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4-(3-Chlorophenyl)-1-(3-chloropropyl)piperazin-1-ium chloride redetermined at 100 K

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Keywords: crystal structure; 5-HT1 serotonin receptor ligands; piperazinium salts; disorder.

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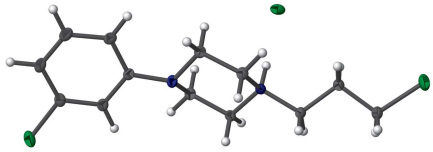
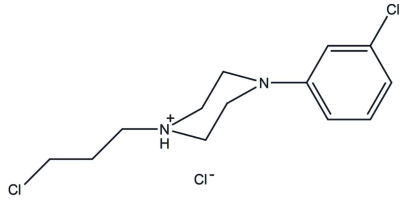
Structural data: full structural data are available from iucrdata.iucr.org

The crystal structure of the title salt, $C_{13}H_{19}Cl_2N_2^+\cdot Cl^-$, has been reported previously [Homrighausen & Krause Bauer (2002). *Acta Cryst.* E**58**, o1395–o1396] based on room-temperature data, where it was found to contain a disordered chloropropyl group. We now present the structure at 100 K in which the chloropropyl group is ordered. The piperazine ring adopts a chair conformation with the exocyclic N—C bonds in equatorial orientations. The dihedral angle between the piperazine ring (all atoms) and the benzene ring is 28.47 (5)°. The chloropropyl group has an extended conformation [N—C—C—C = −177.25 (8) ° and C—C—C—Cl = 174.23 (7)°]. In the crystal, charge-assisted N—H···Cl hydrogen bonds link the cation and anion into ion pairs. Numerous weak C—H···Cl interactions link the ion pairs into a three-dimensional network. Short Cl···Cl contacts [3.2419 (4) Å] are also observed.

3D view



Chemical scheme



Structure description

The title compound $C_{13}H_{19}Cl_2N_2^+Cl^-$ belongs to a class of 5-HT1 (5-hydroxytryptamine1) subtype serotonin receptor ligands (Okamoto *et al.*, 1993; Verdonk *et al.*, 1992; Dalpiaz *et al.*, 1996). The structure of the title compound (Fig. 1) has been previously reported (Homrighausen & Krause Bauer, 2002) but was collected at 296 K and contained a disordered chloropropyl group. This redetermination at 100 K shows that the chloropropyl group is ordered. In the crystal, charge-assisted N—H···Cl hydrogen bonds and C—H···Cl secondary interactions occur (Table 1 and Fig. 2), resulting in a three-dimensional supramolecular architecture.

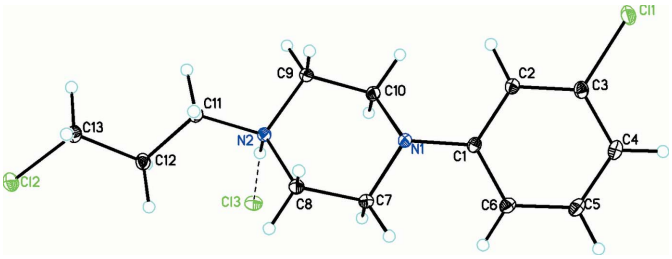


Figure 1
Diagram of $C_{13}H_{19}Cl_2N_2^+Cl^-$, with hydrogen bonds shown as dashed lines. Atomic displacement parameters are shown at the 30% probability level.

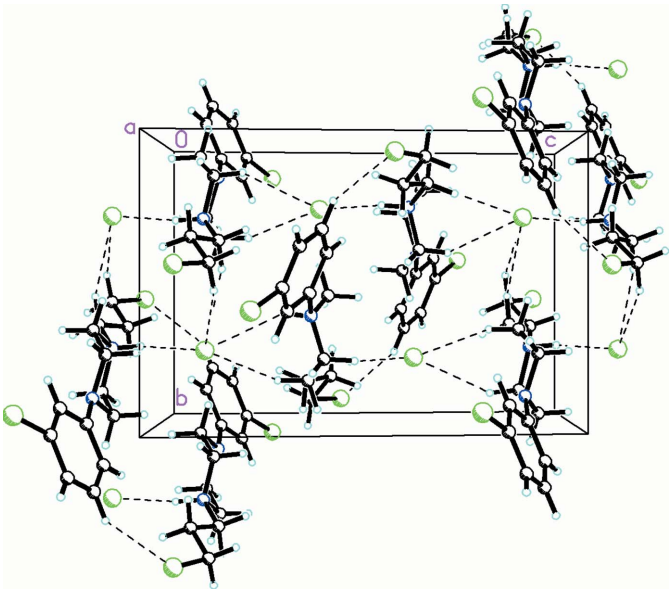


Figure 2
Packing daigram viewed along the *a* axis, showing the extensive network of N—H···Cl hydrogen bonds and C—H···Cl secondary interactions (indicated by dashed lines).

