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Crystal structure studies of 4-ethylpiperazin-1-ium 3,5-dinitrobenzoate, 4-methylpiperazin-1-ium 3,5-dinitrobenzoate and 4-methylpiperazin-1-ium 4-iodobenzoate

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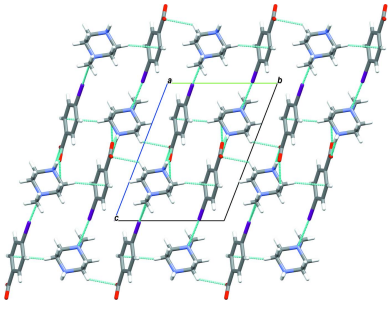
As part of our ongoing investigation on the chemical and biological properties of piperazinium salts, we synthesized three novel compounds: 1-ethylpiperazinium 3,5-dinitrobenzoate (I), 1-methylpiperazinium 3,5-dinitrobenzoate (II) and 1-methylpiperazinium 4-iodobenzoate (III). The crystal structures of these compounds are built up of organic layers formed by the strong connection between the molecules by hydrogen bonds of type N—H···O. These layers are linked through N—H···O hydrogen bonds and C—H···O interactions or C—I···N halogen bonding, leading to the formation of a three-dimensional network.

1. Chemical context

Piperazines and substituted piperazines are important pharmacophores that can be found in many biologically active compounds across a number of different therapeutic areas (Berkheij, 2005) such as antifungal (Upadhayaya *et al.*, 2004), anti-bacterial, anti-malarial and anti-psychotic agents (Choudhary *et al.*, 2006). A valuable insight into recent advances on antimicrobial activity of piperazine derivatives has been reported (Kharb *et al.*, 2012).

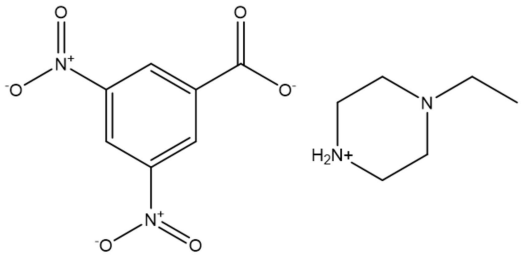
Piperazines are among the most important building blocks in today's drug discovery efforts and are found in biologically active compounds across a number of different therapeutic areas (Brockunier *et al.*, 2004; Bogatcheva *et al.*, 2006). A review of the current pharmacological and toxicological information for piperazine derivatives is given by Elliott (2011).

1-Ethylpiperazine is used in the synthesis of 2-{2-methoxy-5-[(4-methylpiperazin-1-yl)sulfonyl]phenyl}-1*H*-benzo[*d*]-imidazole hydrochloride and 2-{5-[(4-ethylpiperazin-1-yl)-sulfonyl]-2-methoxyphenyl}-1*H*-benzo[*d*]imidazole hydrochloride as benzimidazole analogs of sildenafil, which is marketed for the treatment of erectile dysfunction (Qandil, 2012). It is also employed as an intermediate in veterinary medicine and serves as a precursor in the preparation of dyes. *N*-Ethyl piperazine is used in the synthesis of enrofloxacin, which is an antibiotic used to treat bacterial infections. It is also used in the synthesis of dyes, agrochemicals and other pharmaceutical compounds. The crystal structures of compounds derived from 1-ethylpiperazine, *viz*., chlorobis-

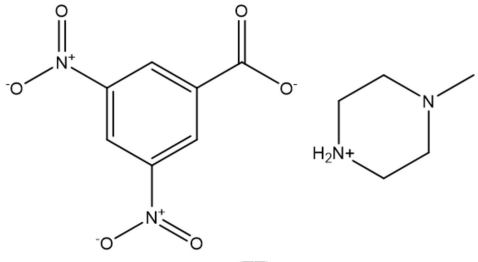


(2-chlorobenzyl)(4-ethylpiperazine-1-dithiocarbamato-κ^2S,S')tin(IV) (Li & Li, 2007), 1-diphenylmethyl-4-ethylpiperazine-1,4-diium dichloride (Qiao *et al.*, 2010), (*S*)-3-chloro-4-(4-ethylpiperazin-1-yl)-5-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy]furan-2(5*H*)-one (Fu *et al.*, 2010), 4-{[5-(4-chlorophenyl)-1-(4-fluorophenyl)-1*H*-pyrazol-3-yl]carbonyl}-*N*-ethylpiperazine-1-carboxamide (Shahani *et al.*, 2011), 2-[4-(2-methoxyphenyl)piperazin-1-yl]-*N*-(pyridin-2-yl)acetamide (Lu & Jiang, 2011), *N*-(4-chlorophenyl)-4-ethylpiperazine-1-carboxamide (Li, 2011) and trichlorido(1-ethylpiperazin-1-ium)cobalt(II) (Dhieb *et al.*, 2014) have been reported.

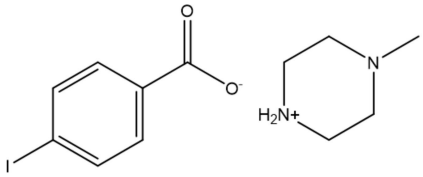
1-Methylpiperazine is used in the preparation of 2-(4-methyl-1-piperazinylmethyl)acrylophenone as an anti-microtubular drug (Mallevais *et al.*, 1984). It is involved in the preparation of 1-(4-methoxyphenyl)-4-methylpiperazine by reaction with 1-chloro-4-methoxy-benzene. It acts as an intermediate in the synthesis of active pharmaceutical ingredients such as ofloxacin, rifampicin, clozapine, sildenafil, trifluoperazine and zopiclone. The crystal structures of 1-methylpiperazine-1,4-diium 4-nitrophthalate(2−) 4-nitrophthalic acid monohydrate (Guo, 2004), (−)-2-methylpiperazin-1-ium perchlorate (Peng, 2010), 1-methylpiperazine-1,4-diium dipicrate (Dutkiewicz *et al.*, 2011), 1-methylpiperazine-1,4-dium bis(hydrogen oxalate) (Essid *et al.*, 2014), 2-methylpiperazine-1,4-diium bis(hydrogen maleate) (Wecharine *et al.*, 2015) and 2-methylpiperazine-1,4-diium bis(hydrogen maleate) (Wecharine & Arto, 2015), have been reported.



(I)



(II)



(III)

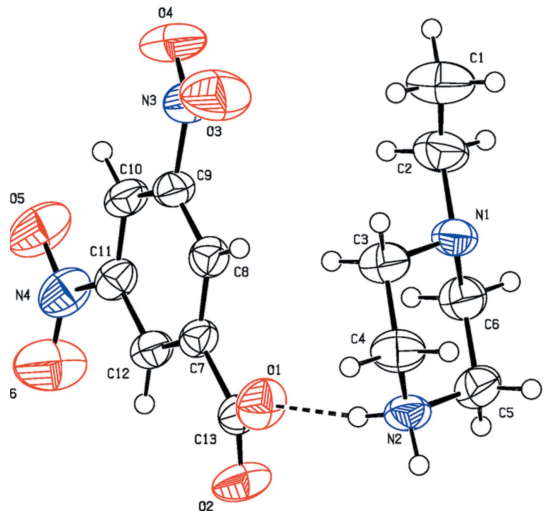


Figure 1
The molecular structure of compound (I), showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

We have recently reported the crystal structures of some salts of 4-methoxyphenylpiperazine (Kiran Kumar *et al.*, 2019) and also 2-methoxyphenylpiperazine (Harish Chinthal *et al.*, 2020). In view of the importance of piperazines in general and the use of 1-ethyl/methylpiperazine in particular, the present paper reports the crystal structure of salts 1-ethylpiperazinium 3,5-dinitrobenzoate (I), 1-methylpiperazinium 3,5-dinitrobenzoate (II) and 1-methylpiperazinium 4-iodobenzoate (III).

