)	O31—C37—C31	123.2 (3)
C22—C21—N4	122.6 (3)	O32—C37—C31	116.7 (3)
C26—C21—N4	120.8 (2)	C37—O32—H32	104.6 (18)
C21—C22—C23	121.8 (3)	C32—O33—H32	99.0 (13)
C21—C22—H22	119.1	O34—N33—O35	122.3 (3)
C23—C22—H22	119.1	O34—N33—C33	119.5 (3)
C24—C23—C22	120.4 (3)	O35—N33—C33	118.2 (3)
C24—C23—H23	119.8	O36—N35—O37	122.8 (2)
C22—C23—H23	119.8	O36—N35—C35	118.8 (3)
C23—C24—C25	118.4 (3)	O37—N35—C35	118.5 (2)
C23—C24—O24	125.6 (3)		

C6—N1—C2—C3	−58.5 (3)	C36—C31—C32—C33	2.6 (4)
N1—C2—C3—N4	54.3 (3)	C37—C31—C32—C33	−176.6 (2)
C2—C3—N4—C21	176.0 (2)	O33—C32—C33—C34	−179.8 (3)
C2—C3—N4—C5	−51.2 (3)	C31—C32—C33—C34	−1.3 (4)
C21—N4—C5—C6	−174.0 (2)	O33—C32—C33—N33	−1.6 (4)
C3—N4—C5—C6	53.0 (3)	C31—C32—C33—N33	176.9 (3)
C2—N1—C6—C5	60.0 (3)	C32—C33—C34—C35	−0.9 (4)
N4—C5—C6—N1	−57.5 (3)	N33—C33—C34—C35	−179.2 (2)

C3—N4—C21—C22	−11.2 (4)	C33—C34—C35—C36	2.0 (4)
C5—N4—C21—C22	−142.9 (3)	C33—C34—C35—N35	−179.4 (2)
C3—N4—C21—C26	170.9 (3)	C32—C31—C36—C35	−1.7 (4)
C5—N4—C21—C26	39.2 (4)	C37—C31—C36—C35	177.5 (3)
C26—C21—C22—C23	0.4 (5)	C34—C35—C36—C31	−0.6 (4)
N4—C21—C22—C23	−177.6 (3)	N35—C35—C36—C31	−179.3 (2)
C21—C22—C23—C24	−0.8 (5)	C36—C31—C37—O31	−0.3 (5)
C22—C23—C24—C25	0.9 (5)	C32—C31—C37—O31	179.0 (3)
C22—C23—C24—O24	−179.3 (3)	C36—C31—C37—O32	179.6 (3)
C23—C24—C25—C26	−0.6 (5)	C32—C31—C37—O32	−1.1 (4)
O24—C24—C25—C26	179.5 (3)	C34—C33—N33—O34	−158.4 (3)
C24—C25—C26—C21	0.3 (5)	C32—C33—N33—O34	23.3 (4)
C22—C21—C26—C25	−0.2 (5)	C34—C33—N33—O35	19.6 (4)
N4—C21—C26—C25	177.9 (3)	C32—C33—N33—O35	−158.7 (3)
C23—C24—O24—C27	0.6 (5)	C34—C35—N35—O36	−7.6 (4)
C25—C24—O24—C27	−179.6 (3)	C36—C35—N35—O36	171.1 (3)
C36—C31—C32—O33	−178.8 (3)	C34—C35—N35—O37	172.5 (3)
C37—C31—C32—O33	2.0 (4)	C36—C35—N35—O37	−8.8 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O32—H32···O33	1.04 (4)	1.47 (4)	2.472 (3)	158 (3)
N1—H11···O33	0.93 (3)	1.98 (3)	2.820 (3)	150 (3)
N1—H11···O34	0.93 (3)	2.27 (3)	2.910 (3)	126 (2)
N1—H12···O31^{i}	0.93 (3)	2.04 (3)	2.931 (3)	160 (3)
N1—H12···O32^{i}	0.93 (3)	2.58 (3)	3.250 (3)	129 (2)
C34—H34···O36^{ii}	0.93	2.53	3.449 (3)	171
C5—H5*B*···*Cg*2^{iii}	0.97	2.84	3.639 (3)	140

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

4-(4-Methoxyphenyl)piperazin-1-ium hydrogensuccinate (VIII)

Crystal data

$C_{11}H_{17}N_2O^+·C_4H_5O_4^-$
M_r = 310.35
Orthorhombic, $Pna2_1$
a = 9.3225 (9) Å
b = 28.261 (3) Å
c = 5.8228 (8) Å
V = 1534.1 (3) Å^3
Z = 4
F(000) = 664
D_x = 1.344 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2423 reflections
θ = 2.6–27.8°
μ = 0.10 mm^{-1}
T = 296 K
Block, colourless
0.44 × 0.42 × 0.24 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.816, T_{max} = 0.976
5828 measured reflections
2419 independent reflections

2053 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.6°$
$h = -6 \rightarrow 11$
$k = -36 \rightarrow 27$
$l = -7 \rightarrow 5$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.104$
$S = 1.14$
2419 reflections
233 parameters
16 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.356P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Absolute structure: Flack *x* determined using 460 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Special details

Experimental. Compound (VIII). IR (KBr , cm^{-1}) 3135 (NH_2), 2836 (OCH_3), 1562 (COO). NMR ($CDCl_3$) δ(^{1}H)) 2.66 (s, 4H, succinate), 3.32 (m, 4H, piperazine), 3.35 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.90 (m, 4H, methoxyphenyl).

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)
N1	0.5210 (3)	0.66867 (8)	0.5428 (5)	0.0395 (6)	
H11	0.580 (3)	0.6921 (11)	0.556 (7)	0.047*	
H12	0.435 (3)	0.6801 (10)	0.623 (7)	0.047*	
C2	0.5853 (3)	0.62541 (9)	0.6443 (7)	0.0435 (7)	
H2A	0.6135	0.6317	0.8018	0.052*	
H2B	0.6704	0.6167	0.5586	0.052*	
C3	0.4786 (3)	0.58515 (9)	0.6388 (6)	0.0414 (7)	
H3A	0.5238	0.5568	0.6992	0.050*	
H3B	0.3981	0.5929	0.7374	0.050*	
N4	0.4259 (2)	0.57556 (7)	0.4075 (5)	0.0347 (5)	
C5	0.3676 (3)	0.61875 (9)	0.3026 (6)	0.0439 (7)	
H5A	0.2824	0.6284	0.3859	0.053*	
H5B	0.3397	0.6120	0.1454	0.053*	
C6	0.4745 (3)	0.65878 (10)	0.3038 (6)	0.0479 (8)	
H6A	0.5570	0.6503	0.2110	0.058*	
H6B	0.4312	0.6869	0.2380	0.058*	
C21	0.3353 (3)	0.53502 (9)	0.3862 (5)	0.0331 (6)	
C22	0.3336 (3)	0.49886 (9)	0.5496 (6)	0.0394 (7)	
H22	0.3926	0.5011	0.6779	0.047*	
C23	0.2451 (3)	0.45967 (10)	0.5241 (6)	0.0440 (7)	
H23	0.2456	0.4361	0.6354	0.053*	
C24	0.1567 (3)	0.45534 (9)	0.3356 (6)	0.0407 (7)	

C25	0.1589 (3)	0.48988 (10)	0.1703 (7)	0.0484 (8)	
H25	0.1013	0.4870	0.0406	0.058*	
C26	0.2469 (3)	0.52924 (10)	0.1961 (6)	0.0464 (8)	
H26	0.2466	0.5524	0.0826	0.056*	
O24	0.0728 (2)	0.41532 (8)	0.3280 (5)	0.0620 (8)	
C27	−0.0230 (4)	0.41098 (13)	0.1399 (9)	0.0729 (12)	
H27A	−0.0790	0.3827	0.1572	0.109*	
H27B	0.0307	0.4094	−0.0005	0.109*	
H27C	−0.0856	0.4379	0.1358	0.109*	
C31	0.7061 (15)	0.7714 (3)	0.797 (3)	0.0296 (18)	0.660 (15)
O31	0.7173 (15)	0.7375 (5)	0.655 (3)	0.0463 (18)	0.660 (15)
O32	0.7811 (18)	0.8079 (5)	0.790 (4)	0.0443 (15)	0.660 (15)
C32	0.5909 (9)	0.7663 (3)	0.9790 (16)	0.0375 (16)	0.660 (15)
H32A	0.6331	0.7517	1.1138	0.045*	0.660 (15)
H32B	0.5175	0.7450	0.9216	0.045*	0.660 (15)
C33	0.5200 (11)	0.8123 (3)	1.0509 (19)	0.056 (3)	0.660 (15)
H33A	0.5933	0.8339	1.1050	0.067*	0.660 (15)
H33B	0.4747	0.8265	0.9178	0.067*	0.660 (15)
C34	0.4093 (16)	0.8060 (6)	1.237 (3)	0.0468 (19)	0.660 (15)
O33	0.3172 (11)	0.8361 (3)	1.279 (2)	0.086 (3)	0.660 (15)
O34	0.4253 (19)	0.7688 (5)	1.359 (2)	0.065 (3)	0.660 (15)
H34	0.3533	0.7647	1.4378	0.098*	0.660 (15)
C41	0.702 (3)	0.7808 (8)	0.792 (6)	0.0296 (18)	0.340 (15)
O41	0.736 (3)	0.7440 (11)	0.678 (7)	0.0463 (18)	0.340 (15)
O42	0.782 (4)	0.8158 (10)	0.816 (8)	0.0443 (15)	0.340 (15)
C42	0.567 (2)	0.7768 (6)	0.934 (3)	0.0375 (16)	0.340 (15)
H42A	0.4853	0.7819	0.8332	0.045*	0.340 (15)
H42B	0.5601	0.7447	0.9916	0.045*	0.340 (15)
C43	0.555 (2)	0.8103 (7)	1.134 (3)	0.056 (3)	0.340 (15)
H43A	0.5570	0.8425	1.0770	0.067*	0.340 (15)
H43B	0.6369	0.8060	1.2337	0.067*	0.340 (15)
C44	0.419 (3)	0.8032 (11)	1.272 (5)	0.0468 (19)	0.340 (15)
O43	0.304 (2)	0.8221 (6)	1.225 (5)	0.086 (3)	0.340 (15)
O44	0.425 (4)	0.7694 (12)	1.418 (5)	0.065 (3)	0.340 (15)
H44	0.3490	0.7681	1.4892	0.098*	0.340 (15)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0367 (12)	0.0305 (11)	0.0512 (17)	−0.0052 (10)	0.0144 (13)	−0.0049 (11)
C2	0.0389 (14)	0.0366 (13)	0.055 (2)	−0.0012 (11)	−0.0002 (16)	−0.0023 (14)
C3	0.0440 (15)	0.0361 (13)	0.0440 (18)	−0.0024 (11)	−0.0032 (15)	0.0033 (13)
N4	0.0388 (12)	0.0296 (10)	0.0357 (13)	−0.0015 (9)	0.0050 (11)	−0.0003 (10)
C5	0.0592 (17)	0.0331 (12)	0.0395 (17)	−0.0042 (12)	−0.0014 (16)	0.0044 (13)
C6	0.0606 (18)	0.0386 (14)	0.0446 (19)	−0.0070 (13)	0.0126 (18)	0.0056 (14)
C21	0.0345 (13)	0.0314 (12)	0.0333 (16)	0.0023 (10)	0.0055 (12)	−0.0008 (11)
C22	0.0421 (15)	0.0354 (13)	0.0406 (17)	0.0004 (11)	−0.0064 (14)	0.0037 (13)
C23	0.0483 (16)	0.0366 (14)	0.0472 (19)	−0.0025 (12)	−0.0064 (16)	0.0123 (13)

