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Chlorpromazinium picrate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.012 Å
R factor = 0.095
wR factor = 0.283
Data-to-parameter ratio = 13.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The title compound [systematic name: *N*-(2-chloro-10*H*-phenothiazin-10-yl)-*N*,*N*-dimethylpropanaminium 2,4,6-trinitrophenolate], $C_{17}H_{20}ClN_2S^+\cdot C_6H_2N_3O_7^-$, belongs to a group of phenothiazine derivatives which exhibit pharmacologic activities. There are two anion–cation pairs in the asymmetric unit. The molecular conformations of the cations differ in the dihedral angles between the two outer aromatic rings of the phenothiazine unit and in two torsion angles of the side chain. The crystal packing is stabilized by N—H···O and C—H···O hydrogen bonds.

Comment

Chlorpromazine, chemically 2-chloro-*N*,*N*-dimethyl-10*H*-phenothiazine-10-propanamine, was the first antipsychotic drug, used during the 1950s and 1960s, and is an aliphatic phenothiazine. The aliphatic phenothiazines are highly sedating, which is often apparent at the start of therapy; with time some tolerance to this effect develops. Chlorpromazine has strong α-adrenergic blocking activity and can cause orthostatic hypotension. Chlorpromazine has moderate anticholinergic activity, manifested as occasional dry mouth, blurred vision, urinary retention and constipation. Chlorpromazine increases prolactin secretion owing to its dopamine receptor blocking action in the pituitary and hypothalamus. Chlorpromazine is considered a typical antipsychotic and acts as an antagonist (blocking agent) on different postsynaptic receptors. Chlorpromazine has a wide range of activity arising from its depressant actions on the central nervous system and its α-adrenergic blocking and weak antimuscarinic activities. Cationic phenothiazine derivatives also act as π-electron donors and can form charge-transfer (CT) complexes with organic compounds. The donor activity of phenothiazines is so high that, even in the ground state, there is practically total transfer of an electron to an acceptor with the formation of CT complexes (Karpinska *et al.*, 1996). The properties and analytical application of chlorpromazine picrate have been reported (Tarasiewicz & Basinska, 1974). A review of various aspects of phenothiazines has been published (Kojilo *et al.*, 2001).

Perspective views of the title compound, (I), are shown in Figs. 1 and 2. The asymmetric unit comprises two cations and two anions. Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 5.28, November 2006; *MOGUL*, Version 1.1; Allen, 2002; Bruno *et al.*, 2004). The dihedral angles between the two aromatic rings of the phenothiazine unit are 30.3 (4) and 38.6 (2)° for the two cations. A least-squares comparison of the chlorpromazinium cations of the title compound (r.m.s. deviation 0.113 Å), fitting only the phenothiazine units, is shown in Fig. 3. Apart from the

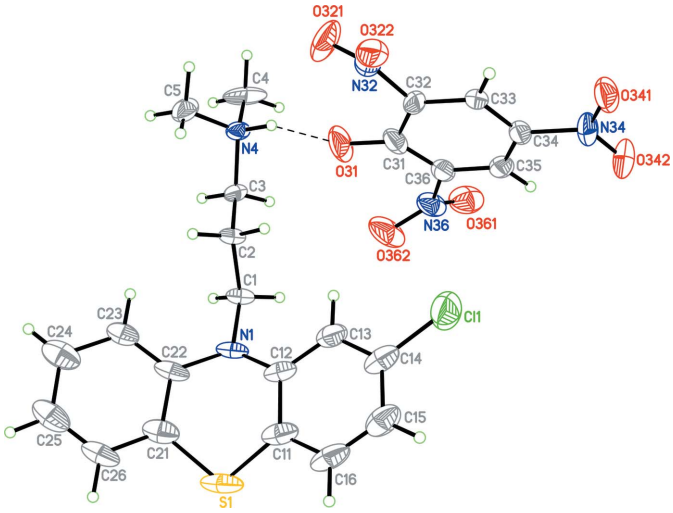


Figure 1
The structure of one ion-pair of the asymmetric unit of the title compound, with the atom numbering. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates a hydrogen bond.

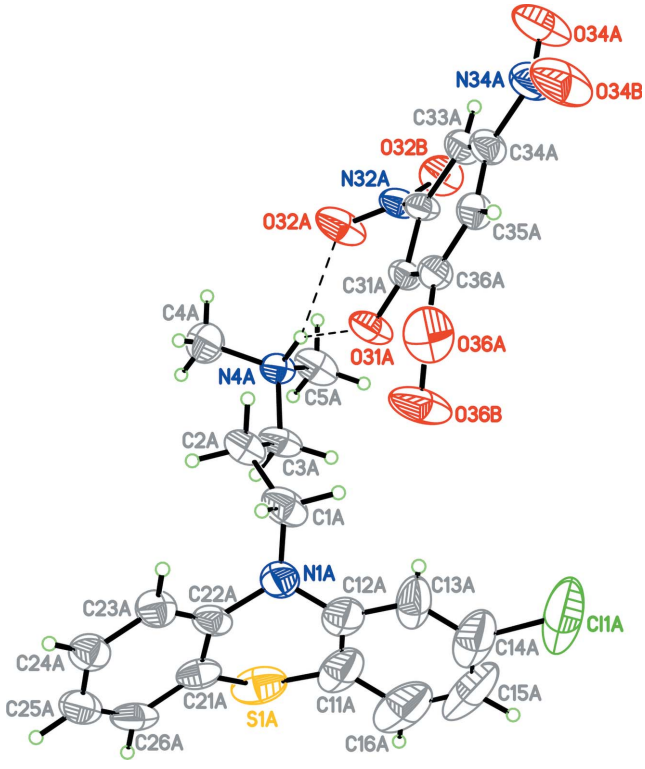


Figure 2
The structure of the other ion-pair of the asymmetric unit of the title compound, with the atom numbering. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

different angles between the two aromatic rings of the phenothiazine unit, the cations differ in two torsion angles of the side chain (Table 1).