2. Structural commentary

The molecular structures of the title salts (I), (II) and (III) are illustrated in Figs. 1, 2 and 3, respectively. The asymmetric unit of compound (I) is composed of one 1-ethylpiperazinium cation and one 3,5-dinitrobenzoate anion while (II) consists of a 1-methylpiperazinium cation and a 3,5-dinitrobenzoate anion. Compound (III) crystallizes with one 1-methylpiperazinium cation and one 4-iodobenzoate anion in the asymmetric unit. In all compounds, the piperazine rings have a

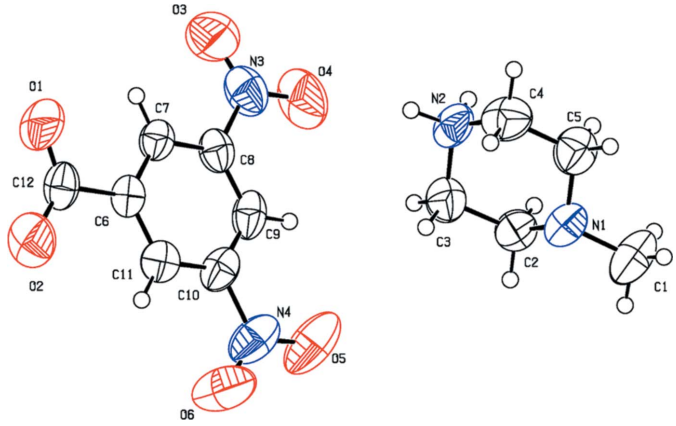


Figure 2
The molecular structure of compound (II), showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

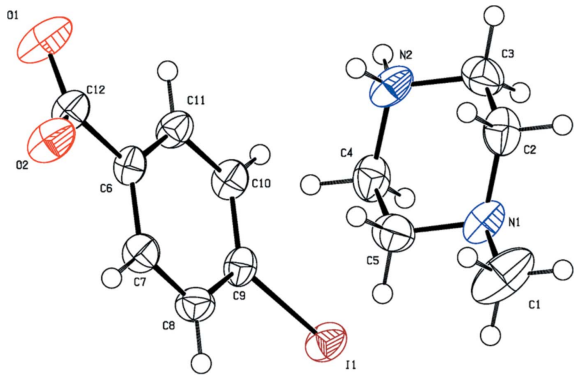


Figure 3
The molecular structure of compound (III), showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

chair conformation with a positively charged protonated N atom with a maximum deviation from their mean plane of 0.239 (2), 0.258 (2) and 0.238 (2) Å at atom N1, for the three title compounds, respectively. The benzene rings are almost planar, with maximum deviations of 0.010 (2), 0.006 (2) and 0.006 (3) Å at atoms C8, C10 and C8 for (I), (II) and (III) respectively. The substituents of the benzene rings in all compounds are approximately in the same plane and do not deviate significantly from planarity.

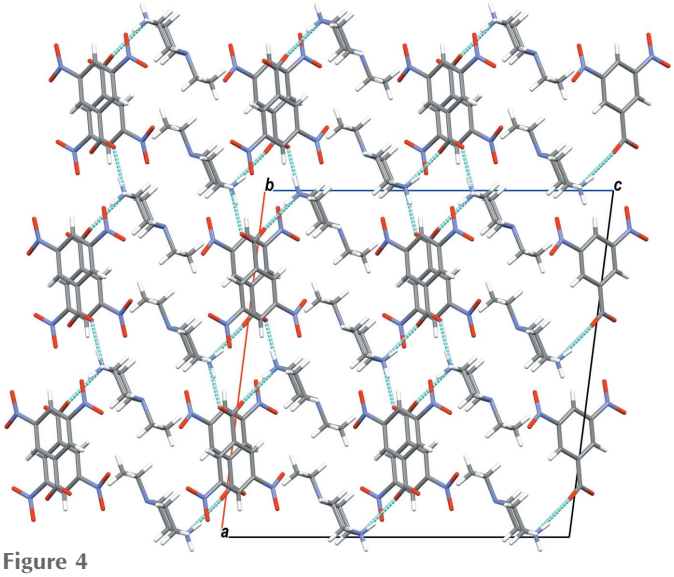


Figure 4
Molecular packing of (I) with hydrogen bonding shown as dashed lines.

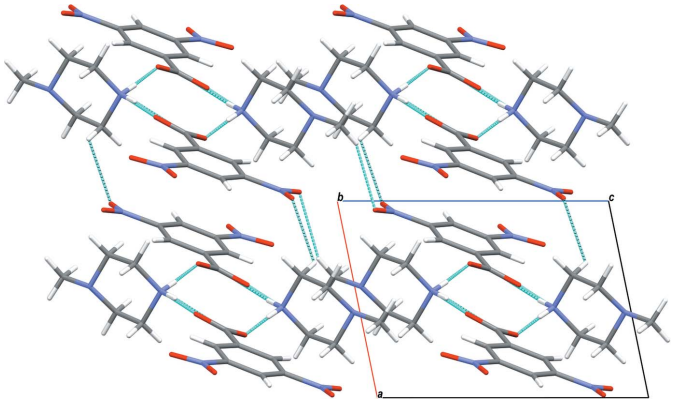


Figure 5
Molecular packing of (II) with hydrogen bonding shown as dashed lines..

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···O1	0.91 (2)	1.88 (2)	2.768 (2)	168 (3)
N2—H22···O2^{i}	0.92 (2)	1.77 (2)	2.684 (2)	171 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···O2^{i}	0.91 (2)	1.82 (2)	2.728 (2)	175 (2)
N2—H22···O1^{ii}	0.91 (2)	1.78 (2)	2.691 (2)	172 (2)

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

Table 3
Hydrogen-bond geometry (Å, °) for (III).

Cg2 is the centroid of the C6–C11 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3*A*···O2^{i}	0.97	2.56	3.272 (3)	130
C5—H5*A*···O1^{ii}	0.97	2.56	3.469 (3)	156
N2—H21···O2^{ii}	0.87 (2)	1.83 (2)	2.696 (3)	172 (3)
N2—H22···O1^{iii}	0.88 (2)	1.83 (2)	2.700 (3)	172 (3)
C4—H4*B*···*Cg*2^{iv}	0.97	2.59	3.473 (3)	152

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

3. Supramolecular features

In the crystal of (I), the cation and anion are linked by N2—H21···O1 hydrogen bonds, forming layers extending along the

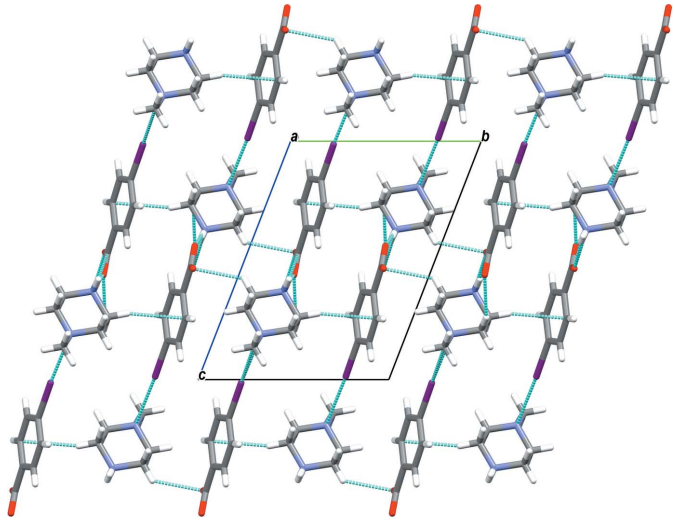


Figure 6
Molecular packing of (III) with hydrogen bonding shown as dashed lines..

