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4-Nitrophenylpiperazinium chloride monohydrate

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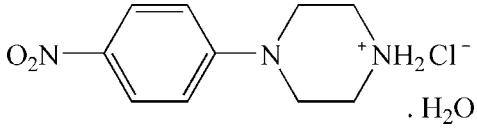
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.042; wR factor = 0.120; data-to-parameter ratio = 14.7.

In the title compound, $C_{10}H_{14}N_3O_2^+\cdot Cl^-\cdot H_2O$, the cation acts with a water molecule as a chloride-ion receptor. The water molecule forms three strong hydrogen bonds. The H atoms of the piperazinium cation form hydrogen bonds to the chloride ion and to a water molecule, giving a three-dimensional hydrogen-bond network. Weak intermolecular C—H···O hydrogen bonds and π–π stacking interactions between pairs of antiparallel benzene rings, with a mean interplanar separation of 3.66 Å, also stabilize the structure.

Related literature

For related literature, see: Chen *et al.* (2000); Hepperle *et al.* (1999); How *et al.* (2007); Lan *et al.* (2005, 2006); Saczewski *et al.* (2006); Sopo & Sillanpää (2007); Wu *et al.* (2005); Zou *et al.* (2005).



Experimental

Crystal data

$C_{10}H_{14}N_3O_2^+\cdot Cl^-\cdot H_2O$
M_r = 261.71
Triclinic, $P\overline{1}$
a = 7.404 (2) Å
b = 9.212 (3) Å
c = 9.757 (3) Å
α = 110.111 (4)°
β = 90.209 (4)°
γ = 96.484 (4)°
V = 620.3 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 293 (2) K
0.15 × 0.10 × 0.10 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997*b*)
T_{min} = 0.955, T_{max} = 0.970
2866 measured reflections
2390 independent reflections
2078 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.120
S = 1.04
2390 reflections
163 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3D···Cl1^{i}	0.853 (18)	2.317 (18)	3.1681 (18)	176 (3)
O3—H3C···Cl1^{ii}	0.871 (18)	2.273 (19)	3.135 (2)	170 (4)
N1—H1D···O3^{iii}	0.90	1.88	2.741 (2)	161
N1—H1C···Cl1	0.90	2.21	3.0994 (17)	168

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2123).

References

Bruker (1999). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, X., Wang, L., Zhao, Z. Z., Zhang, X. Q., Chen, X. H. & Chen, H. S. (2000). *Chin. Chem. Lett.* **11**, 571–572.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Hepperle, M., Eckert, J. & Gala, D. (1999). *Tetrahedron Lett.* **40**, 5655–5659.
How, F. N.-F., Watkin, D. J., Crouse, K. A. & Tahir, M. I. M. (2007). *Acta Cryst.* E**63**, o3023–o3024.
Lan, B.-J., Guo, P., Zou, Z.-G. & Lu, Y.-X. (2005). *Acta Cryst.* E**61**, o3022–o3024.
Lan, B.-J., Guo, P., Zou, Z.-G. & Lu, Y.-X. (2006). *Acta Cryst.* E**62**, o383–o385.
Saczewski, F., Bulakowska, A., Bednarski, P. & Grunert, R. (2006). *Eur. J. Med. Chem.* **41**, 219–225.
Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sopo, H. & Sillanpää, R. (2007). *Acta Cryst.* C**63**, o386–o388.
Wu, B. N., Chen, I. C., Lin, R. J., Chiu, C. C., An, L. M. & Chen, I. J. (2005). *J. Cardiovasc. Pharmacol.* **46**, 600–608.
Zou, Z.-G., Guo, P. & Lu, Y.-X. (2005). *Acta Cryst.* E**61**, o4096–o4098.

