Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N,*N*-Dimethyl-3-oxo-3-(thiophen-2-yl)-propanaminium chloride

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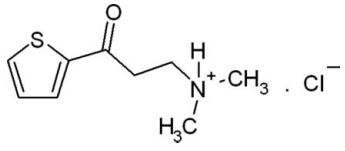
Received 1 August 2011; accepted 2 August 2011

Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.097; data-to-parameter ratio = 28.5.

In the title molecular salt, $C_9H_{14}NOS^+\cdot Cl^-$, the crystal packing is stabilized by weak intermolecular N—H···Cl, C—H···Cl and C—H···π interactions, which lead to the formation of a two-dimensional supramolecular layer which stacks along the b axis.

Related literature

For the management of major depressive disorders, see: Gupta *et al.* (2007). For the dual re-uptake inhibitor drug, duloxetine [systematic name (+)-(*S*)-*N*-methyl-3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propan-1-amine], see: Waitekus & Kirkpatrick, (2004). For related structures, see: Bhadbhade *et al.* (2009); Tao *et al.* (2006, 2008).



Experimental

Crystal data

$C_9H_{14}NOS^+\cdot Cl^-$
M_r = 219.72
Monoclinic, $P2_1/n$
a = 5.8663 (3) Å
b = 27.0109 (9) Å
c = 7.1385 (4) Å
β = 110.767 (6)°
V = 1057.63 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.52 mm^{-1}
T = 173 K
0.24 × 0.21 × 0.11 mm

Data collection

Oxford Diffraction Xcalibur Eos Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2010)
T_{min} = 0.885, T_{max} = 0.945
14443 measured reflections
3538 independent reflections
3290 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.097
S = 1.13
3538 reflections
124 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

*Cg*1 is the centroid of the S1/C1–C4 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···Cl1	0.87 (1)	2.17 (1)	3.0317 (11)	171 (2)
C1—H1*A*···Cl1^{i}	0.95	2.82	3.5641 (13)	136
C6—H6*A*···*Cg*1^{ii}	0.99	2.97	3.8183 (13)	144

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

ASD thanks the University of Mysore for research facilities. JPJ acknowledges the NSF–MRI program (grant No. CHE-1039027) for funds to purchase the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2775).

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supporting information

Acta Cryst. (2011). E**67**, o2271 [doi:10.1107/S1600536811031199]

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S1. Comment

The title salt, (I), $C_9H_{14}NOS^+$, Cl^-, is an intermediate in the synthesis of duloxetine, which is a new generation drug indicated for the management of major depressive disorders as well as for neuropathic pain (Waitekus & Kirkpatrick, 2004). Duloxetine is a dual re-uptake inhibitor with actions on serotonin as well as norepinephrine (Gupta *et al.*, 2007). The crystal structures of related structures, (*R*)-3-hydroxy-*N*,*N*-dimethyl-3-(2-thienyl)-propanamine (Tao *et al.*, 2006), *N*,*N*-dimethyl-3-(1-naphthyloxy)-3-(2-thienyl)propan-1-amine (Tao *et al.*, 2008) and duloxetine hydrochloride (Bhadbhade *et al.*, 2009) have been reported. In view of the importance of duloxetine, the crystal structure of the title compound, (I), is reported.

In the molecular salt, $C_9H_{14}NOS^+$, Cl^-, one cation-anion pair makes up the asymmetric unit (Fig. 1). The crystal packing is stabilized by weak N—H···Cl, C—H···Cl and C—H..*Cg* π-ring intermolecular interactions (Table 1) forming a 2-D supramolecular layer which stacks along the *b* axis (Fig. 2).

S2. Experimental

The title compound was obtained as a gift sample from *R. L*. Fine chem., Bangalore. X-ray quality crystals were obtained from slow evaporation of methanol solution (*M*.pt.: 451–454 K).

S3. Refinement

The N—H atom was located from a difference Fourier map and refined with N—H = 0.87±0.02 Å, and with U_{iso}(H) = 1.19U_{eq}(N). All of the remaining H atoms were placed in their calculated positions and then refined using the riding model with C—H lengths of 0.95 Å (CH), 0.99 Å (CH_2) or 0.98 Å (CH_3). The isotropic displacement parameters for these atoms were set to 1.20 (CH), 1.19 (CH_2) or 1.49–1.51 (CH_3) times U_{eq} of the parent atom.