Table 4
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_6H_{15}N_2^+\cdot C_7H_3N_2O_6^-$	$C_5H_{13}N_2^+\cdot C_7H_3N_2O_6^-$	$C_5H_{13}N_2^+\cdot C_7H_4IO_2^-$
M_r	326.31	312.29	348.17
Crystal system, space group	Monoclinic, $C2/c$	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	293	293	293
a, b, c (Å)	19.362 (1), 8.6279 (7), 19.318 (1)	7.8023 (6), 10.3920 (8), 10.4770 (8)	6.2418 (4), 9.5465 (8), 12.5346 (9)
α, β, γ (°)	90, 97.261 (8), 90	73.578 (8), 74.289 (8), 71.828 (7)	110.708 (8), 90.235 (5), 101.559 (6)
V (Å^3)	3201.3 (4)	758.49 (11)	682.19 (9)
Z	8	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.11	0.11	2.34
Crystal size (mm)	0.46 × 0.28 × 0.24	0.48 × 0.48 × 0.44	0.48 × 0.24 × 0.2
Data collection			
Diffractometer	Oxford Diffraction Xcalibur	Oxford Diffraction Xcalibur	Oxford Diffraction Xcalibur
Absorption correction	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}	0.964, 0.974	0.948, 0.952	0.515, 0.626
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6345, 2943, 1968	4819, 2774, 1935	4189, 2492, 2324
R_{int}	0.016	0.010	0.011
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.602	0.602	0.602
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.123, 1.04	0.044, 0.129, 1.03	0.020, 0.051, 1.11
No. of reflections	2943	2774	2492
No. of parameters	214	206	160
No. of restraints	2	2	2
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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.17	0.28, −0.15	0.37, −0.95

Computer programs: *CrysAlis CCD* (Oxford Diffraction, 2009), *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXT* (Sheldrick, 2015*a*), *Mercury* (Macrae *et al.*, 2020), *SHELXL2014* (Sheldrick, 2015*b*), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

c-axis direction. The layers are connected *via* N2—H22···O2 hydrogen bonds, forming sheets lying parallel to the *ac* plane (Table 1 and Fig. 4). The crystal structure of compound (II) is built up of N2—H21···O2 and N2—H22···O1 hydrogen bonds that connect the molecules in strong layers along the *c*-axis direction. The layers are linked *via* weak interactions of the type C—H···O, giving a three-dimensional network along the *b* axis (Table 2 and Fig. 5). The molecules in the crystal of (III) are linked by N2—H21···O2, N2—H22···O1, C—H···O and C—H···π interactions, forming layers along the *b* axis. The layers are linked through C—I···N halogen bonding with C9—I1 and I1···N1($1-x, 1-y, -z$) bond distnces of 2.103 (2) and 3.073 (2) Å, respectively, and bond angle of 174.33 (8)°, leading to a three-dimensional structure (Table 3 and Fig. 6).

4. Database survey

A search of the Cambridge Structural Database (Version 2020.3.0, last update March 2021; Groom *et al.*, 2016) for the piperazinium cation and benzoate anion involved in the three salts gave 62 hits, 60 of which have branched aromatic substituents either on the piperazinium cation, the benzoate anion or both, that make their structures extremely different from those of the title salts. The other two compounds are quite similar to the title molecules: 4-methylpiperazin-1-ium 2-amino-5-iodobenzoate (MAVMEC: Zhu & Guo, 2005) and 1-methylpiperazine-1,4-diium 4-nitrophthalate(2-) 4-nitrophthalic acid monohydrate (IZEFY: Guo, 2004), which share the cationic part and its chair conformation with salts (II) and (III). The crystal structures of the two compounds are based on differently sized rings formed through hydrogen-bond contacts, which then aggregate into a 3D framework.

5. Synthesis and crystallization

For the synthesis of (I), a solution of commercially available 1-ethylpiperazine (100 mg, 0.88 mol) (from Sigma-Aldrich) in methanol (10 ml) was mixed with an equimolar solution of 3,5-dinitrobenzoic acid (186.6 mg, 0.88 mol). Compounds (II) and (III) were prepared by the same method in which 1-methylpiperazine (100 mg, 1.0 mol) in methanol (10 ml) was mixed with an equimolar solution of 3,5-dinitrobenzoic acid (212 mg, 1.0 mol) for (II) or with an equimolar solution of 4-iodobenzoic acid (248 mg, 1.0 mol) for (III). The corresponding mixtures were stirred for 30 min at 323 K and allowed to stand at room temperature. X-ray quality crystals were formed upon slow evaporation in a week time (m.p. 453–455 K, 459–461 K and 410–412 K, respectively).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The H atoms bound to C were positioned with idealized geometry and refined using a riding model with aromatic C—H = 0.93 Å, 0.96 Å (methyl) or 0.97 Å (methylene). The H atoms of the N atom were located in a difference map and later restrained to the distance N—H = 0.86 (2) Å. All H atoms were refined with isotropic displacement parameters set at $1.2U_{eq}$ (C-aromatic, C-methylene, N) or $1.5U_{eq}$ (C-methyl) of the parent atom.

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supporting information

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Crystal structure studies of 4-ethylpiperazin-1-ium 3,5-dinitrobenzoate, 4-methylpiperazin-1-ium 3,5-dinitrobenzoate and 4-methylpiperazin-1-ium 4-iodobenzoate

Sriramapura D. Archana, Haruvegowda Kiran Kumar, Hemmige S. Yathirajan, Sabine Foro, Mohammed S. M. Abdelbaky and Santiago Garcia-Granda

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: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

4-Ethylpiperazin-1-ium 3,5-dinitrobenzoate (I)

Crystal data

$C_6H_{15}N_2^+·C_7H_3N_2O_6^-$
M_r = 326.31
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 19.362 (1) Å
b = 8.6279 (7) Å
c = 19.318 (1) Å
β = 97.261 (8)°
V = 3201.3 (4) Å^3
Z = 8
F(000) = 1376
D_x = 1.354 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6345 reflections
θ = 2.6–25.4°
μ = 0.11 mm^{-1}
T = 293 K
Prism, orange
0.46 × 0.28 × 0.24 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.964, T_{max} = 0.974
6345 measured reflections
2943 independent reflections
1968 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 25.4°, θ_{min} = 2.6°
h = −23→23
k = −10→10
l = −9→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.123
S = 1.04
2943 reflections
214 parameters
2 restraints

