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4-(*o*-Tolyl)piperazin-1-ium chlorideHoong-Kun Fun,^{a,†} Safra Izuanı Jama Asik,^a
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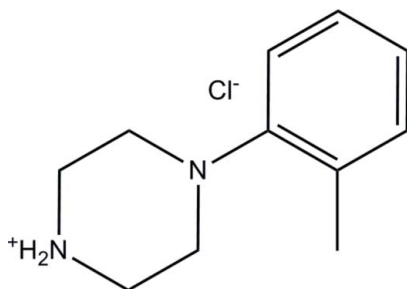
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.032; wR factor = 0.092; data-to-parameter ratio = 38.1.

In the title molecular salt, $\text{C}_{11}\text{H}_{17}\text{N}_2^+\cdot\text{Cl}^-$, the piperazin-1-ium ring adopts a chair conformation with the aromatic ring in a pseudo-equatorial orientation. The dihedral angle between the benzene ring and the mean plane of the piperazin-1-ium ring is $51.22(6)^\circ$. In the crystal, $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds link the molecules into chains propagating in $[100]$. Weak $\text{C}-\text{H}\cdots\pi$ interactions also occur.

Related literature

For the medicinal applications of piperazine derivatives, see: Amir *et al.* (2004); Omar & AboulWafa (1986); El-Emam *et al.* (2004). For conformational analysis, see: Cremer & Pople (1975). For a related structure, see: Ben Gharbia *et al.* (2008).



Experimental

Crystal data

 $\text{C}_{11}\text{H}_{17}\text{N}_2^+\cdot\text{Cl}^-$ $M_r = 212.72$ Orthorhombic, $P2_12_12_1$ $a = 8.1572(2)$ Å $b = 11.2821(3)$ Å $c = 12.4256(3)$ Å $V = 1143.53(5)$ Å³ $Z = 4$ Mo $K\alpha$ radiation
 $\mu = 0.30$ mm⁻¹ $T = 296$ K
 $0.54 \times 0.33 \times 0.23$ mm

Data collection

Bruker APEX DUO CCD
diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)
 $T_{\min} = 0.854$, $T_{\max} = 0.936$ 8246 measured reflections
4871 independent reflections
4172 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.092$
 $S = 0.95$
4871 reflections
128 parameters
H-atom parameters constrained $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³
Absolute structure: Flack (1983),
1943 Friedel pairs
Flack parameter: 0.02 (4)

Table 1

Hydrogen-bond geometry (Å, °).

 Cg2 is the centroid of $\text{C5}-\text{C10}$ ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N1}\cdots\text{CH}^{\text{i}}$	0.87	2.26	3.1155 (10)	167
$\text{N1}-\text{H2N1}\cdots\text{CH}^{\text{ii}}$	0.87	2.23	3.0956 (10)	177
$\text{C3}-\text{H3A}\cdots\text{Cg2}^{\text{iii}}$	0.97	2.79	3.5342 (11)	134

Symmetry codes: (i) $x+1, y+1, z+1$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iii) $-x+\frac{3}{2}, -y+2, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6474).

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† Thomson Reuters ResearcherID: A-3561-2009.

supplementary materials

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4-(*o*-Tolyl)piperazin-1-ium chloride

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Comment

During the past years considerable evidence has been accumulated to demonstrate the efficacy of piperazine derivatives possessing antibacterial and antimicrobial activities (Amir *et al.*, 2004). For instance, Linezolid, Eperezolid, which are currently important antibiotics used for the treatment of microbial infections, contain the piperazine and morpholine ring in their structures (Omar & AboulWafa, 1986, El-Emam *et al.*, 2004).

As shown in Fig. 1, the asymmetric unit of the title compound contains a 4-(*o*-tolyl)piperazin-1-ium cation and a chloride anion. The benzene (C5–C10) ring and the mean plane of 4-(*o*-tolyl) piperazin-1-ium (C1–C4) make a dihedral angle of 51.22 (6)°. The piperazin-1-ium (N1/N2/C1–C4) adopts a chair conformation with puckering parameters $Q = 0.5859$ (11) Å, $\theta = 173.86$ (11)° and $\varphi = 3.0$ (11)° (Cremer & Pople, 1975). It is also noted that the geometric parameters [$d_{av}(C-N) = 1.4653$ (13) Å and $d_{av}(C-C) = 1.5082$ (16) Å for the 4-(*o*-tolyl)piperazin-1-ium moiety are in close agreement with those found in 4-(2,3-dimethylphenyl)piperazin-1-ium chloride monohydrate (Ben Gharbia *et al.*, 2008).

In the crystal (Fig. 2), N1—H1N1...Cl1 and N1—H2N1...Cl1 hydrogen bonds (Table 1) link the molecules into chains along the *a* axis. In addition, the crystal packing features weak intermolecular C—H... π interactions involving the benzene (C5–C10 ; centroid *Cg*2) ring with a distance of 3.5342 (11) Å.