C24	0.0370 (13)	0.0332 (12)	0.052 (2)	−0.0019 (11)	−0.0022 (15)	0.0026 (13)
C25	0.0533 (17)	0.0456 (15)	0.046 (2)	−0.0059 (13)	−0.0156 (17)	0.0056 (15)
C26	0.0587 (18)	0.0414 (14)	0.0391 (19)	−0.0073 (13)	−0.0055 (16)	0.0104 (14)
O24	0.0604 (13)	0.0480 (11)	0.078 (2)	−0.0194 (10)	−0.0266 (15)	0.0143 (12)
C27	0.067 (2)	0.061 (2)	0.090 (3)	−0.0233 (17)	−0.036 (2)	0.011 (2)
C31	0.0307 (14)	0.020 (4)	0.0377 (18)	0.002 (3)	0.0121 (15)	0.002 (4)
O31	0.039 (4)	0.043 (4)	0.056 (4)	−0.018 (2)	0.025 (4)	−0.025 (2)
O32	0.0467 (11)	0.029 (4)	0.057 (5)	−0.011 (3)	0.027 (2)	−0.014 (3)
C32	0.043 (3)	0.025 (3)	0.045 (4)	0.002 (2)	0.019 (3)	0.004 (2)
C33	0.069 (5)	0.0348 (18)	0.064 (7)	0.008 (3)	0.043 (5)	0.009 (4)
C34	0.053 (3)	0.032 (2)	0.055 (5)	0.0033 (16)	0.031 (3)	−0.001 (2)
O33	0.097 (3)	0.054 (5)	0.107 (7)	0.039 (4)	0.067 (4)	0.016 (4)
O34	0.0654 (15)	0.0655 (15)	0.065 (8)	0.0228 (12)	0.054 (5)	0.026 (4)
C41	0.0307 (14)	0.020 (4)	0.0377 (18)	0.002 (3)	0.0121 (15)	0.002 (4)
O41	0.039 (4)	0.043 (4)	0.056 (4)	−0.018 (2)	0.025 (4)	−0.025 (2)
O42	0.0467 (11)	0.029 (4)	0.057 (5)	−0.011 (3)	0.027 (2)	−0.014 (3)
C42	0.043 (3)	0.025 (3)	0.045 (4)	0.002 (2)	0.019 (3)	0.004 (2)
C43	0.069 (5)	0.0348 (18)	0.064 (7)	0.008 (3)	0.043 (5)	0.009 (4)
C44	0.053 (3)	0.032 (2)	0.055 (5)	0.0033 (16)	0.031 (3)	−0.001 (2)
O43	0.097 (3)	0.054 (5)	0.107 (7)	0.039 (4)	0.067 (4)	0.016 (4)
O44	0.0654 (15)	0.0655 (15)	0.065 (8)	0.0228 (12)	0.054 (5)	0.026 (4)

Geometric parameters (Å, º)

N1—C6	1.484 (5)	O24—C27	1.419 (5)
N1—C2	1.484 (4)	C27—H27A	0.9600
N1—H11	0.86 (3)	C27—H27B	0.9600
N1—H12	0.98 (3)	C27—H27C	0.9600
C2—C3	1.512 (4)	C31—O32	1.247 (5)
C2—H2A	0.9700	C31—O31	1.270 (7)
C2—H2B	0.9700	C31—C32	1.513 (6)
C3—N4	1.459 (4)	C32—C33	1.517 (7)
C3—H3A	0.9700	C32—H32A	0.9700
C3—H3B	0.9700	C32—H32B	0.9700
N4—C21	1.429 (3)	C33—C34	1.505 (6)
N4—C5	1.469 (3)	C33—H33A	0.9700
C5—C6	1.508 (4)	C33—H33B	0.9700
C5—H5A	0.9700	C34—O33	1.233 (9)
C5—H5B	0.9700	C34—O34	1.280 (6)
C6—H6A	0.9700	O34—H34	0.8200
C6—H6B	0.9700	C41—O42	1.247 (9)
C21—C26	1.390 (4)	C41—O41	1.271 (10)
C21—C22	1.396 (4)	C41—C42	1.514 (9)
C22—C23	1.388 (4)	C42—C43	1.507 (11)
C22—H22	0.9300	C42—H42A	0.9700
C23—C24	1.378 (5)	C42—H42B	0.9700
C23—H23	0.9300	C43—C44	1.508 (10)
C24—C25	1.371 (4)	C43—H43A	0.9700

C24—O24	1.376 (3)	C43—H43B	0.9700
C25—C26	1.390 (4)	C44—O43	1.235 (13)
C25—H25	0.9300	C44—O44	1.282 (9)
C26—H26	0.9300	O44—H44	0.8200
C6—N1—C2	109.6 (2)	C21—C26—C25	122.0 (3)
C6—N1—H11	114 (3)	C21—C26—H26	119.0
C2—N1—H11	110 (2)	C25—C26—H26	119.0
C6—N1—H12	106 (2)	C24—O24—C27	117.0 (3)
C2—N1—H12	114 (2)	O24—C27—H27A	109.5
H11—N1—H12	103 (3)	O24—C27—H27B	109.5
N1—C2—C3	110.2 (2)	H27A—C27—H27B	109.5
N1—C2—H2A	109.6	O24—C27—H27C	109.5
C3—C2—H2A	109.6	H27A—C27—H27C	109.5
N1—C2—H2B	109.6	H27B—C27—H27C	109.5
C3—C2—H2B	109.6	O32—C31—O31	123.7 (8)
H2A—C2—H2B	108.1	O32—C31—C32	120.0 (6)
N4—C3—C2	112.4 (3)	O31—C31—C32	116.3 (6)
N4—C3—H3A	109.1	C31—C32—C33	114.8 (6)
C2—C3—H3A	109.1	C31—C32—H32A	108.6
N4—C3—H3B	109.1	C33—C32—H32A	108.6
C2—C3—H3B	109.1	C31—C32—H32B	108.6
H3A—C3—H3B	107.9	C33—C32—H32B	108.6
C21—N4—C3	115.3 (2)	H32A—C32—H32B	107.5
C21—N4—C5	114.3 (2)	C34—C33—C32	113.3 (6)
C3—N4—C5	110.7 (2)	C34—C33—H33A	108.9
N4—C5—C6	112.1 (2)	C32—C33—H33A	108.9
N4—C5—H5A	109.2	C34—C33—H33B	108.9
C6—C5—H5A	109.2	C32—C33—H33B	108.9
N4—C5—H5B	109.2	H33A—C33—H33B	107.7
C6—C5—H5B	109.2	O33—C34—O34	122.3 (7)
H5A—C5—H5B	107.9	O33—C34—C33	122.8 (7)
N1—C6—C5	109.8 (3)	O34—C34—C33	114.7 (6)
N1—C6—H6A	109.7	C34—O34—H34	109.5
C5—C6—H6A	109.7	O42—C41—O41	124.3 (15)
N1—C6—H6B	109.7	O42—C41—C42	119.7 (12)
C5—C6—H6B	109.7	O41—C41—C42	115.3 (12)
H6A—C6—H6B	108.2	C43—C42—C41	116.0 (12)
C26—C21—C22	116.7 (2)	C43—C42—H42A	108.3
C26—C21—N4	120.9 (3)	C41—C42—H42A	108.3
C22—C21—N4	122.3 (3)	C43—C42—H42B	108.3
C23—C22—C21	121.2 (3)	C41—C42—H42B	108.3
C23—C22—H22	119.4	H42A—C42—H42B	107.4
C21—C22—H22	119.4	C42—C43—C44	113.1 (15)
C24—C23—C22	120.8 (3)	C42—C43—H43A	109.0
C24—C23—H23	119.6	C44—C43—H43A	109.0
C22—C23—H23	119.6	C42—C43—H43B	109.0
C25—C24—O24	124.8 (3)	C44—C43—H43B	109.0