0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 1.8986P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.18587 (15)	0.3364 (3)	0.30396 (15)	0.0884 (9)
H1A	0.232834	0.339426	0.326863	0.133*
H1B	0.177587	0.424858	0.273903	0.133*
H1C	0.154108	0.338102	0.338302	0.133*
C2	0.17517 (12)	0.1925 (3)	0.26195 (13)	0.0655 (7)
H2A	0.208261	0.190584	0.228215	0.079*
H2B	0.184798	0.103891	0.292568	0.079*
C3	0.08924 (11)	0.2969 (3)	0.17179 (12)	0.0533 (6)
H3A	0.12338	0.291797	0.13919	0.064*
H3B	0.092984	0.397926	0.194012	0.064*
C4	0.01736 (11)	0.2779 (3)	0.13276 (13)	0.0589 (6)
H4A	−0.017049	0.290226	0.164733	0.071*
H4B	0.009231	0.357361	0.097152	0.071*
C5	0.02593 (11)	0.0011 (3)	0.15297 (12)	0.0563 (6)
H5A	0.023563	−0.099603	0.130507	0.068*
H5B	−0.008248	0.003405	0.185592	0.068*
C6	0.09733 (11)	0.0253 (3)	0.19161 (12)	0.0538 (6)
H6A	0.106657	−0.054243	0.227061	0.065*
H6B	0.131632	0.015195	0.159377	0.065*
C7	0.22610 (9)	0.0114 (2)	0.00395 (10)	0.0389 (5)
C8	0.25500 (10)	0.1070 (2)	0.05725 (10)	0.0431 (5)
H8	0.226597	0.164062	0.08315	0.052*
C9	0.32638 (10)	0.1168 (2)	0.07159 (10)	0.0449 (5)
C10	0.37088 (10)	0.0395 (2)	0.03386 (11)	0.0468 (5)
H10	0.418946	0.049122	0.043855	0.056*
C11	0.34091 (9)	−0.0527 (2)	−0.01928 (11)	0.0442 (5)
C12	0.26950 (9)	−0.0699 (2)	−0.03464 (10)	0.0428 (5)
H12	0.250959	−0.135397	−0.070496	0.051*
C13	0.14743 (10)	−0.0038 (3)	−0.01245 (10)	0.0440 (5)
N1	0.10398 (8)	0.1771 (2)	0.22445 (8)	0.0478 (5)
N2	0.00983 (8)	0.1234 (2)	0.09987 (9)	0.0502 (5)
N3	0.35665 (12)	0.2143 (3)	0.13029 (11)	0.0657 (6)

N4	0.38632 (9)	−0.1369 (2)	−0.06158 (12)	0.0612 (5)
O1	0.11149 (7)	0.0962 (2)	0.01190 (8)	0.0621 (5)
O2	0.12597 (7)	−0.1160 (2)	−0.05004 (9)	0.0653 (5)
O3	0.31860 (12)	0.3056 (3)	0.15461 (11)	0.0980 (7)
O4	0.41795 (10)	0.1972 (3)	0.15171 (10)	0.0987 (7)
O5	0.44928 (7)	−0.1316 (2)	−0.04397 (10)	0.0829 (6)
O6	0.35960 (9)	−0.2085 (3)	−0.11194 (11)	0.0962 (7)
H21	0.0381 (14)	0.116 (4)	0.0660 (13)	0.115*
H22	−0.0355 (10)	0.114 (4)	0.0790 (14)	0.115*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.084 (2)	0.088 (2)	0.085 (2)	−0.0122 (16)	−0.0206 (15)	−0.0224 (17)
C2	0.0594 (14)	0.0728 (18)	0.0585 (14)	−0.0020 (12)	−0.0150 (11)	0.0000 (13)
C3	0.0511 (12)	0.0460 (13)	0.0597 (13)	−0.0019 (10)	−0.0053 (10)	−0.0028 (11)
C4	0.0477 (12)	0.0602 (15)	0.0652 (14)	0.0061 (11)	−0.0069 (11)	−0.0037 (13)
C5	0.0538 (13)	0.0543 (14)	0.0608 (14)	−0.0136 (11)	0.0072 (11)	−0.0063 (12)
C6	0.0546 (13)	0.0483 (14)	0.0563 (13)	−0.0017 (10)	−0.0015 (10)	0.0037 (12)
C7	0.0330 (9)	0.0390 (11)	0.0437 (11)	−0.0016 (8)	0.0007 (8)	0.0063 (10)
C8	0.0431 (11)	0.0413 (12)	0.0448 (11)	−0.0019 (9)	0.0053 (9)	0.0024 (10)
C9	0.0460 (11)	0.0423 (12)	0.0439 (11)	−0.0114 (10)	−0.0043 (9)	0.0027 (10)
C10	0.0331 (10)	0.0478 (12)	0.0565 (13)	−0.0072 (9)	−0.0057 (9)	0.0094 (11)
C11	0.0332 (10)	0.0446 (12)	0.0547 (12)	0.0004 (9)	0.0049 (9)	0.0032 (11)
C12	0.0370 (10)	0.0422 (12)	0.0479 (11)	−0.0039 (9)	−0.0002 (9)	0.0008 (10)
C13	0.0329 (10)	0.0542 (14)	0.0443 (11)	−0.0017 (10)	0.0026 (9)	0.0081 (11)
N1	0.0446 (9)	0.0524 (11)	0.0437 (10)	−0.0038 (8)	−0.0048 (8)	−0.0025 (9)
N2	0.0331 (9)	0.0683 (13)	0.0477 (10)	−0.0049 (9)	−0.0013 (7)	−0.0090 (10)
N3	0.0674 (14)	0.0690 (15)	0.0579 (12)	−0.0222 (12)	−0.0030 (11)	−0.0041 (12)
N4	0.0428 (11)	0.0591 (13)	0.0833 (14)	0.0009 (9)	0.0135 (10)	−0.0068 (12)
O1	0.0415 (8)	0.0734 (11)	0.0735 (11)	0.0069 (8)	0.0153 (7)	−0.0026 (9)
O2	0.0340 (8)	0.0748 (11)	0.0837 (11)	−0.0064 (8)	−0.0057 (7)	−0.0170 (10)
O3	0.1085 (17)	0.0929 (16)	0.0892 (15)	−0.0096 (13)	−0.0011 (12)	−0.0405 (13)
O4	0.0675 (12)	0.1305 (19)	0.0900 (14)	−0.0337 (12)	−0.0219 (10)	−0.0182 (13)
O5	0.0337 (9)	0.0929 (14)	0.1238 (16)	0.0008 (9)	0.0167 (9)	−0.0136 (12)
O6	0.0624 (11)	0.1236 (18)	0.1026 (14)	0.0096 (11)	0.0109 (10)	−0.0556 (14)

Geometric parameters (Å, º)

C1—C2	1.484 (3)	C7—C8	1.381 (3)
C1—H1A	0.96	C7—C12	1.383 (3)
C1—H1B	0.96	C7—C13	1.522 (2)
C1—H1C	0.96	C8—C9	1.377 (3)
C2—N1	1.480 (3)	C8—H8	0.93
C2—H2A	0.97	C9—C10	1.370 (3)
C2—H2B	0.97	C9—N3	1.473 (3)
C3—N1	1.453 (3)	C10—C11	1.368 (3)
C3—C4	1.506 (3)	C10—H10	0.93