The crystal packing is stabilized by N—H···O hydrogen bonds and several weak C—H···O contacts (Table 2). It it interesting to note that one cation–anion pair is connected by just one N—H···O hydrogen bond (H4···O321 is 3.02 Å),

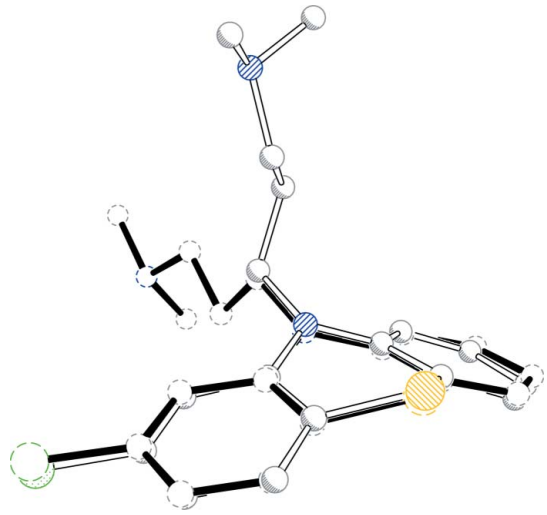
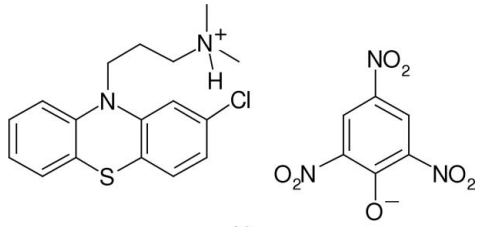


Figure 3
Least-squares fit of the two cations in the asymmetric unit. H atoms have been omitted.

whereas there is a bifurcated N—H···O hydrogen bond in the second pair. In addition, the distance between the amino H atom and the phenol O atom is significantly shorter in the first pair than in the second one.



(I)

Experimental

Chlorpromazine hydrochloride (1.0670 g, 0.03 *M*) and picric acid (0.6885 g, 0.03 *M*) were dissolved separately in doubly distilled water (100 ml). Both solutions were mixed and stirred in a beaker. The phenothiazine derivative formed a salt with picric acid instantaneously at room temperature. The separated orange salt was filtered off, washed thoroughly with doubly distilled water and dried in a vacuum desiccator over phosphorus pentoxide. The compound was recrystallized from acetonitrile (m.p. 434 K).

Crystal data

$C_{17}H_{20}ClN_2S^+\cdot C_6H_2N_3O_7^-$
M_r = 547.97
Triclinic, $P\overline{1}$
a = 12.3355 (14) Å
b = 14.6631 (19) Å
c = 15.5340 (19) Å
α = 108.758 (10)°
β = 104.675 (10)°
γ = 100.922 (9)°
V = 2458.6 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 173 (2) K
0.22 × 0.18 × 0.04 mm

Data collection

Stoe IPDS-II two-circle diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
T_{min} = 0.948, T_{max} = 0.998
30547 measured reflections
8664 independent reflections
4240 reflections with $I > 2\sigma(I)$
R_{int} = 0.089

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.095
$wR(F^2)$ = 0.283
S = 0.98
8664 reflections
667 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.94 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1
Selected torsion angles (°).

C22—N1—C1—C2	81.1 (7)	C22*A*—N1*A*—C1*A*—C2*A*	−77.6 (7)
C1—C2—C3—N4	−170.6 (5)	C1*A*—C2*A*—C3*A*—N4*A*	−147.8 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O31	0.93	1.73	2.605 (9)	156
N4*A*—H4*A*···O31*A*	0.93	1.91	2.723 (7)	145
N4*A*—H4*A*···O32*A*	0.93	2.28	2.940 (7)	127
C1*A*—H1*A*1···O36*B*	0.99	2.45	3.261 (9)	139
C2—H2*B*···O31	0.99	2.56	3.229 (10)	125
C3—H3*A*···Cl1*A*^{i}	0.99	2.70	3.457 (6)	133
C3—H3*B*···O342^{ii}	0.99	2.56	3.477 (8)	154
C4—H4*D*···O36*B*^{iii}	0.98	2.45	3.426 (13)	172
C5—H5*C*···O341^{ii}	0.98	2.57	3.354 (10)	137
C3*A*—H3*A*2···O34*B*^{ii}	0.99	2.41	3.312 (10)	152
C5*A*—H5*A*1···O34*B*^{iv}	0.98	2.48	3.453 (11)	172
C5*A*—H5*A*2···O32*A*	0.98	2.51	3.047 (10)	114
C15*A*—H15*A*···O342^{v}	0.95	2.53	3.315 (11)	140

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

H atoms were found in a difference map, but they were refined using a riding model with C—H ranging from 0.95 to 0.99 Å and N—H = 0.93 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N) or 1.5U_{eq}(C_{methyl}).

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

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