C25—C24—C23	119.1 (3)	H43A—C43—H43B	107.8
O24—C24—C23	116.0 (3)	O43—C44—O44	120.3 (16)
C24—C25—C26	120.2 (3)	O43—C44—C43	123.7 (14)
C24—C25—H25	119.9	O44—C44—C43	114.8 (12)
C26—C25—H25	119.9	C44—O44—H44	109.5
C6—N1—C2—C3	−57.9 (3)	O24—C24—C25—C26	179.3 (3)
N1—C2—C3—N4	56.2 (3)	C23—C24—C25—C26	−1.5 (5)
C2—C3—N4—C21	174.2 (2)	C22—C21—C26—C25	1.0 (4)
C2—C3—N4—C5	−54.0 (3)	N4—C21—C26—C25	179.3 (3)
C21—N4—C5—C6	−172.9 (3)	C24—C25—C26—C21	0.4 (5)
C3—N4—C5—C6	54.8 (3)	C25—C24—O24—C27	−3.1 (5)
C2—N1—C6—C5	58.5 (3)	C23—C24—O24—C27	177.7 (3)
N4—C5—C6—N1	−57.4 (3)	O32—C31—C32—C33	32 (2)
C3—N4—C21—C26	161.9 (3)	O31—C31—C32—C33	−146 (2)
C5—N4—C21—C26	31.8 (4)	C31—C32—C33—C34	−178.3 (12)
C3—N4—C21—C22	−19.9 (4)	C32—C33—C34—O33	−162 (2)
C5—N4—C21—C22	−150.0 (3)	C32—C33—C34—O34	23 (2)
C26—C21—C22—C23	−1.3 (4)	O42—C41—C42—C43	−13 (5)
N4—C21—C22—C23	−179.6 (3)	O41—C41—C42—C43	157 (4)
C21—C22—C23—C24	0.2 (5)	C41—C42—C43—C44	−178 (2)
C22—C23—C24—C25	1.2 (5)	C42—C43—C44—O43	−86 (4)
C22—C23—C24—O24	−179.5 (3)	C42—C43—C44—O44	82 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O31	0.86 (3)	1.90 (3)	2.750 (15)	167 (4)
N1—H12···O32^{i}	0.98 (3)	1.77 (4)	2.741 (19)	171 (3)
O34—H34···O31^{ii}	0.82	1.79	2.60 (2)	168
N1—H11···O41	0.86 (3)	2.18 (4)	3.03 (3)	165 (4)
N1—H12···O42^{i}	0.98 (3)	1.82 (5)	2.77 (4)	163 (3)
O44—H44···O41^{ii}	0.82	1.56	2.35 (2)	161
C3—H3*A*···*Cg*2^{iii}	0.97	2.76	3.652 (3)	154

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

4-(4-Methoxyphenyl)piperazin-1-ium hydrogenfumarate (IX)

Crystal data

$C_{11}H_{17}N_2O^+·C_4H_3O_4^-$
M_r = 308.33
Orthorhombic, *Pna*2$_1$
a = 9.069 (1) Å
b = 28.528 (3) Å
c = 5.8375 (9) Å
V = 1510.3 (3) Å^3
Z = 4
F(000) = 656

D_x = 1.356 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2829 reflections
θ = 2.7–27.7°
μ = 0.10 mm^{-1}
T = 296 K
Plate, colourless
0.48 × 0.48 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.888, T_{max} = 0.992
5834 measured reflections
2827 independent reflections
2316 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 27.5°, θ_{min} = 2.7°
h = −8→11
k = −32→35
l = −7→6

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.101
S = 1.05
2827 reflections
221 parameters
11 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.4265P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Absolute structure: Flack x determined using 769 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Special details

Experimental. Compound (IX). IR (KBr , cm^{-1}) 3001 (NH_2), 2839 (OCH_3), 1562 (COO). NMR ($CDCl_3$) δ(^{1}H)) 3.09 (m, 4H, piperazine), 3.35 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.26 (s, 2H, fumarate), 6.90 (m, 4H, methoxyphenyl).

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)
N1	0.5253 (3)	0.66688 (8)	0.5154 (5)	0.0448 (6)	
H11	0.588 (4)	0.6872 (12)	0.518 (6)	0.054*	
H12	0.440 (4)	0.6776 (11)	0.596 (6)	0.054*	
C2	0.5885 (3)	0.62425 (10)	0.6244 (6)	0.0490 (8)	
H2A	0.6182	0.6315	0.7801	0.059*	
H2B	0.6753	0.6144	0.5403	0.059*	
C3	0.4771 (3)	0.58500 (9)	0.6274 (6)	0.0449 (7)	
H3A	0.5225	0.5572	0.6916	0.054*	
H3B	0.3952	0.5937	0.7254	0.054*	
N4	0.4215 (3)	0.57432 (7)	0.3988 (4)	0.0395 (6)	
C5	0.3637 (4)	0.61653 (10)	0.2869 (6)	0.0505 (8)	
H5A	0.2767	0.6272	0.3685	0.061*	
H5B	0.3344	0.6089	0.1315	0.061*	
C6	0.4751 (4)	0.65530 (10)	0.2808 (6)	0.0540 (9)	
H6A	0.5589	0.6458	0.1886	0.065*	
H6B	0.4317	0.6829	0.2106	0.065*	
C21	0.3300 (3)	0.53374 (9)	0.3824 (5)	0.0372 (6)	

C22	0.3313 (3)	0.49854 (9)	0.5482 (6)	0.0441 (7)	
H22	0.3919	0.5017	0.6758	0.053*	
C23	0.2439 (3)	0.45907 (10)	0.5261 (7)	0.0485 (8)	
H23	0.2468	0.4361	0.6393	0.058*	
C24	0.1529 (3)	0.45301 (10)	0.3401 (6)	0.0456 (8)	
C25	0.1521 (4)	0.48719 (10)	0.1732 (6)	0.0518 (8)	
H25	0.0924	0.4836	0.0448	0.062*	
C26	0.2391 (4)	0.52673 (11)	0.1945 (6)	0.0509 (8)	
H26	0.2366	0.5493	0.0796	0.061*	
O24	0.0698 (3)	0.41291 (8)	0.3349 (5)	0.0668 (8)	
C27	−0.0259 (4)	0.40672 (14)	0.1473 (9)	0.0804 (13)	
H27A	−0.0819	0.3785	0.1680	0.121*	
H27B	0.0307	0.4045	0.0088	0.121*	
H27C	−0.0918	0.4330	0.1373	0.121*	
C31	0.7171 (3)	0.77494 (10)	0.8023 (6)	0.0452 (7)	
O31	0.7323 (3)	0.73835 (7)	0.6832 (5)	0.0673 (8)	
O32	0.7875 (3)	0.81180 (7)	0.7776 (5)	0.0595 (7)	
C32	0.6095 (4)	0.77182 (10)	0.9941 (6)	0.0526 (9)	0.906 (9)
H32	0.5993	0.7427	1.0643	0.063*	0.906 (9)
C33	0.5305 (7)	0.80489 (15)	1.0714 (12)	0.0607 (11)	0.906 (9)
H33	0.5456	0.8345	1.0089	0.073*	0.906 (9)
C34	0.4163 (5)	0.80084 (15)	1.2518 (8)	0.0518 (9)	0.906 (9)
O33	0.3241 (5)	0.83097 (16)	1.2845 (8)	0.0992 (18)	0.906 (9)
O34	0.4218 (4)	0.76290 (13)	1.3671 (8)	0.0734 (13)	0.906 (9)
H34	0.3526	0.7621	1.4574	0.110*	0.906 (9)
C42	0.6095 (4)	0.77182 (10)	0.9941 (6)	0.0526 (9)	0.094 (9)
H42	0.5982	0.7421	1.0566	0.063*	0.094 (9)
C43	0.531 (6)	0.8035 (9)	1.086 (10)	0.0607 (11)	0.094 (9)
H43	0.5533	0.8343	1.0477	0.073*	0.094 (9)
C44	0.407 (4)	0.7961 (12)	1.247 (6)	0.0518 (9)	0.094 (9)
O43	0.280 (4)	0.8058 (15)	1.203 (7)	0.0992 (18)	0.094 (9)
O44	0.444 (4)	0.7801 (13)	1.442 (6)	0.0734 (13)	0.094 (9)
H44	0.3697	0.7743	1.5169	0.110*	0.094 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0436 (14)	0.0378 (12)	0.0531 (18)	−0.0049 (10)	0.0167 (13)	−0.0020 (12)
C2	0.0444 (16)	0.0431 (15)	0.060 (2)	0.0018 (12)	0.0054 (16)	−0.0042 (15)
C3	0.0482 (17)	0.0398 (14)	0.047 (2)	−0.0019 (13)	−0.0013 (15)	0.0052 (13)
N4	0.0466 (13)	0.0348 (11)	0.0371 (14)	0.0016 (10)	0.0048 (12)	−0.0005 (10)
C5	0.072 (2)	0.0403 (14)	0.0396 (19)	−0.0043 (14)	−0.0015 (17)	0.0079 (14)
C6	0.077 (2)	0.0423 (14)	0.043 (2)	−0.0044 (15)	0.0172 (18)	0.0048 (15)
C21	0.0398 (15)	0.0355 (13)	0.0363 (17)	0.0060 (11)	0.0060 (14)	0.0009 (12)
C22	0.0484 (17)	0.0402 (14)	0.0437 (19)	0.0029 (12)	−0.0071 (15)	0.0040 (14)
C23	0.0532 (18)	0.0413 (15)	0.0510 (19)	0.0005 (13)	−0.0054 (17)	0.0123 (15)
C24	0.0391 (15)	0.0409 (14)	0.057 (2)	0.0015 (12)	−0.0036 (15)	0.0009 (14)
C25	0.0560 (19)	0.0519 (17)	0.048 (2)	−0.0013 (15)	−0.0160 (17)	0.0035 (16)