C3—H3A	0.97	C11—C12	1.385 (2)
C3—H3B	0.97	C11—N4	1.467 (3)
C4—N2	1.476 (3)	C12—H12	0.93
C4—H4A	0.97	C13—O1	1.238 (2)
C4—H4B	0.97	C13—O2	1.250 (2)
C5—N2	1.477 (3)	N2—H21	0.907 (17)
C5—C6	1.500 (3)	N2—H22	0.922 (17)
C5—H5A	0.97	N3—O3	1.213 (3)
C5—H5B	0.97	N3—O4	1.216 (2)
C6—N1	1.454 (3)	N4—O6	1.212 (2)
C6—H6A	0.97	N4—O5	1.224 (2)
C6—H6B	0.97		

C2—C1—H1A	109.5	C8—C7—C12	119.22 (17)
C2—C1—H1B	109.5	C8—C7—C13	120.47 (18)
H1A—C1—H1B	109.5	C12—C7—C13	120.31 (18)
C2—C1—H1C	109.5	C9—C8—C7	119.24 (19)
H1A—C1—H1C	109.5	C9—C8—H8	120.4
H1B—C1—H1C	109.5	C7—C8—H8	120.4
N1—C2—C1	113.6 (2)	C10—C9—C8	123.05 (19)
N1—C2—H2A	108.9	C10—C9—N3	118.16 (18)
C1—C2—H2A	108.9	C8—C9—N3	118.8 (2)
N1—C2—H2B	108.9	C11—C10—C9	116.52 (17)
C1—C2—H2B	108.9	C11—C10—H10	121.7
H2A—C2—H2B	107.7	C9—C10—H10	121.7
N1—C3—C4	111.11 (18)	C10—C11—C12	122.71 (19)
N1—C3—H3A	109.4	C10—C11—N4	118.60 (17)
C4—C3—H3A	109.4	C12—C11—N4	118.69 (18)
N1—C3—H3B	109.4	C7—C12—C11	119.23 (19)
C4—C3—H3B	109.4	C7—C12—H12	120.4
H3A—C3—H3B	108	C11—C12—H12	120.4
N2—C4—C3	110.43 (17)	O1—C13—O2	126.81 (18)
N2—C4—H4A	109.6	O1—C13—C7	117.20 (19)
C3—C4—H4A	109.6	O2—C13—C7	115.98 (18)
N2—C4—H4B	109.6	C3—N1—C6	109.69 (16)
C3—C4—H4B	109.6	C3—N1—C2	111.54 (17)
H4A—C4—H4B	108.1	C6—N1—C2	108.66 (17)
N2—C5—C6	110.30 (17)	C4—N2—C5	110.20 (17)
N2—C5—H5A	109.6	C4—N2—H21	110 (2)
C6—C5—H5A	109.6	C5—N2—H21	111 (2)
N2—C5—H5B	109.6	C4—N2—H22	108 (2)
C6—C5—H5B	109.6	C5—N2—H22	110.3 (19)
H5A—C5—H5B	108.1	H21—N2—H22	108 (3)
N1—C6—C5	111.54 (18)	O3—N3—O4	124.2 (2)
N1—C6—H6A	109.3	O3—N3—C9	117.8 (2)
C5—C6—H6A	109.3	O4—N3—C9	118.0 (2)
N1—C6—H6B	109.3	O6—N4—O5	123.5 (2)
C5—C6—H6B	109.3	O6—N4—C11	118.33 (18)

H6A—C6—H6B	108	O5—N4—C11	118.2 (2)
N1—C3—C4—N2	−57.7 (2)	C12—C7—C13—O2	15.6 (3)
N2—C5—C6—N1	57.5 (2)	C4—C3—N1—C6	58.2 (2)
C12—C7—C8—C9	−1.2 (3)	C4—C3—N1—C2	178.59 (18)
C13—C7—C8—C9	179.11 (18)	C5—C6—N1—C3	−58.3 (2)
C7—C8—C9—C10	2.1 (3)	C5—C6—N1—C2	179.54 (18)
C7—C8—C9—N3	−177.62 (17)	C1—C2—N1—C3	65.2 (3)
C8—C9—C10—C11	−1.2 (3)	C1—C2—N1—C6	−173.8 (2)
N3—C9—C10—C11	178.58 (18)	C3—C4—N2—C5	56.1 (2)
C9—C10—C11—C12	−0.6 (3)	C6—C5—N2—C4	−55.9 (2)
C9—C10—C11—N4	179.50 (18)	C10—C9—N3—O3	165.7 (2)
C8—C7—C12—C11	−0.5 (3)	C8—C9—N3—O3	−14.5 (3)
C13—C7—C12—C11	179.18 (18)	C10—C9—N3—O4	−15.0 (3)
C10—C11—C12—C7	1.5 (3)	C8—C9—N3—O4	164.7 (2)
N4—C11—C12—C7	−178.69 (18)	C10—C11—N4—O6	−174.2 (2)
C8—C7—C13—O1	16.0 (3)	C12—C11—N4—O6	5.9 (3)
C12—C7—C13—O1	−163.64 (18)	C10—C11—N4—O5	6.0 (3)
C8—C7—C13—O2	−164.73 (18)	C12—C11—N4—O5	−173.9 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H21···O1	0.91 (2)	1.88 (2)	2.768 (2)	168 (3)
N2—H22···O2^{i}	0.92 (2)	1.77 (2)	2.684 (2)	171 (3)

Symmetry code: (i) −*x*, −*y*, −*z*.

4-Methylpiperazin-1-ium 3,5-dinitrobenzoate (II)

Crystal data

$C_5H_{13}N_2^+·C_7H_3N_2O_6^-$
M_r = 312.29
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.8023 (6) Å
b = 10.3920 (8) Å
c = 10.4770 (8) Å
α = 73.578 (8)°
β = 74.289 (8)°
γ = 71.828 (7)°
V = 758.49 (11) Å^3
Z = 2
F(000) = 328
D_x = 1.367 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 4819 reflections
θ = 2.6–25.4°
μ = 0.11 mm^{-1}
T = 293 K
Prism, orange
0.48 × 0.48 × 0.44 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.948, T_{max} = 0.952
4819 measured reflections
2774 independent reflections
1935 reflections with $I > 2\sigma(I)$
R_{int} = 0.010
θ_{max} = 25.4°, θ_{min} = 2.6°
h = −9→7
k = −12→8
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.129$
$S = 1.03$
2774 reflections
206 parameters
2 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2 + 0.1428P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.4259 (3)	−0.25601 (14)	0.60539 (19)	0.1005 (6)
O2	0.3187 (2)	−0.28191 (15)	0.44153 (17)	0.0950 (5)
O3	0.2206 (3)	0.1945 (2)	0.7260 (2)	0.1219 (7)
O4	0.1284 (3)	0.37901 (16)	0.5805 (2)	0.1139 (7)
O5	0.0144 (3)	0.3389 (2)	0.16451 (19)	0.1237 (7)
O6	0.0455 (3)	0.1363 (3)	0.1329 (2)	0.1293 (8)
N3	0.1771 (3)	0.25321 (19)	0.6173 (2)	0.0806 (5)
N4	0.0540 (3)	0.2122 (3)	0.1988 (2)	0.0877 (6)
C6	0.2667 (2)	−0.05607 (17)	0.47269 (17)	0.0500 (4)
C7	0.2608 (2)	0.02602 (17)	0.55809 (18)	0.0535 (4)
H7	0.307549	−0.013627	0.637091	0.064*
C8	0.1847 (2)	0.16762 (17)	0.52500 (19)	0.0569 (4)
C9	0.1152 (2)	0.23142 (19)	0.4090 (2)	0.0625 (5)
H9	0.064143	0.326656	0.38815	0.075*
C10	0.1249 (2)	0.1477 (2)	0.32539 (19)	0.0606 (5)
C11	0.1974 (2)	0.00621 (19)	0.35514 (18)	0.0568 (5)
H11	0.199786	−0.047271	0.29663	0.068*
C12	0.3453 (3)	−0.21207 (18)	0.5093 (2)	0.0606 (5)
N1	0.4346 (2)	0.71225 (17)	0.02379 (16)	0.0702 (5)
N2	0.4591 (3)	0.52702 (16)	0.28262 (17)	0.0687 (5)
C1	0.3857 (4)	0.8479 (3)	−0.0671 (3)	0.1066 (9)
H1A	0.493157	0.865009	−0.133097	0.16*
H1B	0.338418	0.918742	−0.015173	0.16*
H1C	0.293597	0.849066	−0.112598	0.16*
C2	0.2725 (3)	0.6783 (2)	0.1169 (2)	0.0697 (5)
H2A	0.184008	0.681477	0.06581	0.084*
H2B	0.21612	0.74668	0.172715	0.084*
C3	0.3197 (3)	0.5366 (2)	0.2067 (2)	0.0739 (6)