Experimental

To a stirred solution of 2-fluorotoluene (2g, 0.0181 mol) and anhydrous potassium carbonate (3.7g, 0.027 mol) in dry acetonitrile (20 ml), piperazine-1-carboxylic acid tert butyl ester (3.38g, 0.0181 mol) was added dropwise at RT and reaction mixture was stirred at RT for 5h. After the completion of reaction, the reaction mixture was filtered and the filtrate was concentrated. The product (5g) was then dissolved with HCl in dioxane (25 ml) and stirred at RT for 2 h. The reaction mixture was concentrated through high vacuum. The crude product was recrystallised from hot ethanol to afford title compound as colourless blocks (3.0g, 66%). M.p > 620K.

Refinement

Atom H1N1 and H2N1 were located in a difference Fourier map and fixed to the positions with N–H = 0.8702 and 0.8662 Å. The remaining H atoms were positioned geometrically and refined using a riding model with C–H = 0.93–0.97 Å. The U_{iso} values were constrained to be 1.5 U_{eq} of the carrier atom for methyl H atoms and 1.2 U_{eq} for the remaining H atoms. A rotating group model was used for the methyl groups. 1943 Friedel pairs were used to determine the absolute configuration.

Figures

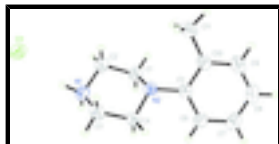


Fig. 1. The structure of the title compound, showing 50% probability displacement ellipsoids.

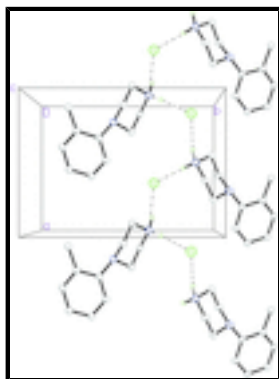


Fig. 2. The crystal packing, viewed along the *c* axis, showing one-dimensional chains along the *a* axis. Hydrogen atoms that not involved in hydrogen bonding (dashed lines) are omitted for clarity.

4-(*o*-Tolyl)piperazin-1-ium chloride

Crystal data

$C_{11}H_{17}N_2^+ \cdot Cl^-$

$M_r = 212.72$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 8.1572$ (2) Å

$b = 11.2821$ (3) Å

$c = 12.4256$ (3) Å

$V = 1143.53$ (5) Å³

$Z = 4$

$F(000) = 456$

$D_x = 1.236$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3871 reflections

$\theta = 2.4$ – 35.1°

$\mu = 0.30$ mm⁻¹

$T = 296$ K

Block, colourless

$0.54 \times 0.33 \times 0.23$ mm

Data collection

Bruker APEX DUO CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)

$T_{\min} = 0.854$, $T_{\max} = 0.936$

8246 measured reflections

4871 independent reflections

4172 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 35.5^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -7 \rightarrow 13$

$k = -10 \rightarrow 18$

$l = -6 \rightarrow 20$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.032$$

$$wR(F^2) = 0.092$$

$$S = 0.95$$

4871 reflections

128 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.0493P]$$

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

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

$$\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 1943 Friedel pairs

Flack parameter: 0.02 (4)

Special details

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

Refinement. 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 $F^2 > 2\sigma(F^2)$ is used only for calculating 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.37470 (3)	0.15197 (3)	0.10255 (2)	0.04298 (7)
N1	1.02356 (12)	1.12619 (8)	1.00673 (8)	0.04027 (19)
H1N1	1.1142	1.1422	1.0407	0.048*
H2N1	0.9841	1.1900	0.9779	0.048*
N2	0.81569 (10)	0.94027 (7)	0.93398 (6)	0.03177 (15)
C1	0.93463 (14)	0.99338 (10)	0.86053 (8)	0.0381 (2)
H1A	0.8839	1.0581	0.8214	0.046*
H1B	0.9713	0.9347	0.8088	0.046*
C2	1.07872 (14)	1.03893 (12)	0.92397 (10)	0.0461 (2)
H2A	1.1337	0.9732	0.9590	0.055*
H2B	1.1563	1.0765	0.8757	0.055*
C3	0.89107 (15)	1.07704 (11)	1.07575 (8)	0.0427 (2)
H3A	0.8502	1.1384	1.1234	0.051*
H3B	0.9346	1.0134	1.1197	0.051*
C4	0.75240 (13)	1.03055 (10)	1.00711 (8)	0.0380 (2)
H4A	0.6679	0.9967	1.0526	0.046*
H4B	0.7042	1.0949	0.9662	0.046*
C5	0.69593 (12)	0.86761 (8)	0.88251 (6)	0.03052 (16)
C6	0.53332 (14)	0.90410 (10)	0.87004 (8)	0.0382 (2)
H6A	0.5015	0.9783	0.8951	0.046*
C7	0.41906 (15)	0.83147 (12)	0.82098 (9)	0.0468 (3)