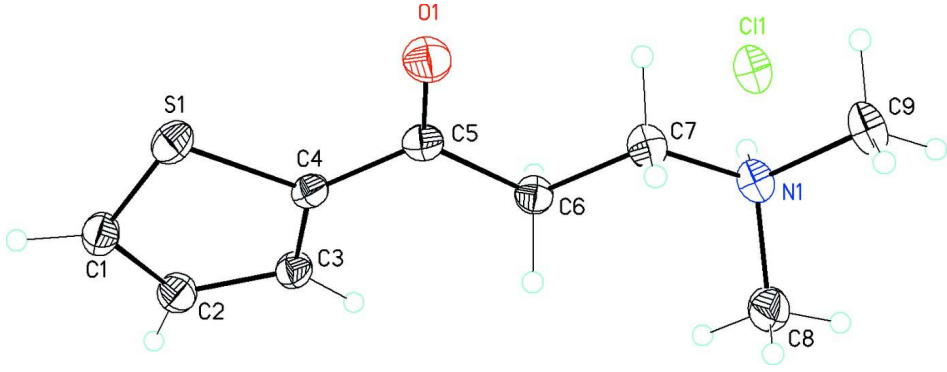

Figure 1

Molecular structure of the ion pair in the title compound showing the atom labeling scheme and 50% probability displacement ellipsoids.

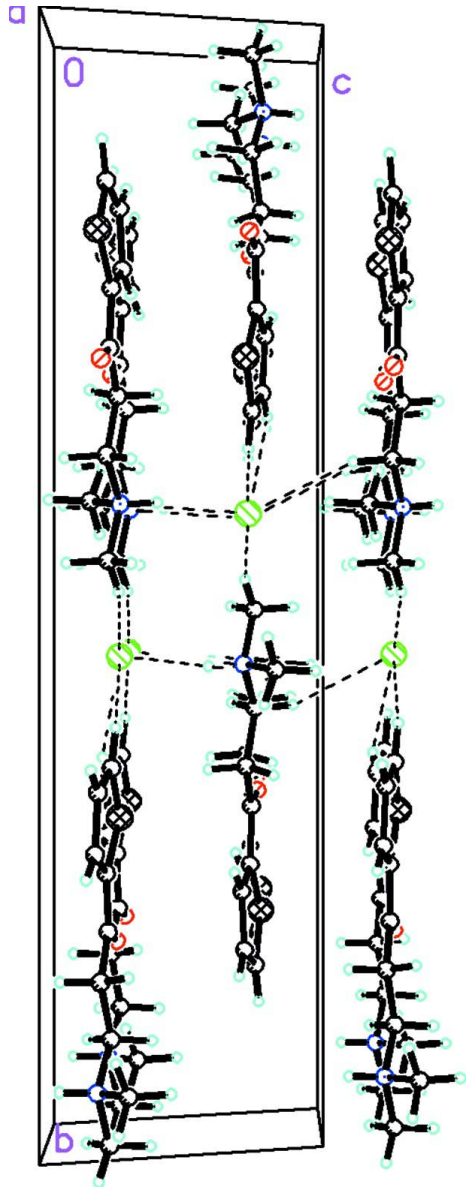

Figure 2

Packing diagram of the title compound viewed down the *a* axis. Dashed lines indicate weak N—H···Cl and C—H···Cl intermolecular interactions forming a 2-D supramolecular layer which stacks along the *b* axis.