Synthesis and crystallization

The title compound was obtained from Sigma Aldrich and crystals suitable for a single-crystal X-ray diffraction study were obtained by dissolving the title compound in ethanol and allowing the solvent to evaporate slowly at room temperature.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

RJB wishes to acknowledge NSF award 1205608, Partnership for Reduced Dimensional Materials, for partial funding of this research. The authors wish to acknowledge the assistance of Dr Matthias Zeller in the collection of the diffraction data and NSF Grant CHE 0087210, Ohio Board of Regents Grant CAP-491, and Youngstown State University for funds to purchase the X-ray diffractometer.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*N*···Cl3	0.929 (15)	2.139 (15)	3.0629 (9)	172.4 (13)
C8—H8*B*···Cl3^{i}	0.99	2.90	3.7757 (10)	147
C9—H9*A*···Cl3^{i}	0.99	2.83	3.7200 (10)	150
C11—H11*A*···Cl3^{ii}	0.99	2.78	3.6981 (11)	155
C12—H12*A*···Cl1^{iii}	0.99	2.87	3.5172 (11)	123
C12—H12*B*···Cl3	0.99	2.94	3.6149 (10)	126
C13—H13*A*···Cl3^{ii}	0.99	2.90	3.7940 (11)	150
C13—H13*B*···Cl1^{iii}	0.99	2.95	3.6095 (12)	125

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{19}Cl_2N_2^+\cdot Cl^-$
M_r	309.65
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	10.9608 (9), 9.5199 (8), 14.0262 (11)
β (°)	95.398 (1)
V (Å^3)	1457.1 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.61
Crystal size (mm)	0.55 × 0.32 × 0.30
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.610, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32810, 4808, 4407
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.748
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.083, 1.08
No. of reflections	4808
No. of parameters	167
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.69, −0.33

Computer programs: *APEX2* (Bruker, 2005), *SAINT* (Bruker, 2002), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *SHELXTL* (Sheldrick, 2008).

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full crystallographic data

IUCrData (2016). **1**, x160168 [https://doi.org/10.1107/S2414314616001681]

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Crystal data

$C_{13}H_{19}Cl_2N_2^+\cdot Cl^-$
M_r = 309.65
Monoclinic, $P2_1/c$
a = 10.9608 (9) Å
b = 9.5199 (8) Å
c = 14.0262 (11) Å
β = 95.398 (1)°
V = 1457.1 (2) Å^3
Z = 4
$F(000)$ = 648
D_x = 1.412 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9973 reflections
θ = 2.6–31.8°
μ = 0.61 mm^{-1}
T = 100 K
Block, colourless
0.55 × 0.32 × 0.30 mm

Data collection

Bruker APEXII diffractometer
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.610, T_{max} = 0.746
32810 measured reflections
4808 independent reflections
4407 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 32.1°, θ_{min} = 2.6°
h = −16→16
k = −14→14
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.08
4808 reflections
167 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.537P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.69 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.19355 (2)	0.41129 (3)	0.74761 (2)	0.02408 (7)
Cl2	0.89868 (2)	0.06195 (3)	0.56586 (2)	0.02604 (7)
Cl3	0.45091 (2)	0.23674 (3)	0.38594 (2)	0.01897 (6)
N1	0.23210 (7)	0.38855 (8)	0.62774 (6)	0.01511 (15)
N2	0.44985 (7)	0.22760 (8)	0.60415 (6)	0.01394 (14)
H2N	0.4481 (13)	0.2217 (15)	0.5379 (11)	0.016 (3)*
C1	0.12197 (9)	0.46460 (10)	0.62867 (7)	0.01423 (16)
C2	0.02649 (9)	0.40667 (10)	0.67638 (7)	0.01616 (17)
H2A	0.0346	0.3152	0.7033	0.019*
C3	−0.07914 (9)	0.48363 (10)	0.68387 (7)	0.01700 (17)
C4	−0.09634 (10)	0.61775 (11)	0.64557 (8)	0.01990 (19)
H4A	−0.1700	0.6685	0.6509	0.024*
C5	−0.00117 (10)	0.67422 (11)	0.59915 (8)	0.02107 (19)
H5A	−0.0097	0.7662	0.5731	0.025*
C6	0.10650 (10)	0.59958 (10)	0.58970 (7)	0.01782 (18)
H6A	0.1695	0.6404	0.5567	0.021*
C7	0.33718 (9)	0.45553 (10)	0.58992 (7)	0.01646 (17)
H7A	0.3409	0.5558	0.6088	0.020*
H7B	0.3285	0.4504	0.5191	0.020*
C8	0.45436 (9)	0.38120 (10)	0.62920 (7)	0.01595 (17)
H8A	0.5254	0.4252	0.6023	0.019*
H8B	0.4654	0.3920	0.6997	0.019*
C9	0.33685 (9)	0.16198 (10)	0.63727 (7)	0.01506 (16)
H9A	0.3424	0.1627	0.7081	0.018*
H9B	0.3309	0.0630	0.6156	0.018*
C10	0.22316 (9)	0.24111 (10)	0.59790 (7)	0.01574 (17)
H10A	0.2145	0.2354	0.5271	0.019*
H10B	0.1498	0.1978	0.6218	0.019*
C11	0.56026 (9)	0.14857 (11)	0.64726 (7)	0.01708 (17)
H11A	0.5382	0.0484	0.6537	0.020*
H11B	0.5840	0.1856	0.7123	0.020*
C12	0.66940 (9)	0.15917 (11)	0.58844 (7)	0.01750 (17)
H12A	0.6965	0.2581	0.5850	0.021*
H12B	0.6468	0.1250	0.5225	0.021*
C13	0.77155 (9)	0.06936 (11)	0.63720 (8)	0.01945 (18)
H13A	0.7406	−0.0268	0.6469	0.023*
H13B	0.7987	0.1095	0.7008	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01963 (12)	0.02193 (12)	0.03227 (14)	0.00122 (8)	0.01077 (10)	−0.00347 (9)
Cl2	0.01862 (12)	0.02468 (13)	0.03645 (15)	0.00401 (9)	0.01116 (10)	0.00181 (10)
Cl3	0.02473 (12)	0.02111 (12)	0.01101 (10)	−0.00293 (8)	0.00141 (8)	0.00052 (7)
N1	0.0135 (3)	0.0116 (3)	0.0205 (4)	0.0004 (3)	0.0030 (3)	0.0001 (3)