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supplementary materials

Acta Cryst. (2007). E**63**, o3611 [**doi:10.1107/S1600536807034666**]

4-Nitrophenylpiperazinium chloride monohydrate

Y.-X. Lu

Comment

4-Nitrophenylpiperazinium chloride monohydrate (I) has been used as an intermediate in the synthesis of anticancer durgs, transcriptase inhibitors and antifungal reagents (Saczewski *et al.*, 2006; Chen *et al.*, 2000; Hepperle *et al.*, 1999). It is also an important reagent for potassium channel openers, which show considerable biomolecular current-voltage rectification characteristics (Wu *et al.*, 2005; Lan *et al.*, 2005, 2006).

The basic structural unit of (I) consists of a 4-nitrophenylpiperazinium cation, a chloride ion and a water molecule. The molecular structure and atom-labeling scheme are shown in Fig. 1. The bonds N3—O1, N3—O2 [1.224 (2), 1.218 (2) Å, respectively] have partial double-bond character. The shorter intramolecular distance of H2b···H6a and H4a···H10*a* [1.97 and 1.98 Å] demonstrates the existence of H···H contacts.

The chloride anion forms one N—H···Cl and two O—H···Cl hydrogen bonds, namely one to piperazinium atom N1H1c, and two to the H atom of the water molecule (O3H3D, O3H3c) (Table 1). The H···Cl1 interaction lengths of the hydrogen bonds range from 2.21 to 2.317 (18) Å (Sopo & Sillanpää, 2007).

The H atoms of the piperazinium cation form hydrogen bonds to the chloride ion and to water atom O3 in an adjacent unit, forming a three-dimensional hydrogen-bond network (Fig. 2). Thus, the piperazinium cation plays an important role by acting as a bridge between the water O atom and the chloride ion.

The NO_2 groups also help to stabilize the crystal structure. The hydrogen bonds C3—H3b···O1^{iv} [symmetry code: (iv) $-x+1, -y+2, -z+1$] are responsible for two-membered aggregates (Fig. 3), and C1—H1b···O2^{v} [symmetry code: (v) $x, y-1, z-1$] for zigzag molecular chains (Fig. 4) (Zou *et al.*, 2005).

π···π Stacking interactions between pairs of antiparallel benzene rings are observed [mean separation of 3.66 Å] (Fig. 5) (How *et al.*, 2007).

Experimental

Crystals suitable for single-crystal X-ray analysis were obtained at room temperature by slow evaporation of an aqueous solution of 4-nitrophenylpiperazine and hydrochloric acid (1:1).

Refinement

H atoms were included using a riding model with C—H = 0.97 or 0.93 Å, O—H = 0.85 or 0.87 Å, N—H = 0.90 Å, and $U_{iso} = 1.2U_{eq}$ of the parent atom.

Figures

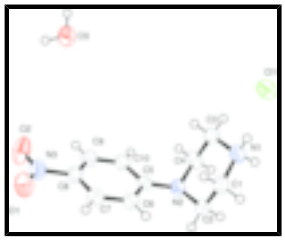

Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius.

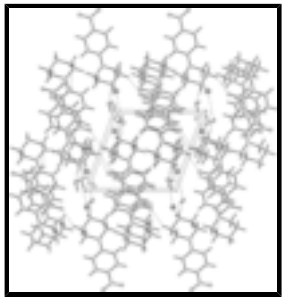

Fig. 2. The crystal structure of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds.

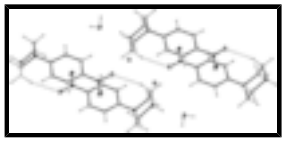

Fig. 3. Two-membered aggregates. Dashed lines indicate hydrogen bonds.

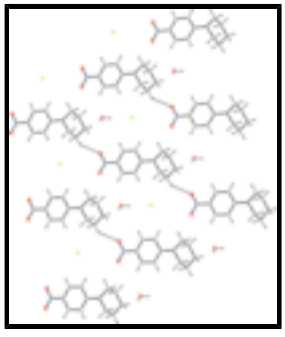

Fig. 4. Zigzag molecular chains. Dashed lines indicate hydrogen bonds.