H3A	0.209494	0.517861	0.270132	0.089*
H3B	0.366896	0.467313	0.15165	0.089*
C4	0.6227 (3)	0.5678 (2)	0.1885 (2)	0.0809 (6)
H4A	0.684243	0.501297	0.131159	0.097*
H4B	0.708662	0.568073	0.240126	0.097*
C5	0.5641 (3)	0.7102 (2)	0.1016 (2)	0.0767 (6)
H5A	0.50716	0.777105	0.15895	0.092*
H5B	0.671413	0.736436	0.040146	0.092*
H21	0.412 (3)	0.586 (2)	0.340 (2)	0.092*
H22	0.494 (3)	0.4374 (18)	0.329 (2)	0.092*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1400 (15)	0.0432 (8)	0.1110 (13)	0.0019 (8)	−0.0587 (12)	−0.0017 (8)
O2	0.1243 (14)	0.0579 (9)	0.0982 (12)	−0.0057 (8)	−0.0139 (10)	−0.0373 (9)
O3	0.188 (2)	0.0895 (13)	0.1115 (15)	−0.0329 (13)	−0.0574 (15)	−0.0344 (12)
O4	0.1277 (14)	0.0523 (10)	0.1664 (18)	−0.0016 (9)	−0.0407 (13)	−0.0441 (11)
O5	0.1127 (14)	0.1017 (15)	0.1015 (13)	0.0206 (11)	−0.0330 (11)	0.0208 (11)
O6	0.1450 (19)	0.149 (2)	0.0972 (14)	−0.0207 (14)	−0.0625 (13)	−0.0148 (14)
N3	0.0813 (12)	0.0582 (11)	0.1069 (16)	−0.0145 (9)	−0.0177 (11)	−0.0297 (11)
N4	0.0675 (12)	0.0988 (16)	0.0703 (13)	−0.0021 (10)	−0.0176 (9)	0.0047 (12)
C6	0.0438 (9)	0.0429 (9)	0.0544 (10)	−0.0084 (7)	−0.0007 (7)	−0.0086 (8)
C7	0.0489 (9)	0.0469 (10)	0.0578 (10)	−0.0098 (7)	−0.0088 (8)	−0.0053 (8)
C8	0.0514 (10)	0.0439 (10)	0.0721 (12)	−0.0111 (7)	−0.0067 (9)	−0.0140 (9)
C9	0.0484 (10)	0.0435 (10)	0.0788 (13)	−0.0071 (7)	−0.0067 (9)	0.0018 (9)
C10	0.0448 (10)	0.0617 (12)	0.0590 (11)	−0.0073 (8)	−0.0074 (8)	0.0023 (9)
C11	0.0487 (10)	0.0597 (11)	0.0562 (10)	−0.0122 (8)	−0.0013 (8)	−0.0142 (9)
C12	0.0630 (11)	0.0420 (10)	0.0627 (12)	−0.0068 (8)	0.0020 (9)	−0.0110 (9)
N1	0.0768 (11)	0.0689 (11)	0.0543 (9)	−0.0116 (8)	−0.0144 (8)	−0.0036 (8)
N2	0.0975 (13)	0.0401 (8)	0.0587 (10)	0.0023 (8)	−0.0235 (9)	−0.0102 (7)
C1	0.123 (2)	0.0942 (19)	0.0786 (16)	−0.0234 (15)	−0.0293 (15)	0.0223 (14)
C2	0.0695 (13)	0.0647 (12)	0.0737 (13)	−0.0130 (10)	−0.0253 (10)	−0.0075 (10)
C3	0.0870 (15)	0.0604 (12)	0.0751 (13)	−0.0214 (10)	−0.0180 (11)	−0.0115 (10)
C4	0.0717 (14)	0.0743 (14)	0.0922 (16)	0.0063 (11)	−0.0325 (12)	−0.0237 (12)
C5	0.0638 (12)	0.0790 (14)	0.0780 (14)	−0.0189 (10)	−0.0099 (11)	−0.0061 (11)

Geometric parameters (Å, º)

O1—C12	1.233 (2)	N1—C5	1.452 (3)
O2—C12	1.241 (2)	N1—C1	1.464 (3)
O3—N3	1.213 (3)	N2—C3	1.477 (3)
O4—N3	1.219 (2)	N2—C4	1.483 (3)
O5—N4	1.224 (3)	N2—H21	0.906 (16)
O6—N4	1.212 (3)	N2—H22	0.913 (16)
N3—C8	1.467 (3)	C1—H1A	0.96
N4—C10	1.475 (3)	C1—H1B	0.96
C6—C7	1.384 (2)	C1—H1C	0.96

C6—C11	1.386 (2)	C2—C3	1.502 (3)
C6—C12	1.519 (2)	C2—H2A	0.97
C7—C8	1.384 (2)	C2—H2B	0.97
C7—H7	0.93	C3—H3A	0.97
C8—C9	1.374 (3)	C3—H3B	0.97
C9—C10	1.373 (3)	C4—C5	1.506 (3)
C9—H9	0.93	C4—H4A	0.97
C10—C11	1.377 (2)	C4—H4B	0.97
C11—H11	0.93	C5—H5A	0.97
N1—C2	1.446 (2)	C5—H5B	0.97