N2	0.0142 (3)	0.0143 (3)	0.0136 (3)	0.0015 (3)	0.0030 (3)	0.0010 (3)
C1	0.0152 (4)	0.0133 (4)	0.0140 (4)	0.0014 (3)	0.0002 (3)	−0.0016 (3)
C2	0.0162 (4)	0.0148 (4)	0.0176 (4)	0.0015 (3)	0.0023 (3)	−0.0006 (3)
C3	0.0160 (4)	0.0173 (4)	0.0178 (4)	0.0009 (3)	0.0023 (3)	−0.0037 (3)
C4	0.0196 (4)	0.0188 (4)	0.0209 (4)	0.0062 (3)	0.0002 (3)	−0.0022 (3)
C5	0.0239 (5)	0.0166 (4)	0.0225 (5)	0.0051 (4)	0.0008 (4)	0.0021 (3)
C6	0.0200 (4)	0.0154 (4)	0.0179 (4)	0.0014 (3)	0.0012 (3)	0.0022 (3)
C7	0.0152 (4)	0.0136 (4)	0.0208 (4)	−0.0006 (3)	0.0026 (3)	0.0019 (3)
C8	0.0149 (4)	0.0141 (4)	0.0189 (4)	−0.0006 (3)	0.0018 (3)	−0.0005 (3)
C9	0.0152 (4)	0.0134 (4)	0.0171 (4)	0.0001 (3)	0.0044 (3)	0.0010 (3)
C10	0.0150 (4)	0.0127 (4)	0.0196 (4)	−0.0002 (3)	0.0018 (3)	−0.0013 (3)
C11	0.0158 (4)	0.0193 (4)	0.0165 (4)	0.0044 (3)	0.0032 (3)	0.0036 (3)
C12	0.0158 (4)	0.0215 (4)	0.0156 (4)	0.0032 (3)	0.0035 (3)	0.0020 (3)
C13	0.0165 (4)	0.0207 (4)	0.0216 (5)	0.0042 (3)	0.0045 (3)	0.0028 (3)

Geometric parameters (Å, º)