N,*N*-Dimethyl-3-oxo-3-(thiophen-2-yl)propanaminium chloride

Crystal data

$C_9H_{14}NOS^+·Cl^-$
M_r = 219.72
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 5.8663 (3) Å
b = 27.0109 (9) Å
c = 7.1385 (4) Å
β = 110.767 (6)°
V = 1057.63 (9) Å^3
Z = 4
F(000) = 464
D_x = 1.380 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6745 reflections
θ = 3.1–32.2°
μ = 0.52 mm^{-1}

T = 173 K
Block, colorless

0.24 × 0.21 × 0.11 mm

Data collection

Oxford Diffraction Xcalibur Eos Gemini diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1500 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2010)
T_{min} = 0.885, T_{max} = 0.945

14443 measured reflections
3538 independent reflections
3290 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 32.3°, θ_{min} = 3.1°
h = −8→8
k = −39→40
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.097
S = 1.13
3538 reflections
124 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.4408P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0190 (18)

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.52202 (6)	0.201976 (12)	0.22248 (5)	0.02281 (9)
Cl1	0.25260 (7)	0.437297 (12)	0.73047 (5)	0.02698 (10)
O1	0.59639 (18)	0.31119 (4)	0.23658 (16)	0.0269 (2)
N1	0.1628 (2)	0.42989 (4)	0.28618 (16)	0.0202 (2)
H1N	0.185 (3)	0.4283 (6)	0.413 (2)	0.024*
C1	0.3315 (2)	0.15653 (5)	0.24400 (19)	0.0232 (2)
H1A	0.3584	0.1222	0.2307	0.028*
C2	0.1360 (2)	0.17494 (5)	0.2825 (2)	0.0232 (2)
H2A	0.0125	0.1549	0.3008	0.028*
C3	0.1380 (2)	0.22742 (4)	0.29226 (19)	0.0200 (2)
H3A	0.0157	0.2465	0.3172	0.024*
C4	0.3377 (2)	0.24739 (4)	0.26137 (17)	0.0176 (2)

C5	0.4056 (2)	0.29935 (4)	0.25738 (17)	0.0183 (2)
C6	0.2273 (2)	0.33779 (4)	0.27755 (18)	0.0193 (2)
H6A	0.0631	0.3312	0.1780	0.023*
H6B	0.2174	0.3358	0.4129	0.023*
C7	0.3098 (2)	0.38907 (4)	0.24408 (19)	0.0209 (2)
H7A	0.4826	0.3934	0.3311	0.025*
H7B	0.3006	0.3918	0.1033	0.025*
C8	−0.1028 (3)	0.42606 (5)	0.1722 (2)	0.0301 (3)
H8A	−0.1859	0.4550	0.2009	0.045*
H8B	−0.1665	0.3959	0.2118	0.045*
H8C	−0.1313	0.4248	0.0284	0.045*
C9	0.2585 (3)	0.47836 (5)	0.2479 (2)	0.0278 (3)
H9A	0.1668	0.5052	0.2806	0.042*
H9B	0.2405	0.4806	0.1063	0.042*
H9C	0.4313	0.4812	0.3315	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01902 (15)	0.02573 (16)	0.02610 (16)	0.00399 (11)	0.01097 (12)	−0.00015 (11)
Cl1	0.03912 (19)	0.02268 (15)	0.02328 (15)	−0.00231 (12)	0.01617 (13)	−0.00105 (11)
O1	0.0213 (4)	0.0274 (5)	0.0360 (5)	−0.0029 (4)	0.0150 (4)	−0.0012 (4)
N1	0.0250 (5)	0.0182 (4)	0.0199 (5)	−0.0021 (4)	0.0109 (4)	−0.0013 (4)
C1	0.0259 (6)	0.0205 (5)	0.0226 (6)	0.0040 (4)	0.0078 (5)	0.0007 (4)
C2	0.0221 (6)	0.0213 (5)	0.0265 (6)	−0.0012 (4)	0.0090 (5)	0.0012 (5)
C3	0.0169 (5)	0.0199 (5)	0.0243 (5)	0.0010 (4)	0.0086 (4)	0.0001 (4)
C4	0.0149 (5)	0.0197 (5)	0.0174 (5)	0.0016 (4)	0.0050 (4)	0.0003 (4)
C5	0.0173 (5)	0.0221 (5)	0.0156 (5)	−0.0002 (4)	0.0060 (4)	−0.0002 (4)
C6	0.0187 (5)	0.0196 (5)	0.0209 (5)	−0.0008 (4)	0.0086 (4)	0.0006 (4)
C7	0.0228 (5)	0.0200 (5)	0.0234 (5)	−0.0008 (4)	0.0126 (5)	−0.0007 (4)
C8	0.0240 (6)	0.0232 (6)	0.0421 (8)	0.0012 (5)	0.0106 (6)	−0.0032 (5)
C9	0.0377 (7)	0.0177 (5)	0.0315 (7)	−0.0056 (5)	0.0167 (6)	−0.0020 (5)