supplementary materials

H7A	0.3115	0.8571	0.8125	0.056*
C8	0.46538 (18)	0.72070 (12)	0.78461 (10)	0.0507 (3)
H8A	0.3895	0.6718	0.7507	0.061*
C9	0.62468 (18)	0.68295 (10)	0.79889 (9)	0.0451 (2)
H9A	0.6539	0.6076	0.7754	0.054*
C10	0.74324 (14)	0.75387 (9)	0.84727 (7)	0.03504 (18)
C11	0.91432 (17)	0.70764 (11)	0.86458 (11)	0.0482 (3)
H11A	0.9117	0.6227	0.8691	0.072*
H11B	0.9577	0.7396	0.9303	0.072*
H11C	0.9827	0.7312	0.8054	0.072*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.03237 (11)	0.04279 (13)	0.05376 (13)	-0.00052 (10)	0.00001 (10)	0.00279 (11)
N1	0.0329 (4)	0.0355 (4)	0.0524 (5)	-0.0008 (3)	-0.0083 (3)	-0.0036 (3)
N2	0.0313 (4)	0.0318 (4)	0.0322 (3)	-0.0009 (3)	0.0029 (3)	-0.0031 (3)
C1	0.0336 (5)	0.0428 (5)	0.0377 (4)	-0.0050 (4)	0.0063 (4)	-0.0029 (4)
C2	0.0295 (4)	0.0507 (6)	0.0580 (6)	-0.0033 (4)	0.0039 (4)	-0.0098 (5)
C3	0.0469 (6)	0.0424 (5)	0.0388 (4)	-0.0020 (5)	-0.0015 (4)	-0.0088 (4)
C4	0.0343 (4)	0.0393 (5)	0.0404 (4)	-0.0028 (4)	0.0055 (4)	-0.0101 (4)
C5	0.0328 (4)	0.0306 (4)	0.0282 (3)	-0.0023 (3)	0.0012 (3)	0.0013 (3)
C6	0.0340 (4)	0.0396 (5)	0.0410 (4)	-0.0005 (4)	-0.0011 (4)	0.0005 (4)
C7	0.0363 (5)	0.0571 (7)	0.0470 (5)	-0.0074 (5)	-0.0054 (4)	0.0010 (5)
C8	0.0522 (7)	0.0509 (7)	0.0489 (5)	-0.0197 (6)	-0.0047 (5)	-0.0018 (5)
C9	0.0574 (7)	0.0347 (5)	0.0433 (5)	-0.0106 (5)	0.0040 (5)	-0.0040 (4)
C10	0.0425 (5)	0.0295 (4)	0.0331 (4)	-0.0009 (4)	0.0021 (3)	0.0016 (3)
C11	0.0518 (7)	0.0381 (5)	0.0548 (6)	0.0117 (5)	-0.0019 (5)	-0.0026 (5)

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

N1—C3	1.4869 (15)	C4—H4B	0.9700
N1—C2	1.4930 (15)	C5—C6	1.3974 (14)
N1—H1N1	0.8702	C5—C10	1.4098 (13)
N1—H2N1	0.8662	C6—C7	1.3827 (16)
N2—C5	1.4267 (12)	C6—H6A	0.9300
N2—C4	1.4593 (12)	C7—C8	1.382 (2)
N2—C1	1.4606 (13)	C7—H7A	0.9300
C1—C2	1.5056 (16)	C8—C9	1.379 (2)
C1—H1A	0.9700	C8—H8A	0.9300
C1—H1B	0.9700	C9—C10	1.3918 (16)
C2—H2A	0.9700	C9—H9A	0.9300
C2—H2B	0.9700	C10—C11	1.5053 (17)
C3—C4	1.5107 (15)	C11—H11A	0.9600
C3—H3A	0.9700	C11—H11B	0.9600
C3—H3B	0.9700	C11—H11C	0.9600
C4—H4A	0.9700		
C3—N1—C2	111.74 (9)	C3—C4—H4A	109.8