C26	0.065 (2)	0.0455 (15)	0.042 (2)	−0.0041 (14)	−0.0061 (16)	0.0115 (14)
O24	0.0633 (15)	0.0532 (12)	0.084 (2)	−0.0163 (11)	−0.0224 (15)	0.0125 (13)
C27	0.064 (2)	0.070 (2)	0.107 (4)	−0.0205 (19)	−0.034 (3)	0.012 (2)
C31	0.0431 (16)	0.0435 (15)	0.049 (2)	0.0003 (12)	0.0227 (15)	−0.0016 (14)
O31	0.0655 (15)	0.0577 (13)	0.079 (2)	−0.0153 (11)	0.0428 (14)	−0.0234 (13)
O32	0.0632 (14)	0.0469 (11)	0.0684 (17)	−0.0123 (10)	0.0369 (13)	−0.0050 (11)
C32	0.0564 (19)	0.0380 (14)	0.063 (2)	−0.0018 (14)	0.0321 (18)	−0.0001 (15)
C33	0.067 (2)	0.0474 (16)	0.067 (3)	0.0048 (16)	0.034 (2)	0.0065 (17)
C34	0.0558 (19)	0.0416 (18)	0.058 (2)	0.0052 (15)	0.0280 (18)	−0.0037 (15)
O33	0.115 (3)	0.064 (2)	0.119 (3)	0.045 (2)	0.081 (3)	0.028 (2)
O34	0.081 (2)	0.0502 (19)	0.089 (3)	0.0215 (17)	0.061 (2)	0.0185 (17)
C42	0.0564 (19)	0.0380 (14)	0.063 (2)	−0.0018 (14)	0.0321 (18)	−0.0001 (15)
C43	0.067 (2)	0.0474 (16)	0.067 (3)	0.0048 (16)	0.034 (2)	0.0065 (17)
C44	0.0558 (19)	0.0416 (18)	0.058 (2)	0.0052 (15)	0.0280 (18)	−0.0037 (15)
O43	0.115 (3)	0.064 (2)	0.119 (3)	0.045 (2)	0.081 (3)	0.028 (2)
O44	0.081 (2)	0.0502 (19)	0.089 (3)	0.0215 (17)	0.061 (2)	0.0185 (17)

Geometric parameters (Å, º)

N1—C6	1.481 (4)	C24—C25	1.378 (4)
N1—C2	1.487 (4)	C25—C26	1.382 (4)
N1—H11	0.81 (3)	C25—H25	0.9300
N1—H12	0.96 (4)	C26—H26	0.9300
C2—C3	1.508 (4)	O24—C27	1.409 (5)
C2—H2A	0.9700	C27—H27A	0.9600
C2—H2B	0.9700	C27—H27B	0.9600
C3—N4	1.459 (4)	C27—H27C	0.9600
C3—H3A	0.9700	C31—O32	1.239 (3)
C3—H3B	0.9700	C31—O31	1.262 (4)
N4—C21	1.428 (3)	C31—C32	1.488 (4)
N4—C5	1.467 (4)	C32—C33	1.268 (4)
C5—C6	1.499 (4)	C32—H32	0.9300
C5—H5A	0.9700	C33—C34	1.481 (5)
C5—H5B	0.9700	C33—H33	0.9300
C6—H6A	0.9700	C34—O33	1.214 (4)
C6—H6B	0.9700	C34—O34	1.276 (5)
C21—C26	1.387 (4)	O34—H34	0.8200
C21—C22	1.395 (4)	C43—C44	1.479 (12)
C22—C23	1.383 (4)	C43—H43	0.9300
C22—H22	0.9300	C44—O43	1.212 (12)
C23—C24	1.375 (5)	C44—O44	1.274 (12)
C23—H23	0.9300	O44—H44	0.8200
C24—O24	1.370 (3)		

C6—N1—C2	109.4 (2)	C21—C22—H22	119.4
C6—N1—H11	113 (3)	C24—C23—C22	121.3 (3)
C2—N1—H11	108 (2)	C24—C23—H23	119.3
C6—N1—H12	106 (2)	C22—C23—H23	119.3

C2—N1—H12	111 (2)	O24—C24—C23	116.9 (3)
H11—N1—H12	109 (3)	O24—C24—C25	124.9 (3)
N1—C2—C3	110.7 (3)	C23—C24—C25	118.2 (3)
N1—C2—H2A	109.5	C24—C25—C26	120.7 (3)
C3—C2—H2A	109.5	C24—C25—H25	119.7
N1—C2—H2B	109.5	C26—C25—H25	119.7
C3—C2—H2B	109.5	C25—C26—C21	121.9 (3)
H2A—C2—H2B	108.1	C25—C26—H26	119.0
N4—C3—C2	112.1 (3)	C21—C26—H26	119.0
N4—C3—H3A	109.2	C24—O24—C27	117.4 (3)
C2—C3—H3A	109.2	O24—C27—H27A	109.5
N4—C3—H3B	109.2	O24—C27—H27B	109.5
C2—C3—H3B	109.2	H27A—C27—H27B	109.5
H3A—C3—H3B	107.9	O24—C27—H27C	109.5
C21—N4—C3	115.6 (2)	H27A—C27—H27C	109.5
C21—N4—C5	115.3 (2)	H27B—C27—H27C	109.5
C3—N4—C5	111.1 (2)	O32—C31—O31	125.6 (3)
N4—C5—C6	112.0 (3)	O32—C31—C32	118.5 (3)
N4—C5—H5A	109.2	O31—C31—C32	115.9 (2)
C6—C5—H5A	109.2	C33—C32—C31	126.4 (3)
N4—C5—H5B	109.2	C33—C32—H32	116.8
C6—C5—H5B	109.2	C31—C32—H32	116.8
H5A—C5—H5B	107.9	C32—C33—C34	126.2 (4)
N1—C6—C5	110.5 (3)	C32—C33—H33	116.9
N1—C6—H6A	109.6	C34—C33—H33	116.9
C5—C6—H6A	109.6	O33—C34—O34	123.0 (4)
N1—C6—H6B	109.6	O33—C34—C33	122.5 (4)
C5—C6—H6B	109.6	O34—C34—C33	114.5 (3)
H6A—C6—H6B	108.1	C34—O34—H34	109.5
C26—C21—C22	116.7 (3)	C44—C43—H43	116.8
C26—C21—N4	121.0 (3)	O43—C44—O44	121.3 (18)
C22—C21—N4	122.2 (3)	O43—C44—C43	124 (2)
C23—C22—C21	121.1 (3)	O44—C44—C43	114.9 (18)
C23—C22—H22	119.4	C44—O44—H44	109.5

C6—N1—C2—C3	−57.2 (3)	C22—C23—C24—O24	−179.4 (3)
N1—C2—C3—N4	55.8 (3)	C22—C23—C24—C25	0.8 (5)
C2—C3—N4—C21	172.3 (2)	O24—C24—C25—C26	179.4 (3)
C2—C3—N4—C5	−53.8 (3)	C23—C24—C25—C26	−0.9 (5)
C21—N4—C5—C6	−171.4 (3)	C24—C25—C26—C21	0.0 (5)
C3—N4—C5—C6	54.7 (3)	C22—C21—C26—C25	0.9 (5)
C2—N1—C6—C5	57.9 (3)	N4—C21—C26—C25	178.6 (3)
N4—C5—C6—N1	−57.2 (4)	C23—C24—O24—C27	178.8 (3)
C3—N4—C21—C26	162.4 (3)	C25—C24—O24—C27	−1.4 (5)
C5—N4—C21—C26	30.5 (4)	O32—C31—C32—C33	34.7 (7)
C3—N4—C21—C22	−20.1 (4)	O31—C31—C32—C33	−148.0 (6)
C5—N4—C21—C22	−151.9 (3)	C31—C32—C33—C34	175.5 (5)
C26—C21—C22—C23	−0.9 (4)	C32—C33—C34—O33	−164.1 (8)

N4—C21—C22—C23	−178.6 (3)	C32—C33—C34—O34	14.9 (10)
C21—C22—C23—C24	0.1 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O31	0.81 (4)	2.18 (3)	2.940 (4)	155 (3)
N1—H12···O32^{i}	0.96 (4)	1.77 (4)	2.714 (4)	169 (3)
O34—H34···O31^{ii}	0.82	1.71	2.522 (5)	170
O44—H44···O31^{ii}	0.82	1.62	2.44 (2)	175
C3—H3*A*···*Cg*2^{iii}	0.97	2.76	3.650 (3)	153

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

4-(4-Methoxyphenyl)piperazin-1-ium hydrogenmaleate (X)

Crystal data

$C_{11}H_{17}N_2O^+·C_4H_3O_4^-$
M_r = 308.33
Monoclinic, $P2_1/c$
a = 9.063 (1) Å
b = 6.4956 (9) Å
c = 26.093 (3) Å
β = 93.18 (1)°
V = 1533.7 (3) Å^3
Z = 4
$F(000)$ = 656
D_x = 1.335 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3315 reflections
θ = 2.7–27.8°
μ = 0.10 mm^{-1}
T = 296 K
Block, colourless
0.48 × 0.44 × 0.32 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.871, T_{max} = 0.968
6112 measured reflections
3311 independent reflections
2459 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 27.6°, θ_{min} = 2.7°
h = −11→11
k = −6→8
l = −26→33

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.111
S = 1.05
3311 reflections
210 parameters
0 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.3046P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0192 (18)

Special details

Experimental. Compound (X). IR (KBr , cm^{-1}) 3073 (NH_2), 2836 (OCH_3), 1565 (COO). NMR ($CDCl_3$) δ(^{1}H)) 3.34 (m, 4H, piperazine), 3.41 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.29 (s, 2H, maleate), 6.90 (m, 4H, methoxyphenyl).