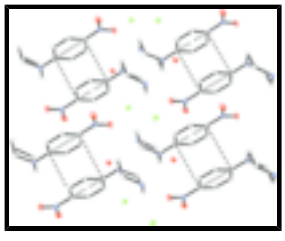

Fig. 5. π···π Stacking interactions. Dashed lines indicate the pairs of antiparallel benzene rings.

4-Nitrophenylpiperazinium chloride monohydrate

Crystal data

$C_{10}H_{14}N_3O_2^+\cdot Cl^-\cdot H_2O$	$Z = 2$
$M_r = 261.71$	$F_{000} = 276$
Triclinic, $P\overline{1}$	$D_x = 1.401$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation

	λ = 0.71073 Å
a = 7.404 (2) Å	Cell parameters from 899 reflections
b = 9.212 (3) Å	θ = 3.5–27.1º
c = 9.757 (3) Å	μ = 0.31 mm^{-1}
α = 110.111 (4)º	*T* = 293 (2) K
β = 90.209 (4)º	Prism, brown
γ = 96.484 (4)º	0.15 × 0.10 × 0.10 mm
V = 620.3 (3) $Å^3$	

Data collection

Bruker APEX CCD area-detector diffractometer	2390 independent reflections
Radiation source: fine-focus sealed tube	2078 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.020
T = 293(2) K	θ_{max} = 26.0º
φ and ω scans	θ_{min} = 2.2º
Absorption correction: multi-scan (SADABS; Sheldrick, 1997b)	*h* = −8→9
T_{min} = 0.955, T_{max} = 0.970	*k* = −9→11
2866 measured reflections	*l* = −10→12

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.042	$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 0.1053P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.120	$(\Delta/\sigma)_{max} < 0.001$
S = 1.04	$\Delta\rho_{max}$ = 0.27 e $Å^{-3}$
2390 reflections	$\Delta\rho_{min}$ = −0.30 e $Å^{-3}$
163 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997a), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.085 (9)
Secondary atom site location: difference Fourier map	

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculat-

ing *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.21896 (6)	0.24305 (5)	0.06332 (5)	0.0512 (2)
N1	0.6240 (2)	0.36182 (16)	0.15956 (17)	0.0453 (4)
H1C	0.5109	0.3277	0.1189	0.054*
H1D	0.6921	0.2830	0.1256	0.054*
N2	0.8687 (2)	0.61144 (16)	0.35096 (15)	0.0406 (4)
N3	0.6741 (2)	1.20158 (19)	0.66763 (19)	0.0527 (4)
O1	0.6553 (2)	1.29264 (17)	0.60370 (19)	0.0710 (5)
O2	0.6467 (3)	1.2324 (2)	0.79697 (18)	0.0825 (6)
O3	0.1758 (2)	0.88143 (18)	0.8816 (2)	0.0721 (5)
C1	0.7023 (3)	0.4943 (2)	0.11475 (19)	0.0460 (4)
H1A	0.6205	0.5738	0.1384	0.055*
H1B	0.7165	0.4581	0.0100	0.055*
C2	0.8841 (3)	0.5617 (2)	0.19315 (19)	0.0450 (4)
H2A	0.9681	0.4841	0.1632	0.054*
H2B	0.9327	0.6501	0.1665	0.054*
C3	0.6164 (3)	0.4062 (2)	0.3206 (2)	0.0456 (4)
H3A	0.5761	0.3147	0.3454	0.055*
H3B	0.5295	0.4805	0.3564	0.055*
C4	0.8020 (3)	0.4773 (2)	0.3922 (2)	0.0458 (4)
H4A	0.7947	0.5100	0.4975	0.055*
H4B	0.8864	0.4001	0.3625	0.055*
C5	0.8183 (2)	0.75675 (18)	0.42769 (17)	0.0354 (4)
C6	0.8009 (2)	0.86723 (19)	0.36100 (18)	0.0403 (4)
H6A	0.8202	0.8418	0.2618	0.048*
C7	0.7560 (2)	1.0121 (2)	0.4393 (2)	0.0416 (4)
H7A	0.7459	1.0846	0.3937	0.050*
C8	0.7259 (2)	1.04990 (19)	0.58589 (19)	0.0402 (4)
C9	0.7443 (2)	0.9451 (2)	0.65606 (19)	0.0436 (4)
H9A	0.7259	0.9725	0.7556	0.052*
C10	0.7898 (2)	0.8006 (2)	0.57808 (19)	0.0412 (4)
H10A	0.8022	0.7301	0.6255	0.049*
H3C	0.070 (4)	0.851 (4)	0.908 (4)	0.161 (17)*
H3D	0.192 (4)	0.978 (2)	0.932 (4)	0.119 (12)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0505 (3)	0.0478 (3)	0.0549 (3)	−0.0029 (2)	−0.0015 (2)	0.0202 (2)
N1	0.0411 (8)	0.0349 (7)	0.0528 (9)	0.0034 (6)	−0.0028 (7)	0.0068 (6)
N2	0.0429 (8)	0.0333 (7)	0.0426 (8)	0.0026 (6)	0.0010 (6)	0.0099 (6)
N3	0.0486 (9)	0.0427 (9)	0.0552 (10)	0.0057 (7)	−0.0011 (7)	0.0021 (7)
O1	0.0838 (12)	0.0447 (8)	0.0861 (11)	0.0203 (8)	0.0102 (9)	0.0208 (8)