O3—N3—O4	123.6 (2)	C3—N2—H22	108.4 (15)
O3—N3—C8	117.95 (18)	C4—N2—H22	109.2 (14)
O4—N3—C8	118.4 (2)	H21—N2—H22	111 (2)
O6—N4—O5	124.2 (2)	N1—C1—H1A	109.5
O6—N4—C10	117.9 (2)	N1—C1—H1B	109.5
O5—N4—C10	117.8 (2)	H1A—C1—H1B	109.5
C7—C6—C11	118.91 (16)	N1—C1—H1C	109.5
C7—C6—C12	120.13 (16)	H1A—C1—H1C	109.5
C11—C6—C12	120.95 (17)	H1B—C1—H1C	109.5
C6—C7—C8	119.47 (17)	N1—C2—C3	111.25 (17)
C6—C7—H7	120.3	N1—C2—H2A	109.4
C8—C7—H7	120.3	C3—C2—H2A	109.4
C9—C8—C7	122.55 (18)	N1—C2—H2B	109.4
C9—C8—N3	118.53 (17)	C3—C2—H2B	109.4
C7—C8—N3	118.92 (18)	H2A—C2—H2B	108
C10—C9—C8	116.73 (16)	N2—C3—C2	110.67 (16)
C10—C9—H9	121.6	N2—C3—H3A	109.5
C8—C9—H9	121.6	C2—C3—H3A	109.5
C9—C10—C11	122.66 (18)	N2—C3—H3B	109.5
C9—C10—N4	118.52 (19)	C2—C3—H3B	109.5
C11—C10—N4	118.8 (2)	H3A—C3—H3B	108.1
C10—C11—C6	119.67 (18)	N2—C4—C5	109.78 (16)
C10—C11—H11	120.2	N2—C4—H4A	109.7
C6—C11—H11	120.2	C5—C4—H4A	109.7
O1—C12—O2	126.92 (18)	N2—C4—H4B	109.7
O1—C12—C6	116.25 (18)	C5—C4—H4B	109.7
O2—C12—C6	116.81 (19)	H4A—C4—H4B	108.2
C2—N1—C5	108.81 (15)	N1—C5—C4	110.61 (18)
C2—N1—C1	110.74 (18)	N1—C5—H5A	109.5
C5—N1—C1	110.91 (18)	C4—C5—H5A	109.5
C3—N2—C4	110.66 (16)	N1—C5—H5B	109.5
C3—N2—H21	110.0 (15)	C4—C5—H5B	109.5
C4—N2—H21	107.1 (14)	H5A—C5—H5B	108.1

C11—C6—C7—C8	0.5 (2)	C9—C10—C11—C6	−1.0 (3)
C12—C6—C7—C8	−178.42 (15)	N4—C10—C11—C6	179.18 (15)
C6—C7—C8—C9	−0.6 (3)	C7—C6—C11—C10	0.2 (2)

C6—C7—C8—N3	179.23 (15)	C12—C6—C11—C10	179.17 (15)
O3—N3—C8—C9	172.3 (2)	C7—C6—C12—O1	−10.5 (2)
O4—N3—C8—C9	−8.0 (3)	C11—C6—C12—O1	170.56 (17)
O3—N3—C8—C7	−7.5 (3)	C7—C6—C12—O2	168.17 (16)
O4—N3—C8—C7	172.18 (18)	C11—C6—C12—O2	−10.8 (2)
C7—C8—C9—C10	−0.2 (3)	C5—N1—C2—C3	−60.3 (2)
N3—C8—C9—C10	−179.99 (15)	C1—N1—C2—C3	177.52 (19)
C8—C9—C10—C11	1.0 (3)	C4—N2—C3—C2	−54.0 (2)
C8—C9—C10—N4	−179.21 (15)	N1—C2—C3—N2	57.2 (2)
O6—N4—C10—C9	−172.5 (2)	C3—N2—C4—C5	54.9 (2)
O5—N4—C10—C9	10.3 (3)	C2—N1—C5—C4	61.4 (2)
O6—N4—C10—C11	7.3 (3)	C1—N1—C5—C4	−176.53 (19)
O5—N4—C10—C11	−169.91 (18)	N2—C4—C5—N1	−59.1 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H21···O2^{i}	0.91 (2)	1.82 (2)	2.728 (2)	175 (2)
N2—H22···O1^{ii}	0.91 (2)	1.78 (2)	2.691 (2)	172 (2)

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

4-Methylpiperazin-1-ium 4-iodobenzoate (III)

Crystal data

$C_5H_{13}N_2^+·C_7H_4IO_2^-$
M_r = 348.17
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 6.2418 (4) Å
b = 9.5465 (8) Å
c = 12.5346 (9) Å
α = 110.708 (8)°
β = 90.235 (5)°
γ = 101.559 (6)°
V = 682.19 (9) Å^3
Z = 2
F(000) = 344
D_x = 1.695 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 4189 reflections
θ = 3.3–25.4°
μ = 2.34 mm^{-1}
T = 293 K
Rods, colourless
0.48 × 0.24 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)
T_{min} = 0.515, T_{max} = 0.626
4189 measured reflections
2492 independent reflections
2324 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
θ_{max} = 25.4°, θ_{min} = 3.3°
h = −7→7
k = −11→11
l = −15→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.051
S = 1.11
2492 reflections
160 parameters
2 restraints
0 constraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 0.2845P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	1.2514 (5)	0.7762 (5)	0.1396 (3)	0.0712 (11)
H1A	1.242455	0.690853	0.068934	0.107*
H1B	1.283901	0.870031	0.124947	0.107*
H1C	1.365551	0.776131	0.19115	0.107*
C2	1.0513 (4)	0.8911 (3)	0.2981 (2)	0.0429 (6)
H2A	1.085517	0.986567	0.284191	0.051*
H2B	1.167221	0.892502	0.350502	0.051*
C3	0.8371 (4)	0.8786 (3)	0.3512 (2)	0.0428 (6)
H3A	0.847548	0.963711	0.423379	0.051*
H3B	0.722435	0.883465	0.301016	0.051*
C4	0.7745 (4)	0.6017 (3)	0.2629 (2)	0.0432 (6)
H4A	0.656473	0.596833	0.210215	0.052*
H4B	0.745692	0.506984	0.277895	0.052*
C5	0.9887 (4)	0.6188 (3)	0.2099 (2)	0.0424 (6)
H5A	1.10447	0.614721	0.259906	0.051*
H5B	0.980005	0.534325	0.137531	0.051*
C6	0.6076 (4)	0.2567 (3)	0.3636 (2)	0.0296 (5)
C7	0.6850 (4)	0.1909 (3)	0.2577 (2)	0.0339 (5)
H7	0.812059	0.153084	0.253927	0.041*
C8	0.5770 (4)	0.1804 (3)	0.1574 (2)	0.0355 (5)
H8	0.629598	0.134593	0.086951	0.043*
C9	0.3881 (4)	0.2396 (3)	0.1635 (2)	0.0312 (5)
C10	0.3100 (4)	0.3057 (3)	0.2684 (2)	0.0332 (5)
H10	0.184232	0.345025	0.272511	0.04*
C11	0.4189 (4)	0.3135 (3)	0.3679 (2)	0.0336 (5)
H11	0.364548	0.357276	0.438151	0.04*
C12	0.7285 (4)	0.2674 (3)	0.4722 (2)	0.0345 (5)
I1	0.22668 (3)	0.23210 (2)	0.01333 (2)	0.03947 (7)
N1	1.0417 (3)	0.7631 (3)	0.19094 (18)	0.0384 (5)
N2	0.7815 (3)	0.7327 (3)	0.37083 (19)	0.0393 (5)
O1	0.6295 (3)	0.2895 (3)	0.56080 (16)	0.0567 (6)
O2	0.9237 (3)	0.2528 (3)	0.46569 (16)	0.0467 (5)