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.54059 (15)	0.1806 (2)	0.56144 (5)	0.0431 (3)
H11	0.6147 (19)	0.166 (3)	0.5393 (6)	0.052*
H12	0.452 (2)	0.174 (3)	0.5426 (7)	0.052*
C2	0.5537 (2)	0.3928 (3)	0.58165 (6)	0.0531 (4)
H2A	0.5428	0.4903	0.5535	0.064*
H2B	0.6506	0.4121	0.5986	0.064*
C3	0.43600 (18)	0.4321 (2)	0.61930 (6)	0.0468 (4)
H3A	0.4472	0.5706	0.6329	0.056*
H3B	0.3392	0.4222	0.6016	0.056*
N4	0.44597 (13)	0.28484 (17)	0.66144 (4)	0.0362 (3)
C5	0.43395 (19)	0.0748 (2)	0.64123 (6)	0.0481 (4)
H5A	0.3370	0.0559	0.6243	0.058*
H5B	0.4438	−0.0222	0.6695	0.058*
C6	0.55084 (18)	0.0302 (2)	0.60367 (6)	0.0468 (4)
H6A	0.6480	0.0377	0.6211	0.056*
H6B	0.5373	−0.1077	0.5900	0.056*
C21	0.35362 (15)	0.3268 (2)	0.70263 (5)	0.0354 (3)
C22	0.26577 (18)	0.5006 (2)	0.70426 (6)	0.0481 (4)
H22	0.2632	0.5920	0.6768	0.058*
C23	0.18120 (18)	0.5421 (3)	0.74593 (6)	0.0530 (4)
H23	0.1247	0.6616	0.7463	0.064*
C24	0.18071 (17)	0.4076 (3)	0.78649 (5)	0.0489 (4)
C25	0.2673 (2)	0.2332 (3)	0.78540 (6)	0.0537 (4)
H25	0.2679	0.1410	0.8127	0.064*
C26	0.35276 (18)	0.1936 (3)	0.74451 (6)	0.0464 (4)
H326	0.4110	0.0757	0.7448	0.056*
O24	0.10103 (14)	0.4323 (2)	0.82944 (4)	0.0706 (4)
C27	0.0207 (2)	0.6185 (4)	0.83401 (7)	0.0844 (7)
H27A	−0.0231	0.6219	0.8667	0.127*
H27B	−0.0556	0.6260	0.8070	0.127*
H27C	0.0864	0.7334	0.8314	0.127*
C31	0.81864 (16)	0.2456 (2)	0.48041 (7)	0.0439 (4)
C32	0.93279 (17)	0.2644 (2)	0.44164 (6)	0.0460 (4)
H32	0.8951	0.2815	0.4080	0.055*
C33	1.07926 (16)	0.2605 (2)	0.44719 (6)	0.0429 (4)
H33	1.1274	0.2743	0.4168	0.052*
C34	1.17846 (15)	0.2380 (2)	0.49393 (6)	0.0370 (3)

O31	0.68826 (12)	0.23449 (19)	0.46522 (5)	0.0627 (4)
O32	0.85878 (12)	0.23939 (18)	0.52832 (4)	0.0520 (3)
O33	1.12495 (12)	0.23595 (18)	0.53839 (4)	0.0488 (3)
H33A	0.996 (2)	0.240 (3)	0.5354 (8)	0.073*
O34	1.31216 (11)	0.22095 (17)	0.48789 (4)	0.0495 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0357 (6)	0.0568 (8)	0.0375 (7)	0.0007 (6)	0.0084 (5)	−0.0023 (6)
C2	0.0645 (10)	0.0474 (9)	0.0493 (9)	−0.0055 (8)	0.0214 (8)	0.0037 (7)
C3	0.0590 (10)	0.0388 (8)	0.0440 (8)	0.0018 (7)	0.0146 (7)	0.0034 (7)
N4	0.0396 (6)	0.0349 (6)	0.0346 (6)	0.0002 (5)	0.0054 (5)	0.0009 (5)
C5	0.0591 (10)	0.0385 (8)	0.0484 (9)	−0.0012 (7)	0.0186 (7)	0.0000 (7)
C6	0.0507 (9)	0.0450 (9)	0.0454 (8)	0.0080 (7)	0.0087 (7)	−0.0013 (7)
C21	0.0340 (7)	0.0391 (7)	0.0329 (7)	−0.0023 (6)	0.0007 (5)	−0.0016 (6)
C22	0.0550 (9)	0.0482 (9)	0.0419 (8)	0.0101 (7)	0.0106 (7)	0.0080 (7)
C23	0.0539 (10)	0.0584 (10)	0.0472 (9)	0.0176 (8)	0.0085 (7)	0.0009 (8)
C24	0.0435 (8)	0.0715 (11)	0.0316 (7)	0.0060 (8)	0.0023 (6)	−0.0037 (7)
C25	0.0645 (10)	0.0662 (11)	0.0305 (7)	0.0109 (9)	0.0042 (7)	0.0111 (7)
C26	0.0525 (9)	0.0508 (9)	0.0358 (8)	0.0120 (7)	0.0001 (6)	0.0044 (6)
O24	0.0722 (8)	0.1024 (11)	0.0386 (6)	0.0251 (7)	0.0175 (6)	0.0033 (6)
C27	0.0759 (13)	0.126 (2)	0.0528 (11)	0.0418 (14)	0.0177 (10)	−0.0042 (12)
C31	0.0357 (8)	0.0337 (8)	0.0631 (10)	0.0035 (6)	0.0104 (7)	0.0045 (7)
C32	0.0425 (8)	0.0529 (9)	0.0427 (8)	0.0026 (7)	0.0035 (6)	0.0069 (7)
C33	0.0411 (8)	0.0493 (9)	0.0395 (8)	0.0003 (7)	0.0118 (6)	0.0033 (7)
C34	0.0352 (7)	0.0300 (7)	0.0463 (8)	−0.0020 (6)	0.0071 (6)	−0.0005 (6)
O31	0.0334 (6)	0.0690 (8)	0.0858 (9)	0.0036 (5)	0.0040 (6)	0.0110 (7)
O32	0.0418 (6)	0.0641 (8)	0.0517 (7)	0.0009 (5)	0.0172 (5)	0.0003 (5)
O33	0.0427 (6)	0.0647 (8)	0.0393 (6)	0.0007 (5)	0.0056 (4)	−0.0020 (5)
O34	0.0337 (5)	0.0572 (7)	0.0580 (7)	−0.0010 (5)	0.0069 (5)	0.0012 (5)

Geometric parameters (Å, º)

N1—C6	1.472 (2)	C23—H23	0.9300
N1—C2	1.478 (2)	C24—O24	1.3759 (17)
N1—H11	0.915 (17)	C24—C25	1.379 (2)
N1—H12	0.917 (18)	C25—C26	1.377 (2)
C2—C3	1.511 (2)	C25—H25	0.9300
C2—H2A	0.9700	C26—H326	0.9300
C2—H2B	0.9700	O24—C27	1.420 (3)
C3—N4	1.4567 (18)	C27—H27A	0.9600
C3—H3A	0.9700	C27—H27B	0.9600
C3—H3B	0.9700	C27—H27C	0.9600
N4—C21	1.4248 (17)	C31—O31	1.2274 (19)
N4—C5	1.4645 (19)	C31—O32	1.283 (2)
C5—C6	1.511 (2)	C31—C32	1.492 (2)
C5—H5A	0.9700	C32—C33	1.328 (2)

C5—H5B	0.9700	C32—H32	0.9300
C6—H6A	0.9700	C33—C34	1.482 (2)
C6—H6B	0.9700	C33—H33	0.9300
C21—C22	1.383 (2)	C34—O34	1.2355 (17)
C21—C26	1.394 (2)	C34—O33	1.2820 (17)
C22—C23	1.391 (2)	O32—H33A	1.25 (2)
C22—H22	0.9300	O33—H33A	1.17 (2)
C23—C24	1.373 (2)		

C6—N1—C2	110.57 (12)	C21—C22—C23	121.70 (14)
C6—N1—H11	112.8 (11)	C21—C22—H22	119.2
C2—N1—H11	105.8 (11)	C23—C22—H22	119.2
C6—N1—H12	112.6 (11)	C24—C23—C22	120.31 (15)
C2—N1—H12	106.8 (11)	C24—C23—H23	119.8
H11—N1—H12	107.8 (15)	C22—C23—H23	119.8
N1—C2—C3	110.13 (13)	C23—C24—O24	125.33 (15)
N1—C2—H2A	109.6	C23—C24—C25	118.74 (14)
C3—C2—H2A	109.6	O24—C24—C25	115.93 (14)
N1—C2—H2B	109.6	C26—C25—C24	120.98 (15)
C3—C2—H2B	109.6	C26—C25—H25	119.5
H2A—C2—H2B	108.1	C24—C25—H25	119.5
N4—C3—C2	111.29 (13)	C25—C26—C21	121.25 (15)
N4—C3—H3A	109.4	C25—C26—H326	119.4
C2—C3—H3A	109.4	C21—C26—H326	119.4
N4—C3—H3B	109.4	C24—O24—C27	117.53 (15)
C2—C3—H3B	109.4	O24—C27—H27A	109.5
H3A—C3—H3B	108.0	O24—C27—H27B	109.5
C21—N4—C3	115.42 (11)	H27A—C27—H27B	109.5
C21—N4—C5	114.50 (11)	O24—C27—H27C	109.5
C3—N4—C5	109.87 (12)	H27A—C27—H27C	109.5
N4—C5—C6	111.79 (12)	H27B—C27—H27C	109.5
N4—C5—H5A	109.3	O31—C31—O32	121.90 (14)
C6—C5—H5A	109.3	O31—C31—C32	118.52 (15)
N4—C5—H5B	109.3	O32—C31—C32	119.57 (14)
C6—C5—H5B	109.3	C33—C32—C31	130.65 (15)
H5A—C5—H5B	107.9	C33—C32—H32	114.7
N1—C6—C5	109.95 (13)	C31—C32—H32	114.7
N1—C6—H6A	109.7	C32—C33—C34	130.48 (13)
C5—C6—H6A	109.7	C32—C33—H33	114.8
N1—C6—H6B	109.7	C34—C33—H33	114.8
C5—C6—H6B	109.7	O34—C34—O33	122.51 (14)
H6A—C6—H6B	108.2	O34—C34—C33	117.29 (13)
C22—C21—C26	117.01 (13)	O33—C34—C33	120.20 (12)
C22—C21—N4	122.86 (13)	C31—O32—H33A	111.7 (9)
C26—C21—N4	120.09 (13)	C34—O33—H33A	111.5 (10)