O2	0.1138 (15)	0.0672 (10)	0.0509 (9)	0.0295 (10)	0.0062 (9)	−0.0054 (8)
O3	0.0616 (10)	0.0425 (8)	0.1024 (13)	0.0119 (7)	0.0190 (9)	0.0109 (8)
C1	0.0560 (11)	0.0383 (9)	0.0385 (9)	0.0058 (8)	0.0029 (8)	0.0068 (7)
C2	0.0470 (10)	0.0372 (9)	0.0463 (10)	0.0077 (7)	0.0134 (8)	0.0078 (7)
C3	0.0466 (10)	0.0373 (9)	0.0548 (11)	0.0042 (7)	0.0057 (8)	0.0186 (8)
C4	0.0515 (11)	0.0353 (8)	0.0520 (10)	0.0068 (7)	−0.0044 (8)	0.0165 (8)
C5	0.0315 (8)	0.0347 (8)	0.0372 (8)	−0.0006 (6)	−0.0005 (6)	0.0104 (7)
C6	0.0455 (10)	0.0403 (9)	0.0340 (8)	0.0025 (7)	0.0034 (7)	0.0125 (7)
C7	0.0435 (9)	0.0368 (8)	0.0459 (10)	0.0021 (7)	0.0009 (7)	0.0170 (7)
C8	0.0369 (9)	0.0352 (8)	0.0426 (9)	0.0024 (7)	−0.0002 (7)	0.0068 (7)
C9	0.0462 (10)	0.0460 (9)	0.0341 (8)	0.0008 (7)	0.0021 (7)	0.0097 (7)
C10	0.0449 (10)	0.0410 (9)	0.0386 (9)	0.0017 (7)	0.0001 (7)	0.0159 (7)

Geometric parameters (Å, °)