H21	0.876 (4)	0.728 (4)	0.420 (2)	0.056*
H22	0.653 (4)	0.728 (4)	0.400 (3)	0.056*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0331 (15)	0.135 (3)	0.056 (2)	0.0112 (18)	0.0100 (14)	0.051 (2)
C2	0.0390 (14)	0.0381 (14)	0.0506 (16)	−0.0024 (11)	−0.0094 (12)	0.0208 (12)
C3	0.0459 (14)	0.0405 (14)	0.0395 (14)	0.0171 (12)	−0.0055 (11)	0.0075 (12)
C4	0.0434 (14)	0.0365 (14)	0.0484 (16)	−0.0033 (11)	−0.0035 (12)	0.0204 (12)
C5	0.0455 (15)	0.0428 (14)	0.0373 (14)	0.0159 (12)	0.0009 (11)	0.0092 (12)
C6	0.0241 (10)	0.0347 (12)	0.0346 (12)	0.0059 (9)	0.0019 (9)	0.0183 (10)
C7	0.0272 (11)	0.0423 (13)	0.0378 (13)	0.0142 (10)	0.0040 (9)	0.0174 (11)
C8	0.0362 (13)	0.0404 (13)	0.0311 (12)	0.0142 (10)	0.0056 (10)	0.0110 (11)
C9	0.0291 (11)	0.0343 (12)	0.0326 (12)	0.0050 (9)	−0.0031 (9)	0.0162 (10)
C10	0.0239 (11)	0.0430 (13)	0.0380 (13)	0.0108 (10)	0.0029 (9)	0.0193 (11)
C11	0.0299 (11)	0.0446 (14)	0.0321 (12)	0.0117 (10)	0.0066 (9)	0.0186 (11)
C12	0.0258 (11)	0.0471 (14)	0.0354 (13)	0.0087 (10)	0.0017 (9)	0.0203 (11)
I1	0.03737 (10)	0.05212 (12)	0.03188 (10)	0.01315 (7)	−0.00148 (7)	0.01691 (8)
N1	0.0269 (10)	0.0595 (14)	0.0346 (11)	0.0059 (9)	0.0023 (8)	0.0260 (10)
N2	0.0279 (10)	0.0639 (14)	0.0327 (11)	0.0124 (10)	0.0036 (8)	0.0241 (11)
O1	0.0371 (10)	0.1100 (18)	0.0370 (11)	0.0261 (11)	0.0097 (8)	0.0379 (12)
O2	0.0319 (9)	0.0780 (14)	0.0400 (10)	0.0216 (9)	0.0035 (8)	0.0278 (10)

Geometric parameters (Å, º)

C1—N1	1.464 (3)	C5—H5B	0.97
C1—H1A	0.96	C6—C11	1.386 (3)
C1—H1B	0.96	C6—C7	1.388 (3)
C1—H1C	0.96	C6—C12	1.514 (3)
C2—N1	1.453 (4)	C7—C8	1.386 (4)
C2—C3	1.498 (4)	C7—H7	0.93
C2—H2A	0.97	C8—C9	1.398 (3)
C2—H2B	0.97	C8—H8	0.93
C3—N2	1.474 (4)	C9—C10	1.381 (3)
C3—H3A	0.97	C9—I1	2.103 (2)
C3—H3B	0.97	C10—C11	1.389 (3)
C4—N2	1.475 (4)	C10—H10	0.93
C4—C5	1.501 (4)	C11—H11	0.93
C4—H4A	0.97	C12—O1	1.246 (3)
C4—H4B	0.97	C12—O2	1.254 (3)
C5—N1	1.454 (4)	N2—H21	0.874 (18)
C5—H5A	0.97	N2—H22	0.881 (18)
N1—C1—H1A	109.5	C11—C6—C7	118.6 (2)
N1—C1—H1B	109.5	C11—C6—C12	120.8 (2)
H1A—C1—H1B	109.5	C7—C6—C12	120.6 (2)
N1—C1—H1C	109.5	C8—C7—C6	121.5 (2)

H1A—C1—H1C	109.5	C8—C7—H7	119.3
H1B—C1—H1C	109.5	C6—C7—H7	119.3
N1—C2—C3	110.8 (2)	C7—C8—C9	119.1 (2)
N1—C2—H2A	109.5	C7—C8—H8	120.4
C3—C2—H2A	109.5	C9—C8—H8	120.4
N1—C2—H2B	109.5	C10—C9—C8	119.9 (2)
C3—C2—H2B	109.5	C10—C9—I1	120.07 (17)
H2A—C2—H2B	108.1	C8—C9—I1	120.00 (18)
N2—C3—C2	110.0 (2)	C9—C10—C11	120.1 (2)
N2—C3—H3A	109.7	C9—C10—H10	119.9
C2—C3—H3A	109.7	C11—C10—H10	119.9
N2—C3—H3B	109.7	C6—C11—C10	120.8 (2)
C2—C3—H3B	109.7	C6—C11—H11	119.6
H3A—C3—H3B	108.2	C10—C11—H11	119.6
N2—C4—C5	110.2 (2)	O1—C12—O2	124.5 (2)
N2—C4—H4A	109.6	O1—C12—C6	118.7 (2)
C5—C4—H4A	109.6	O2—C12—C6	116.7 (2)
N2—C4—H4B	109.6	C2—N1—C5	110.3 (2)
C5—C4—H4B	109.6	C2—N1—C1	110.5 (2)
H4A—C4—H4B	108.1	C5—N1—C1	109.6 (2)
N1—C5—C4	111.1 (2)	C3—N2—C4	110.6 (2)
N1—C5—H5A	109.4	C3—N2—H21	112 (2)
C4—C5—H5A	109.4	C4—N2—H21	108 (2)
N1—C5—H5B	109.4	C3—N2—H22	108 (2)
C4—C5—H5B	109.4	C4—N2—H22	111 (2)
H5A—C5—H5B	108	H21—N2—H22	108 (3)

N1—C2—C3—N2	58.1 (3)	C9—C10—C11—C6	0.6 (4)
N2—C4—C5—N1	−56.7 (3)	C11—C6—C12—O1	18.7 (4)
C11—C6—C7—C8	−0.4 (4)	C7—C6—C12—O1	−161.8 (2)
C12—C6—C7—C8	−179.8 (2)	C11—C6—C12—O2	−161.4 (2)
C6—C7—C8—C9	1.0 (4)	C7—C6—C12—O2	18.0 (4)
C7—C8—C9—C10	−0.8 (4)	C3—C2—N1—C5	−58.7 (3)
C7—C8—C9—I1	177.94 (18)	C3—C2—N1—C1	180.0 (2)
C8—C9—C10—C11	0.0 (4)	C4—C5—N1—C2	58.0 (3)
I1—C9—C10—C11	−178.72 (18)	C4—C5—N1—C1	179.9 (2)
C7—C6—C11—C10	−0.4 (4)	C2—C3—N2—C4	−56.8 (3)
C12—C6—C11—C10	179.0 (2)	C5—C4—N2—C3	56.1 (3)

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of the C6–C11 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···O2^{i}	0.97	2.56	3.272 (3)	130
C5—H5*A*···O1^{ii}	0.97	2.56	3.469 (3)	156
N2—H21···O2^{ii}	0.87 (2)	1.83 (2)	2.696 (3)	172 (3)

N2—H22···O1^{iii}	0.88 (2)	1.83 (2)	2.700 (3)	172 (3)
C4—H4*B*···*Cg*2^{iv}	0.97	2.59	3.473 (3)	152

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