C6—N1—C2—C3	−57.07 (18)	C22—C23—C24—O24	−179.65 (16)
N1—C2—C3—N4	57.68 (18)	C22—C23—C24—C25	1.0 (3)

C2—C3—N4—C21	171.43 (13)	C23—C24—C25—C26	−0.1 (3)
C2—C3—N4—C5	−57.26 (17)	O24—C24—C25—C26	−179.42 (16)
C21—N4—C5—C6	−171.06 (12)	C24—C25—C26—C21	−0.7 (3)
C3—N4—C5—C6	57.15 (17)	C22—C21—C26—C25	0.4 (2)
C2—N1—C6—C5	56.57 (17)	N4—C21—C26—C25	178.39 (14)
N4—C5—C6—N1	−57.02 (18)	C23—C24—O24—C27	−4.6 (3)
C3—N4—C21—C22	−3.3 (2)	C25—C24—O24—C27	174.67 (18)
C5—N4—C21—C22	−132.32 (16)	O31—C31—C32—C33	−173.24 (17)
C3—N4—C21—C26	178.91 (14)	O32—C31—C32—C33	6.0 (2)
C5—N4—C21—C26	49.85 (18)	C31—C32—C33—C34	−0.5 (3)
C26—C21—C22—C23	0.6 (2)	C32—C33—C34—O34	173.69 (16)
N4—C21—C22—C23	−177.33 (14)	C32—C33—C34—O33	−6.1 (2)
C21—C22—C23—C24	−1.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O33—H33*A*···O32	1.167 (18)	1.247 (18)	2.4121 (16)	175 (2)
N1—H11···O31	0.915 (17)	2.126 (16)	2.9309 (19)	146.2 (15)
N1—H11···O32	0.915 (17)	2.296 (17)	3.0798 (18)	143.5 (14)
N1—H12···O34^{i}	0.919 (18)	1.881 (18)	2.7563 (17)	158.5 (17)
C2—H2*A*···O34^{ii}	0.97	2.56	3.363 (2)	140

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

4-(4-Methoxyphenyl)piperazin-1-ium trichloroacetate (XI)

Crystal data

$C_{11}H_{17}N_2O^+·C_2Cl_3O_2^-$
M_r = 355.64
Orthorhombic, $Pca2_1$
a = 10.6117 (11) Å
b = 13.808 (1) Å
c = 10.9137 (8) Å
V = 1599.1 (2) Å^3
Z = 4
F(000) = 736
D_x = 1.477 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2428 reflections
θ = 3.0–27.7°
μ = 0.58 mm^{-1}
T = 296 K
Block, colourless
0.48 × 0.48 × 0.20 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.476, T_{max} = 0.892
6173 measured reflections
2428 independent reflections
2278 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.7°, θ_{min} = 3.0°
h = −5→13
k = −16→17
l = −14→5

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.086$
$S = 1.08$
2428 reflections
198 parameters
1 restraint
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.3843P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.023 (2)
Absolute structure: Classical Flack method preferred over Parsons because s.u. lower
Absolute structure parameter: 0.11 (7)

Special details

Experimental. Compound (XI). IR (KBr , cm^{-1}) 3073 (NH_2), 2829 (OCH_3), 1561 (COO). NMR ($CDCl_3$) δ(^{1}H)) 3.07 (m, 4H, piperazine), 3.19 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.89 (m, 4H, methoxyphenyl).
Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.1394 (2)	0.44188 (17)	0.2473 (3)	0.0301 (5)
H11	0.168 (3)	0.495 (3)	0.204 (3)	0.036*
H12	0.061 (3)	0.426 (3)	0.206 (4)	0.036*
C2	0.1158 (3)	0.4667 (2)	0.3775 (3)	0.0343 (7)
H2A	0.0542	0.5185	0.3822	0.041*
H2B	0.1933	0.4895	0.4148	0.041*
C3	0.0680 (3)	0.37961 (19)	0.4468 (3)	0.0320 (6)
H3A	0.0546	0.3967	0.5320	0.038*
H3B	−0.0121	0.3591	0.4126	0.038*
N4	0.1586 (2)	0.30039 (15)	0.4389 (2)	0.0261 (5)
C5	0.1815 (3)	0.2750 (2)	0.3106 (3)	0.0311 (6)
H5A	0.1037	0.2523	0.2738	0.037*
H5B	0.2424	0.2227	0.3067	0.037*
C6	0.2304 (2)	0.3607 (2)	0.2392 (3)	0.0324 (6)
H6A	0.3112	0.3808	0.2721	0.039*
H6B	0.2423	0.3426	0.1541	0.039*
C21	0.1350 (2)	0.22071 (19)	0.5194 (3)	0.0269 (6)
C22	0.0345 (3)	0.2170 (2)	0.5993 (3)	0.0347 (6)
H22	−0.0265	0.2653	0.5959	0.042*
C23	0.0216 (3)	0.1433 (2)	0.6846 (3)	0.0396 (7)
H23	−0.0468	0.1430	0.7379	0.048*
C24	0.1103 (3)	0.0700 (2)	0.6906 (3)	0.0398 (7)
C25	0.2088 (3)	0.0707 (2)	0.6074 (4)	0.0388 (7)
H25	0.2671	0.0205	0.6083	0.047*

C26	0.2220 (3)	0.14432 (19)	0.5235 (3)	0.0324 (6)
H26	0.2892	0.1434	0.4689	0.039*
O24	0.1108 (3)	−0.00368 (18)	0.7747 (3)	0.0587 (8)
C27	0.0095 (6)	−0.0086 (4)	0.8579 (5)	0.0733 (13)
H27A	0.0234	−0.0608	0.9145	0.110*
H27B	−0.0675	−0.0197	0.8138	0.110*
H27C	0.0035	0.0513	0.9022	0.110*
C31	0.3163 (2)	0.61757 (18)	0.1132 (3)	0.0266 (5)
O31	0.20314 (18)	0.60081 (16)	0.1045 (3)	0.0444 (6)
O32	0.39463 (19)	0.57402 (18)	0.1749 (3)	0.0464 (6)
C32	0.3653 (3)	0.7076 (2)	0.0383 (3)	0.0304 (6)
Cl1	0.52532 (7)	0.69160 (6)	−0.00662 (9)	0.0426 (2)
Cl2	0.35730 (10)	0.80958 (5)	0.13523 (10)	0.0505 (3)
Cl3	0.27618 (8)	0.72790 (7)	−0.09480 (9)	0.0540 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0286 (11)	0.0228 (11)	0.0389 (15)	−0.0020 (8)	−0.0003 (11)	0.0038 (11)
C2	0.0433 (14)	0.0199 (13)	0.0398 (18)	0.0022 (11)	−0.0004 (14)	−0.0032 (12)
C3	0.0354 (13)	0.0242 (13)	0.0364 (16)	0.0059 (11)	0.0060 (12)	−0.0015 (12)
N4	0.0304 (11)	0.0178 (10)	0.0300 (13)	0.0008 (8)	0.0049 (9)	−0.0026 (9)
C5	0.0370 (14)	0.0234 (13)	0.0331 (15)	0.0034 (11)	0.0027 (13)	−0.0025 (12)
C6	0.0308 (14)	0.0307 (14)	0.0356 (16)	0.0041 (10)	0.0064 (13)	0.0002 (13)
C21	0.0295 (11)	0.0196 (11)	0.0316 (16)	−0.0051 (9)	0.0001 (11)	−0.0022 (11)
C22	0.0335 (13)	0.0295 (13)	0.0411 (18)	−0.0016 (11)	0.0036 (13)	−0.0032 (13)
C23	0.0455 (15)	0.0342 (15)	0.0392 (19)	−0.0102 (13)	0.0117 (14)	−0.0011 (14)
C24	0.0628 (19)	0.0206 (12)	0.0361 (18)	−0.0128 (13)	−0.0005 (15)	−0.0005 (13)
C25	0.0487 (15)	0.0198 (12)	0.048 (2)	0.0005 (11)	−0.0002 (16)	0.0004 (13)
C26	0.0336 (13)	0.0229 (13)	0.0408 (18)	−0.0009 (10)	0.0034 (12)	−0.0015 (13)
O24	0.0943 (19)	0.0332 (12)	0.0485 (17)	−0.0085 (13)	0.0079 (15)	0.0129 (13)
C27	0.095 (3)	0.064 (3)	0.061 (3)	−0.028 (2)	0.008 (3)	0.023 (2)
C31	0.0303 (12)	0.0190 (11)	0.0305 (15)	−0.0017 (9)	0.0033 (12)	0.0005 (11)
O31	0.0301 (9)	0.0391 (11)	0.0640 (17)	−0.0070 (8)	−0.0039 (11)	0.0214 (12)
O32	0.0328 (11)	0.0421 (12)	0.0643 (18)	−0.0046 (9)	−0.0072 (11)	0.0244 (12)
C32	0.0320 (12)	0.0260 (13)	0.0332 (15)	−0.0049 (10)	−0.0009 (12)	0.0029 (12)
Cl1	0.0343 (3)	0.0457 (4)	0.0478 (5)	−0.0125 (3)	0.0085 (3)	−0.0007 (4)
Cl2	0.0714 (6)	0.0236 (3)	0.0565 (6)	−0.0017 (3)	0.0089 (5)	−0.0065 (4)
Cl3	0.0514 (5)	0.0652 (6)	0.0455 (5)	−0.0134 (4)	−0.0124 (4)	0.0233 (5)

Geometric parameters (Å, º)