N1—C3	1.484 (2)	C2—H2B	0.970
N1—C1	1.491 (2)	C3—C4	1.510 (3)
N1—H1C	0.900	C3—H3A	0.970
N1—H1D	0.900	C3—H3B	0.970
N2—C5	1.385 (2)	C4—H4A	0.970
N2—C2	1.457 (2)	C4—H4B	0.970
N2—C4	1.462 (2)	C5—C6	1.400 (2)
N3—O2	1.218 (2)	C5—C10	1.405 (2)
N3—O1	1.224 (2)	C6—C7	1.370 (2)
N3—C8	1.446 (2)	C6—H6A	0.930
O3—H3C	0.871 (18)	C7—C8	1.376 (2)
O3—H3D	0.853 (18)	C7—H7A	0.930
C1—C2	1.503 (3)	C8—C9	1.379 (3)
C1—H1A	0.970	C9—C10	1.368 (2)
C1—H1B	0.970	C9—H9A	0.930
C2—H2A	0.970	C10—H10A	0.930
C3—N1—C1	112.33 (13)	N1—C3—H3B	109.6
C3—N1—H1C	109.1	C4—C3—H3B	109.6
C1—N1—H1C	109.1	H3A—C3—H3B	108.2
C3—N1—H1D	109.1	N2—C4—C3	110.52 (14)
C1—N1—H1D	109.1	N2—C4—H4A	109.5
H1C—N1—H1D	107.9	C3—C4—H4A	109.5
C5—N2—C2	120.40 (14)	N2—C4—H4B	109.5
C5—N2—C4	119.96 (14)	C3—C4—H4B	109.5
C2—N2—C4	109.57 (13)	H4A—C4—H4B	108.1
O2—N3—O1	122.48 (17)	N2—C5—C6	121.83 (15)
O2—N3—C8	118.60 (17)	N2—C5—C10	120.60 (14)
O1—N3—C8	118.90 (17)	C6—C5—C10	117.52 (15)
H3C—O3—H3D	103 (2)	C7—C6—C5	121.15 (15)
N1—C1—C2	109.55 (15)	C7—C6—H6A	119.4
N1—C1—H1A	109.8	C5—C6—H6A	119.4
C2—C1—H1A	109.8	C6—C7—C8	119.67 (16)
N1—C1—H1B	109.8	C6—C7—H7A	120.2
C2—C1—H1B	109.8	C8—C7—H7A	120.2

H1A—C1—H1B	108.2	C7—C8—C9	120.92 (16)
N2—C2—C1	111.17 (15)	C7—C8—N3	119.60 (16)
N2—C2—H2A	109.4	C9—C8—N3	119.48 (16)
C1—C2—H2A	109.4	C10—C9—C8	119.44 (16)
N2—C2—H2B	109.4	C10—C9—H9A	120.3
C1—C2—H2B	109.4	C8—C9—H9A	120.3
H2A—C2—H2B	108.0	C9—C10—C5	121.27 (15)
N1—C3—C4	110.06 (15)	C9—C10—H10A	119.4
N1—C3—H3A	109.6	C5—C10—H10A	119.4
C4—C3—H3A	109.6		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3D···Cl1^{i}	0.853 (18)	2.317 (18)	3.1681 (18)	176 (3)
O3—H3C···Cl1^{ii}	0.871 (18)	2.273 (19)	3.135 (2)	170 (4)
N1—H1D···O3^{iii}	0.90	1.88	2.741 (2)	161
N1—H1C···Cl1	0.90	2.21	3.0994 (17)	168