Cl1—C3	1.7485 (11)	C7—C8	1.5234 (13)
Cl2—C13	1.7918 (11)	C7—H7A	0.9900
N1—C1	1.4087 (12)	C7—H7B	0.9900
N1—C7	1.4592 (12)	C8—H8A	0.9900
N1—C10	1.4654 (12)	C8—H8B	0.9900
N2—C9	1.4995 (12)	C9—C10	1.5151 (13)
N2—C11	1.5029 (12)	C9—H9A	0.9900
N2—C8	1.5037 (12)	C9—H9B	0.9900
N2—H2N	0.929 (15)	C10—H10A	0.9900
C1—C6	1.4005 (13)	C10—H10B	0.9900
C1—C2	1.4067 (14)	C11—C12	1.5191 (14)
C2—C3	1.3824 (13)	C11—H11A	0.9900
C2—H2A	0.9500	C11—H11B	0.9900
C3—C4	1.3912 (14)	C12—C13	1.5193 (14)
C4—C5	1.3888 (16)	C12—H12A	0.9900
C4—H4A	0.9500	C12—H12B	0.9900
C5—C6	1.3945 (14)	C13—H13A	0.9900
C5—H5A	0.9500	C13—H13B	0.9900
C6—H6A	0.9500		
C1—N1—C7	119.02 (8)	C7—C8—H8A	109.4
C1—N1—C10	117.42 (8)	N2—C8—H8B	109.4
C7—N1—C10	110.40 (8)	C7—C8—H8B	109.4
C9—N2—C11	108.92 (7)	H8A—C8—H8B	108.0
C9—N2—C8	110.04 (7)	N2—C9—C10	110.79 (7)
C11—N2—C8	112.66 (8)	N2—C9—H9A	109.5
C9—N2—H2N	110.1 (9)	C10—C9—H9A	109.5
C11—N2—H2N	108.2 (9)	N2—C9—H9B	109.5
C8—N2—H2N	106.8 (9)	C10—C9—H9B	109.5
C6—C1—C2	118.50 (9)	H9A—C9—H9B	108.1
C6—C1—N1	122.71 (9)	N1—C10—C9	109.97 (8)

C2—C1—N1	118.65 (8)	N1—C10—H10A	109.7
C3—C2—C1	119.62 (9)	C9—C10—H10A	109.7
C3—C2—H2A	120.2	N1—C10—H10B	109.7
C1—C2—H2A	120.2	C9—C10—H10B	109.7
C2—C3—C4	122.76 (9)	H10A—C10—H10B	108.2
C2—C3—Cl1	118.44 (8)	N2—C11—C12	113.18 (8)
C4—C3—Cl1	118.77 (8)	N2—C11—H11A	108.9
C5—C4—C3	117.12 (9)	C12—C11—H11A	108.9
C5—C4—H4A	121.4	N2—C11—H11B	108.9
C3—C4—H4A	121.4	C12—C11—H11B	108.9
C4—C5—C6	121.80 (10)	H11A—C11—H11B	107.8
C4—C5—H5A	119.1	C11—C12—C13	107.62 (8)
C6—C5—H5A	119.1	C11—C12—H12A	110.2
C5—C6—C1	120.20 (10)	C13—C12—H12A	110.2
C5—C6—H6A	119.9	C11—C12—H12B	110.2
C1—C6—H6A	119.9	C13—C12—H12B	110.2
N1—C7—C8	109.46 (8)	H12A—C12—H12B	108.5
N1—C7—H7A	109.8	C12—C13—Cl2	110.47 (7)
C8—C7—H7A	109.8	C12—C13—H13A	109.6
N1—C7—H7B	109.8	Cl2—C13—H13A	109.6
C8—C7—H7B	109.8	C12—C13—H13B	109.6
H7A—C7—H7B	108.2	Cl2—C13—H13B	109.6
N2—C8—C7	111.04 (8)	H13A—C13—H13B	108.1
N2—C8—H8A	109.4		

C7—N1—C1—C6	3.76 (14)	C1—N1—C7—C8	158.63 (8)
C10—N1—C1—C6	−133.72 (10)	C10—N1—C7—C8	−61.16 (10)
C7—N1—C1—C2	−171.80 (9)	C9—N2—C8—C7	−54.39 (10)
C10—N1—C1—C2	50.72 (12)	C11—N2—C8—C7	−176.15 (8)
C6—C1—C2—C3	−0.17 (14)	N1—C7—C8—N2	57.77 (10)
N1—C1—C2—C3	175.57 (9)	C11—N2—C9—C10	178.29 (8)
C1—C2—C3—C4	0.26 (15)	C8—N2—C9—C10	54.33 (10)
C1—C2—C3—Cl1	−177.57 (7)	C1—N1—C10—C9	−157.53 (8)
C2—C3—C4—C5	−0.65 (15)	C7—N1—C10—C9	61.56 (10)
Cl1—C3—C4—C5	177.17 (8)	N2—C9—C10—N1	−57.91 (10)
C3—C4—C5—C6	0.98 (16)	C9—N2—C11—C12	154.36 (8)
C4—C5—C6—C1	−0.93 (16)	C8—N2—C11—C12	−83.25 (10)
C2—C1—C6—C5	0.50 (14)	N2—C11—C12—C13	−177.25 (8)
N1—C1—C6—C5	−175.06 (9)	C11—C12—C13—Cl2	174.23 (7)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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Symmetry codes: (i) x, $-y+1/2$, $z+1/2$; (ii) $-x+1$, $-y$, $-z+1$; (iii) $x+1$, y, z.