N1—C6	1.482 (3)	C22—C23	1.386 (5)
N1—C2	1.484 (4)	C22—H22	0.9300
N1—H11	0.92 (4)	C23—C24	1.383 (5)
N1—H12	0.97 (3)	C23—H23	0.9300
C2—C3	1.509 (4)	C24—O24	1.370 (4)
C2—H2A	0.9700	C24—C25	1.385 (5)

C2—H2B	0.9700	C25—C26	1.375 (4)
C3—N4	1.459 (3)	C25—H25	0.9300
C3—H3A	0.9700	C26—H26	0.9300
C3—H3B	0.9700	O24—C27	1.410 (6)
N4—C21	1.430 (4)	C27—H27A	0.9600
N4—C5	1.464 (4)	C27—H27B	0.9600
C5—C6	1.509 (4)	C27—H27C	0.9600
C5—H5A	0.9700	C31—O31	1.227 (3)
C5—H5B	0.9700	C31—O32	1.227 (4)
C6—H6A	0.9700	C31—C32	1.576 (4)
C6—H6B	0.9700	C32—Cl3	1.756 (3)
C21—C22	1.379 (4)	C32—Cl2	1.763 (3)
C21—C26	1.402 (4)	C32—Cl1	1.781 (3)

C6—N1—C2	110.0 (2)	C22—C21—N4	123.5 (3)
C6—N1—H11	111 (2)	C26—C21—N4	118.9 (2)
C2—N1—H11	111 (2)	C21—C22—C23	121.9 (3)
C6—N1—H12	111 (2)	C21—C22—H22	119.0
C2—N1—H12	111 (2)	C23—C22—H22	119.0
H11—N1—H12	103 (3)	C24—C23—C22	120.1 (3)
N1—C2—C3	110.6 (2)	C24—C23—H23	119.9
N1—C2—H2A	109.5	C22—C23—H23	119.9
C3—C2—H2A	109.5	O24—C24—C23	125.3 (3)
N1—C2—H2B	109.5	O24—C24—C25	116.2 (3)
C3—C2—H2B	109.5	C23—C24—C25	118.5 (3)
H2A—C2—H2B	108.1	C26—C25—C24	121.3 (3)
N4—C3—C2	110.3 (2)	C26—C25—H25	119.4
N4—C3—H3A	109.6	C24—C25—H25	119.4
C2—C3—H3A	109.6	C25—C26—C21	120.7 (3)
N4—C3—H3B	109.6	C25—C26—H26	119.7
C2—C3—H3B	109.6	C21—C26—H26	119.7
H3A—C3—H3B	108.1	C24—O24—C27	117.7 (3)
C21—N4—C3	115.2 (2)	O24—C27—H27A	109.5
C21—N4—C5	115.6 (2)	O24—C27—H27B	109.5
C3—N4—C5	110.2 (2)	H27A—C27—H27B	109.5
N4—C5—C6	111.3 (2)	O24—C27—H27C	109.5
N4—C5—H5A	109.4	H27A—C27—H27C	109.5
C6—C5—H5A	109.4	H27B—C27—H27C	109.5
N4—C5—H5B	109.4	O31—C31—O32	127.8 (3)
C6—C5—H5B	109.4	O31—C31—C32	115.6 (2)
H5A—C5—H5B	108.0	O32—C31—C32	116.6 (2)
N1—C6—C5	109.8 (2)	C31—C32—Cl3	112.15 (19)
N1—C6—H6A	109.7	C31—C32—Cl2	107.6 (2)
C5—C6—H6A	109.7	Cl3—C32—Cl2	110.05 (16)
N1—C6—H6B	109.7	C31—C32—Cl1	111.06 (19)
C5—C6—H6B	109.7	Cl3—C32—Cl1	107.82 (18)
H6A—C6—H6B	108.2	Cl2—C32—Cl1	108.08 (15)
C22—C21—C26	117.4 (3)		

C6—N1—C2—C3	−57.4 (3)	C22—C23—C24—O24	176.6 (3)
N1—C2—C3—N4	58.2 (3)	C22—C23—C24—C25	−2.1 (5)
C2—C3—N4—C21	168.8 (3)	O24—C24—C25—C26	−176.2 (3)
C2—C3—N4—C5	−58.2 (3)	C23—C24—C25—C26	2.6 (5)
C21—N4—C5—C6	−168.7 (2)	C24—C25—C26—C21	−0.4 (5)
C3—N4—C5—C6	58.5 (3)	C22—C21—C26—C25	−2.3 (4)
C2—N1—C6—C5	56.6 (3)	N4—C21—C26—C25	174.1 (3)
N4—C5—C6—N1	−57.6 (3)	C23—C24—O24—C27	3.5 (5)
C3—N4—C21—C22	0.2 (4)	C25—C24—O24—C27	−177.7 (4)
C5—N4—C21—C22	−130.3 (3)	O31—C31—C32—Cl3	−29.9 (3)
C3—N4—C21—C26	−175.9 (3)	O32—C31—C32—Cl3	151.5 (3)
C5—N4—C21—C26	53.6 (3)	O31—C31—C32—Cl2	91.3 (3)
C26—C21—C22—C23	2.8 (5)	O32—C31—C32—Cl2	−87.3 (3)
N4—C21—C22—C23	−173.3 (3)	O31—C31—C32—Cl1	−150.6 (2)
C21—C22—C23—C24	−0.7 (5)	O32—C31—C32—Cl1	30.8 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O31	0.92 (4)	1.86 (4)	2.775 (4)	172 (3)
N1—H12···O32^{i}	0.97 (3)	1.80 (3)	2.724 (3)	158 (3)

Symmetry code: (i) $x-1/2, -y+1, z$.

Bis(4-(4-methoxyphenyl)piperazin-1-ium) chloranilate(2-) dihydrate (XII)

Crystal data

$C_{11}H_{17}N_2O^+\cdot 0.5C_6Cl_2O_4^{2-}\cdot H_2O$
$M_r = 314.76$
Monoclinic, $P2_1/n$
$a = 9.1597$ (5) Å
$b = 15.1434$ (8) Å
$c = 10.8742$ (6) Å
$\beta = 102.067$ (5)°
$V = 1475.02$ (14) Å^3
$Z = 4$
$F(000) = 664$
$D_x = 1.417$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3253 reflections
$\theta = 2.6$–$28.0°$
$\mu = 0.28$ mm^{-1}
$T = 296$ K
Block, colourless
0.44 × 0.24 × 0.20 mm

Data collection

Oxford Diffraction Xcalibur with Sapphire CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
$T_{min} = 0.892$, $T_{max} = 0.947$
9650 measured reflections
9650 independent reflections
7444 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.6°$, $\theta_{min} = 2.6°$
$h = -11\rightarrow11$
$k = -19\rightarrow19$
$l = -13\rightarrow14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.105$
$S = 1.02$
9650 reflections

204 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.263P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Hydrogen site location: mixed	$(\Delta/\sigma)_{max} < 0.001$
H atoms treated by a mixture of independent and constrained refinement	$\Delta\rho_{max} = 0.23$ e Å^{-3}
	$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Experimental. Compound (XII). IR (KBr , cm^{-1}) 3311 (OH), 3073 (NH_2), 2825 (OCH_3), 1561 (COO), 793 and 741 (CCl) . NMR ($CDCl_3$) $\delta(^1H)$) 3.11 (m, 4H, piperazine), 3.40 (m, 4H, piperazine), 3.77 (s, 3H, OCH_3), 6.88 (m, 4H, methoxyphenyl).

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.4381 (2)	0.32824 (14)	0.35576 (19)	0.0420 (5)
H11	0.437 (2)	0.3477 (15)	0.278 (3)	0.050*
H12	0.420 (3)	0.3725 (16)	0.405 (2)	0.050*
C2	0.5890 (2)	0.29024 (17)	0.4015 (2)	0.0472 (6)
H2A	0.6629	0.3370	0.4125	0.057*
H2B	0.6115	0.2490	0.3397	0.057*
C3	0.5965 (2)	0.24346 (16)	0.5241 (2)	0.0427 (6)
H3A	0.6939	0.2164	0.5509	0.051*
H3B	0.5827	0.2856	0.5878	0.051*
N4	0.48097 (19)	0.17569 (13)	0.51047 (18)	0.0398 (5)
C5	0.3334 (2)	0.21513 (17)	0.4745 (2)	0.0455 (6)
H5A	0.3186	0.2572	0.5381	0.055*
H5B	0.2576	0.1696	0.4681	0.055*
C6	0.3188 (2)	0.26139 (16)	0.3494 (2)	0.0454 (6)
H6A	0.3256	0.2184	0.2847	0.054*
H6B	0.2221	0.2899	0.3271	0.054*
C21	0.5025 (2)	0.10929 (15)	0.6041 (2)	0.0357 (5)
C22	0.6331 (2)	0.05976 (16)	0.6228 (2)	0.0432 (6)
H22	0.7033	0.0719	0.5744	0.052*
C23	0.6610 (2)	−0.00626 (16)	0.7103 (2)	0.0457 (6)
H23	0.7503	−0.0375	0.7222	0.055*
C24	0.5565 (2)	−0.02672 (15)	0.7812 (2)	0.0418 (6)
C25	0.4243 (2)	0.01896 (16)	0.7614 (2)	0.0452 (6)
H25	0.3516	0.0040	0.8059	0.054*
C26	0.3991 (2)	0.08760 (16)	0.6747 (2)	0.0419 (6)
H26	0.3106	0.1195	0.6641	0.050*
O24	0.59700 (19)	−0.09318 (12)	0.86827 (19)	0.0615 (5)
C27	0.4842 (3)	−0.12833 (17)	0.9257 (3)	0.0577 (7)
H27A	0.5208	−0.1806	0.9720	0.086*
H27B	0.3980	−0.1429	0.8621	0.086*