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

Fig. 1

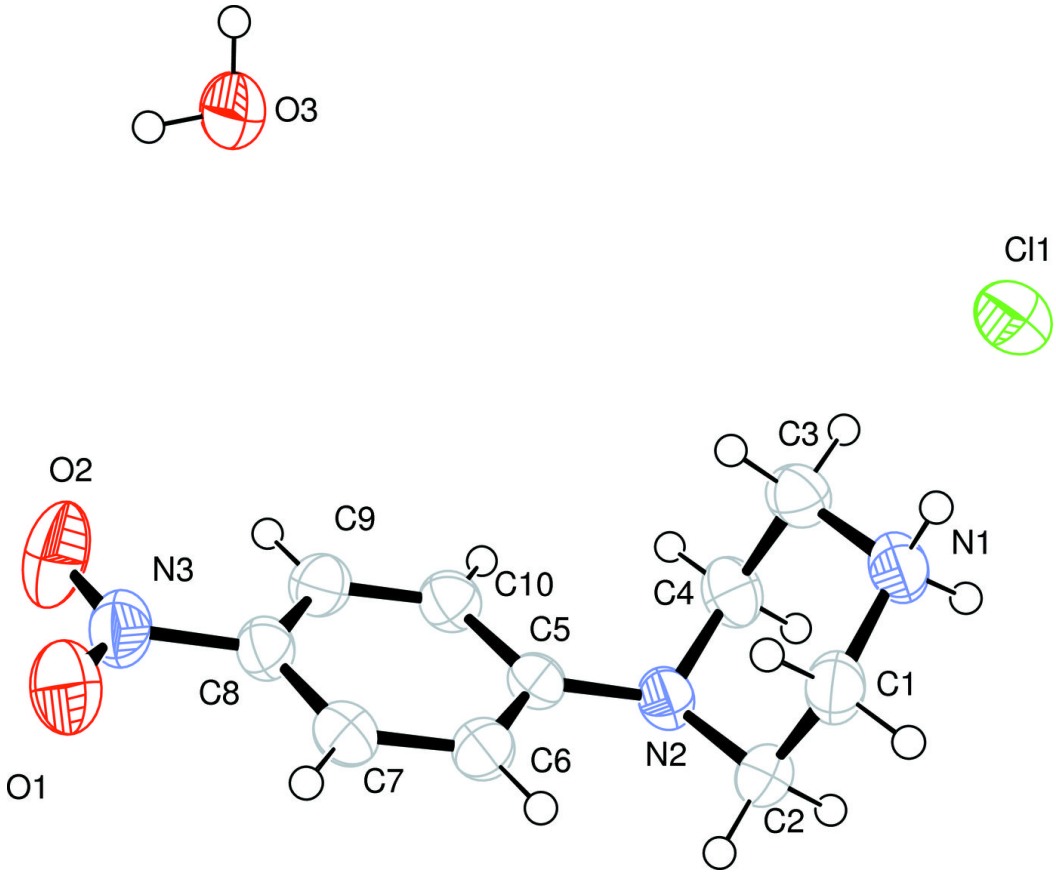