Geometric parameters (Å, º)

S1—C1	1.7032 (14)	C4—C5	1.4620 (16)
S1—C4	1.7216 (12)	C5—C6	1.5165 (16)
O1—C5	1.2224 (15)	C6—C7	1.5139 (16)
N1—C8	1.4834 (18)	C6—H6A	0.9900
N1—C9	1.4876 (16)	C6—H6B	0.9900
N1—C7	1.4947 (16)	C7—H7A	0.9900
N1—H1N	0.870 (13)	C7—H7B	0.9900
C1—C2	1.3647 (18)	C8—H8A	0.9800
C1—H1A	0.9500	C8—H8B	0.9800
C2—C3	1.4191 (17)	C8—H8C	0.9800
C2—H2A	0.9500	C9—H9A	0.9800
C3—C4	1.3769 (16)	C9—H9B	0.9800
C3—H3A	0.9500	C9—H9C	0.9800

C1—S1—C4	91.69 (6)	C7—C6—H6A	109.7
C8—N1—C9	110.60 (11)	C5—C6—H6A	109.7
C8—N1—C7	114.01 (10)	C7—C6—H6B	109.7
C9—N1—C7	109.27 (10)	C5—C6—H6B	109.7
C8—N1—H1N	108.0 (12)	H6A—C6—H6B	108.2
C9—N1—H1N	107.8 (11)	N1—C7—C6	113.80 (9)
C7—N1—H1N	106.8 (11)	N1—C7—H7A	108.8
C2—C1—S1	112.38 (10)	C6—C7—H7A	108.8
C2—C1—H1A	123.8	N1—C7—H7B	108.8
S1—C1—H1A	123.8	C6—C7—H7B	108.8
C1—C2—C3	112.40 (11)	H7A—C7—H7B	107.7
C1—C2—H2A	123.8	N1—C8—H8A	109.5
C3—C2—H2A	123.8	N1—C8—H8B	109.5
C4—C3—C2	112.10 (11)	H8A—C8—H8B	109.5
C4—C3—H3A	124.0	N1—C8—H8C	109.5
C2—C3—H3A	124.0	H8A—C8—H8C	109.5
C3—C4—C5	129.24 (11)	H8B—C8—H8C	109.5
C3—C4—S1	111.43 (9)	N1—C9—H9A	109.5
C5—C4—S1	119.33 (9)	N1—C9—H9B	109.5
O1—C5—C4	121.40 (11)	H9A—C9—H9B	109.5
O1—C5—C6	121.64 (11)	N1—C9—H9C	109.5
C4—C5—C6	116.96 (10)	H9A—C9—H9C	109.5
C7—C6—C5	109.97 (9)	H9B—C9—H9C	109.5

C4—S1—C1—C2	−0.93 (11)	S1—C4—C5—O1	−3.55 (17)
S1—C1—C2—C3	0.86 (15)	C3—C4—C5—C6	−4.03 (19)
C1—C2—C3—C4	−0.29 (16)	S1—C4—C5—C6	175.70 (8)
C2—C3—C4—C5	179.34 (12)	O1—C5—C6—C7	6.42 (16)
C2—C3—C4—S1	−0.40 (14)	C4—C5—C6—C7	−172.82 (10)
C1—S1—C4—C3	0.75 (10)	C8—N1—C7—C6	−55.48 (14)
C1—S1—C4—C5	−179.02 (10)	C9—N1—C7—C6	−179.79 (11)
C3—C4—C5—O1	176.73 (13)	C5—C6—C7—N1	−172.73 (10)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the S1/C1–C4 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···Cl1	0.87 (1)	2.17 (1)	3.0317 (11)	171 (2)
C1—H1*A*···Cl1^{i}	0.95	2.82	3.5641 (13)	136
C6—H6*A*···*Cg*1^{ii}	0.99	2.97	3.8183 (13)	144

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