H27C	0.4573	−0.0853	0.9820	0.086*
C31	0.4846 (2)	0.41334 (14)	0.0515 (2)	0.0301 (5)
O31	0.46952 (17)	0.34242 (10)	0.10569 (14)	0.0429 (4)
C32	0.4674 (2)	0.42353 (14)	−0.0785 (2)	0.0313 (5)
Cl32	0.42518 (7)	0.33070 (4)	−0.17371 (6)	0.04725 (19)
O33	0.54043 (16)	0.48217 (10)	0.25106 (14)	0.0419 (4)
C33	0.5224 (2)	0.49523 (14)	0.13592 (19)	0.0297 (5)
O41	0.3458 (2)	0.45297 (16)	0.5134 (2)	0.0698 (6)
H41	0.383 (4)	0.464 (2)	0.589 (4)	0.105*
H42	0.295 (4)	0.497 (2)	0.492 (3)	0.105*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0531 (12)	0.0465 (13)	0.0271 (11)	0.0008 (11)	0.0101 (9)	0.0103 (10)
C2	0.0458 (13)	0.0526 (15)	0.0447 (15)	−0.0023 (12)	0.0132 (11)	0.0145 (13)
C3	0.0397 (12)	0.0497 (14)	0.0362 (14)	−0.0084 (12)	0.0026 (10)	0.0099 (12)
N4	0.0358 (10)	0.0461 (11)	0.0344 (11)	−0.0073 (9)	0.0003 (8)	0.0123 (9)
C5	0.0372 (12)	0.0559 (16)	0.0411 (14)	−0.0077 (12)	0.0028 (10)	0.0152 (13)
C6	0.0462 (13)	0.0509 (15)	0.0343 (14)	−0.0037 (12)	−0.0026 (10)	0.0082 (12)
C21	0.0368 (12)	0.0404 (13)	0.0280 (12)	−0.0096 (11)	0.0027 (9)	0.0032 (10)
C22	0.0374 (13)	0.0471 (15)	0.0472 (15)	−0.0058 (11)	0.0139 (11)	0.0057 (12)
C23	0.0358 (12)	0.0451 (14)	0.0566 (17)	0.0018 (11)	0.0103 (11)	0.0088 (13)
C24	0.0462 (13)	0.0399 (14)	0.0375 (14)	−0.0005 (12)	0.0043 (10)	0.0093 (11)
C25	0.0429 (13)	0.0540 (16)	0.0413 (15)	−0.0008 (12)	0.0146 (10)	0.0123 (12)
C26	0.0358 (12)	0.0498 (15)	0.0398 (14)	0.0045 (11)	0.0070 (10)	0.0125 (12)
O24	0.0567 (11)	0.0620 (12)	0.0673 (14)	0.0079 (9)	0.0164 (9)	0.0339 (11)
C27	0.0752 (18)	0.0480 (16)	0.0522 (18)	−0.0012 (15)	0.0190 (14)	0.0151 (14)
C31	0.0292 (10)	0.0331 (12)	0.0290 (12)	0.0005 (9)	0.0083 (8)	0.0032 (10)
O31	0.0612 (10)	0.0355 (9)	0.0327 (9)	−0.0024 (8)	0.0115 (7)	0.0066 (7)
C32	0.0368 (11)	0.0315 (11)	0.0256 (11)	−0.0004 (10)	0.0060 (8)	−0.0010 (9)
Cl32	0.0648 (4)	0.0407 (3)	0.0347 (3)	−0.0058 (3)	0.0068 (3)	−0.0065 (3)
O33	0.0582 (9)	0.0456 (10)	0.0215 (8)	−0.0073 (8)	0.0073 (7)	0.0036 (7)
C33	0.0282 (10)	0.0381 (12)	0.0232 (11)	0.0019 (9)	0.0065 (8)	0.0014 (9)
O41	0.0876 (16)	0.0781 (15)	0.0408 (12)	0.0001 (12)	0.0066 (10)	−0.0146 (12)

Geometric parameters (Å, º)

N1—C6	1.481 (3)	C23—C24	1.384 (3)
N1—C2	1.484 (3)	C23—H23	0.9300
N1—H11	0.89 (3)	C24—C25	1.372 (3)
N1—H12	0.89 (2)	C24—O24	1.379 (3)
C2—C3	1.498 (3)	C25—C26	1.390 (3)
C2—H2A	0.9700	C25—H25	0.9300
C2—H2B	0.9700	C26—H26	0.9300
C3—N4	1.459 (3)	O24—C27	1.419 (3)
C3—H3A	0.9700	C27—H27A	0.9600
C3—H3B	0.9700	C27—H27B	0.9600

N4—C21	1.415 (3)	C27—H27C	0.9600
N4—C5	1.455 (3)	C31—O31	1.246 (2)
C5—C6	1.511 (3)	C31—C32	1.398 (3)
C5—H5A	0.9700	C31—C33	1.539 (3)
C5—H5B	0.9700	C32—C33^{i}	1.392 (3)
C6—H6A	0.9700	C32—Cl32	1.741 (2)
C6—H6B	0.9700	O33—C33	1.244 (2)
C21—C26	1.378 (3)	C33—C32^{i}	1.392 (3)
C21—C22	1.390 (3)	O41—H41	0.83 (4)
C22—C23	1.367 (3)	O41—H42	0.82 (3)
C22—H22	0.9300		

C6—N1—C2	112.16 (18)	C26—C21—N4	124.1 (2)
C6—N1—H11	108.7 (15)	C22—C21—N4	118.3 (2)
C2—N1—H11	105.7 (14)	C23—C22—C21	121.7 (2)
C6—N1—H12	108.2 (15)	C23—C22—H22	119.1
C2—N1—H12	111.7 (16)	C21—C22—H22	119.1
H11—N1—H12	110 (2)	C22—C23—C24	120.1 (2)
N1—C2—C3	110.34 (18)	C22—C23—H23	120.0
N1—C2—H2A	109.6	C24—C23—H23	120.0
C3—C2—H2A	109.6	C25—C24—O24	125.3 (2)
N1—C2—H2B	109.6	C25—C24—C23	119.4 (2)
C3—C2—H2B	109.6	O24—C24—C23	115.3 (2)
H2A—C2—H2B	108.1	C24—C25—C26	120.0 (2)
N4—C3—C2	110.20 (19)	C24—C25—H25	120.0
N4—C3—H3A	109.6	C26—C25—H25	120.0
C2—C3—H3A	109.6	C21—C26—C25	121.3 (2)
N4—C3—H3B	109.6	C21—C26—H26	119.4
C2—C3—H3B	109.6	C25—C26—H26	119.4
H3A—C3—H3B	108.1	C24—O24—C27	117.40 (19)
C21—N4—C5	117.85 (18)	O24—C27—H27A	109.5
C21—N4—C3	115.96 (17)	O24—C27—H27B	109.5
C5—N4—C3	110.60 (18)	H27A—C27—H27B	109.5
N4—C5—C6	109.54 (18)	O24—C27—H27C	109.5
N4—C5—H5A	109.8	H27A—C27—H27C	109.5
C6—C5—H5A	109.8	H27B—C27—H27C	109.5
N4—C5—H5B	109.8	O31—C31—C32	125.0 (2)
C6—C5—H5B	109.8	O31—C31—C33	116.47 (18)
H5A—C5—H5B	108.2	C32—C31—C33	118.55 (18)
N1—C6—C5	110.47 (18)	C31—C32—C33^{i}	123.2 (2)
N1—C6—H6A	109.6	C31—C32—Cl32	118.45 (17)
C5—C6—H6A	109.6	C33^{i}—C32—Cl32	118.31 (16)
N1—C6—H6B	109.6	O33—C33—C32^{i}	125.8 (2)
C5—C6—H6B	109.6	O33—C33—C31	115.99 (19)
H6A—C6—H6B	108.1	C32^{i}—C33—C31	118.20 (17)
C26—C21—C22	117.5 (2)	H41—O41—H42	102 (3)

C6—N1—C2—C3	−53.5 (3)	C22—C23—C24—O24	−178.8 (2)

N1—C2—C3—N4	56.5 (3)	O24—C24—C25—C26	176.9 (2)
C2—C3—N4—C21	161.1 (2)	C23—C24—C25—C26	−2.8 (4)
C2—C3—N4—C5	−61.3 (3)	C22—C21—C26—C25	0.1 (3)
C21—N4—C5—C6	−162.3 (2)	N4—C21—C26—C25	177.1 (2)
C3—N4—C5—C6	61.0 (3)	C24—C25—C26—C21	2.3 (4)
C2—N1—C6—C5	53.7 (3)	C25—C24—O24—C27	12.2 (4)
N4—C5—C6—N1	−56.7 (3)	C23—C24—O24—C27	−168.1 (2)
C5—N4—C21—C26	−8.7 (3)	O31—C31—C32—C33^{i}	176.5 (2)
C3—N4—C21—C26	125.7 (2)	C33—C31—C32—C33^{i}	−2.4 (3)
C5—N4—C21—C22	168.2 (2)	O31—C31—C32—Cl32	−1.3 (3)
C3—N4—C21—C22	−57.4 (3)	C33—C31—C32—Cl32	179.81 (14)
C26—C21—C22—C23	−2.0 (3)	O31—C31—C33—O33	2.8 (3)
N4—C21—C22—C23	−179.1 (2)	C32—C31—C33—O33	−178.16 (18)
C21—C22—C23—C24	1.5 (4)	O31—C31—C33—C32^{i}	−176.76 (18)
C22—C23—C24—C25	0.9 (4)	C32—C31—C33—C32^{i}	2.2 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O31	0.89 (3)	1.96 (3)	2.802 (3)	157 (2)
N1—H11···O33	0.89 (3)	2.29 (2)	2.838 (3)	119 (2)
N1—H12···O41	0.90 (2)	1.92 (2)	2.798 (3)	168 (3)
O41—H41···O33^{ii}	0.84 (4)	1.92 (4)	2.738 (3)	166 (3)
O41—H42···O24^{iii}	0.82 (3)	2.49 (3)	3.269 (3)	160 (3)

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