Fig. 2

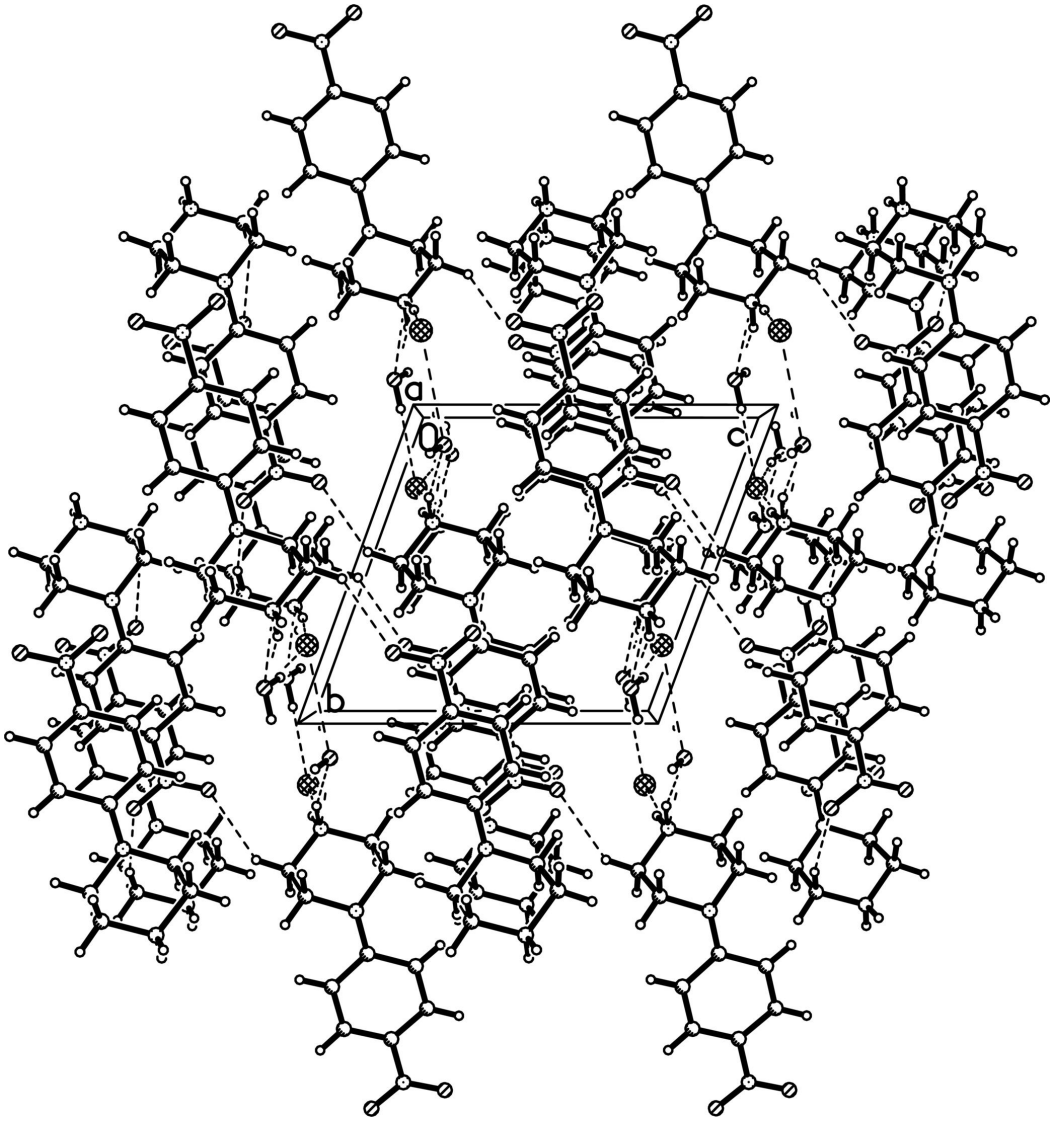

Fig. 3