C3—N1—H1N1	114.6	N2—C4—H4B	109.8
C2—N1—H1N1	102.4	C3—C4—H4B	109.8
C3—N1—H2N1	106.2	H4A—C4—H4B	108.3
C2—N1—H2N1	112.0	C6—C5—C10	119.57 (9)
H1N1—N1—H2N1	110.1	C6—C5—N2	122.03 (9)
C5—N2—C4	115.97 (8)	C10—C5—N2	118.35 (9)
C5—N2—C1	114.24 (7)	C7—C6—C5	120.94 (11)
C4—N2—C1	109.74 (8)	C7—C6—H6A	119.5
N2—C1—C2	109.36 (9)	C5—C6—H6A	119.5
N2—C1—H1A	109.8	C6—C7—C8	119.73 (12)
C2—C1—H1A	109.8	C6—C7—H7A	120.1
N2—C1—H1B	109.8	C8—C7—H7A	120.1
C2—C1—H1B	109.8	C9—C8—C7	119.67 (11)
H1A—C1—H1B	108.3	C9—C8—H8A	120.2
N1—C2—C1	110.51 (9)	C7—C8—H8A	120.2
N1—C2—H2A	109.5	C8—C9—C10	122.20 (11)
C1—C2—H2A	109.5	C8—C9—H9A	118.9
N1—C2—H2B	109.5	C10—C9—H9A	118.9
C1—C2—H2B	109.5	C9—C10—C5	117.86 (11)
H2A—C2—H2B	108.1	C9—C10—C11	120.45 (10)
N1—C3—C4	110.37 (8)	C5—C10—C11	121.65 (10)
N1—C3—H3A	109.6	C10—C11—H11A	109.5
C4—C3—H3A	109.6	C10—C11—H11B	109.5
N1—C3—H3B	109.6	H11A—C11—H11B	109.5
C4—C3—H3B	109.6	C10—C11—H11C	109.5
H3A—C3—H3B	108.1	H11A—C11—H11C	109.5
N2—C4—C3	109.21 (9)	H11B—C11—H11C	109.5
N2—C4—H4A	109.8		
C5—N2—C1—C2	-164.57 (9)	C10—C5—C6—C7	-1.76 (15)
C4—N2—C1—C2	63.23 (11)	N2—C5—C6—C7	-179.23 (10)
C3—N1—C2—C1	53.08 (13)	C5—C6—C7—C8	0.65 (17)
N2—C1—C2—N1	-57.39 (13)	C6—C7—C8—C9	0.87 (18)
C2—N1—C3—C4	-53.24 (12)	C7—C8—C9—C10	-1.31 (18)
C5—N2—C4—C3	165.32 (8)	C8—C9—C10—C5	0.20 (16)
C1—N2—C4—C3	-63.38 (11)	C8—C9—C10—C11	177.96 (11)
N1—C3—C4—N2	57.89 (12)	C6—C5—C10—C9	1.32 (13)
C4—N2—C5—C6	22.41 (12)	N2—C5—C10—C9	178.88 (9)
C1—N2—C5—C6	-106.74 (10)	C6—C5—C10—C11	-176.42 (10)
C4—N2—C5—C10	-155.10 (9)	N2—C5—C10—C11	1.14 (13)
C1—N2—C5—C10	75.76 (11)		

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

Cg2 is the centroid of C5—C10 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N1 \cdots C11 ⁱ	0.87	2.26	3.1155 (10)	167
N1—H2N1 \cdots C11 ⁱⁱ	0.87	2.23	3.0956 (10)	177
C3—H3A \cdots Cg2 ⁱⁱⁱ	0.97	2.79	3.5342 (11)	134

supplementary materials

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

Fig. 1

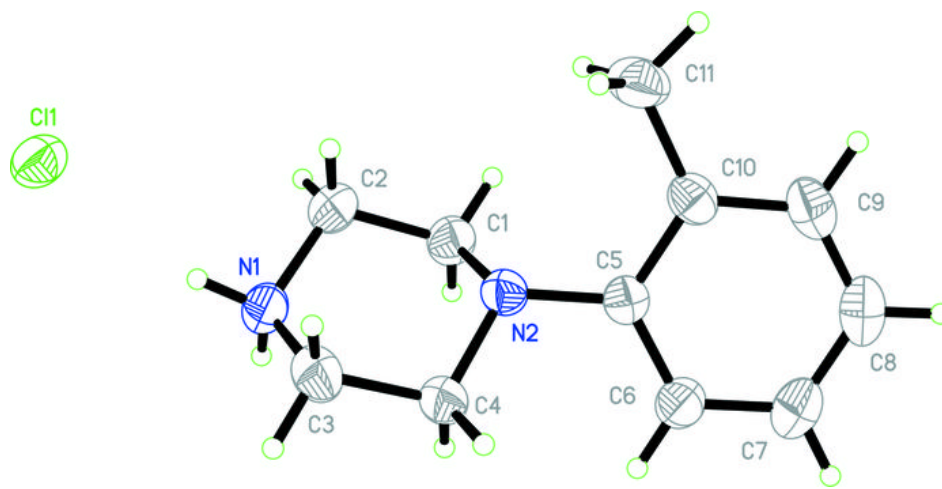


Fig. 2