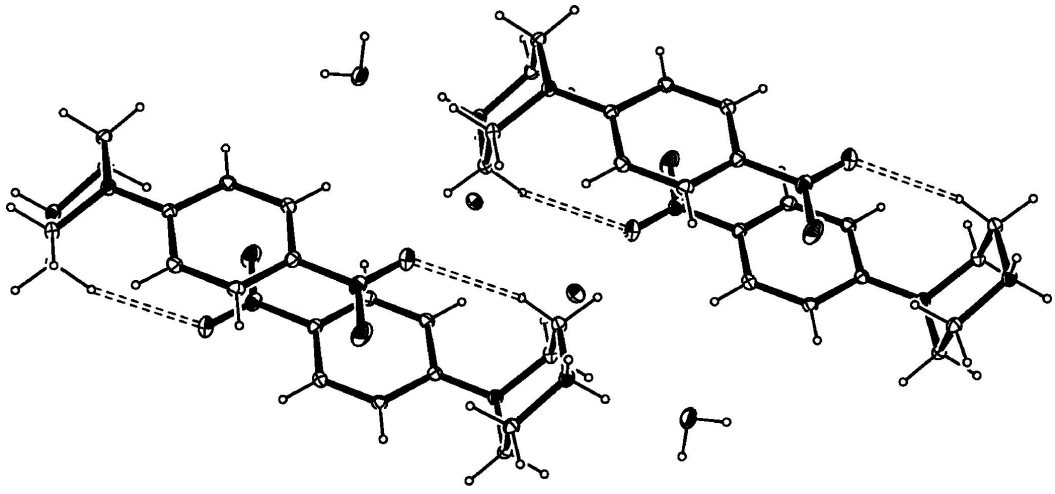

Fig. 4

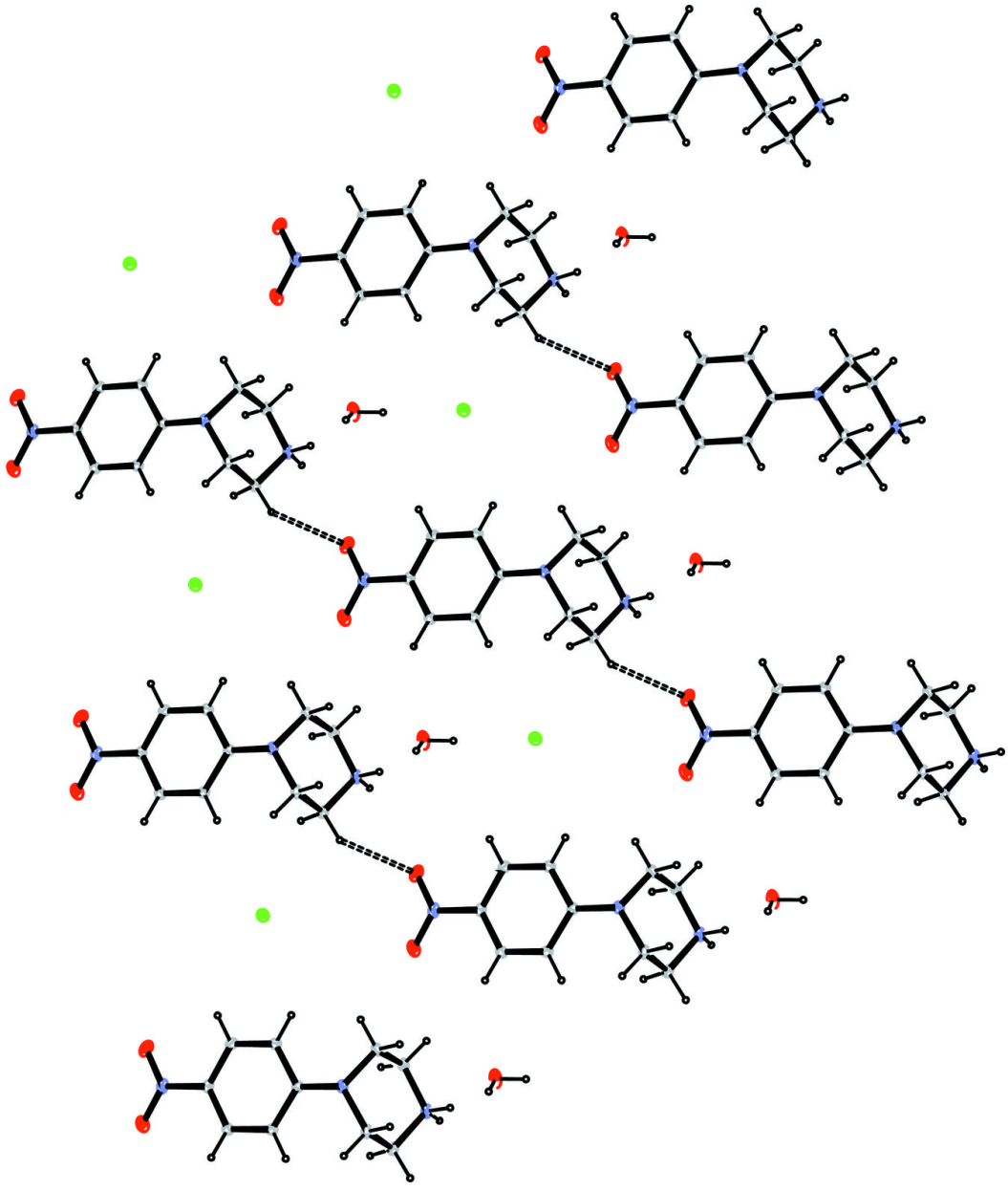

Fig. 5