

Trifluoperazinium dipicrate

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Key indicators

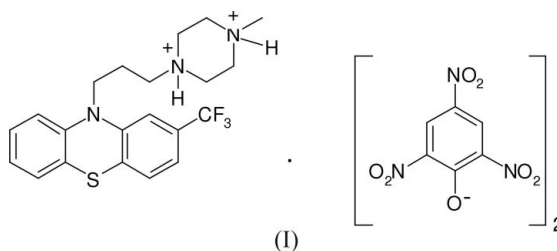
Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.055
 wR factor = 0.149
Data-to-parameter ratio = 12.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound [systematic name: 1-methyl-4-[3-[2-(trifluoromethyl)-10*H*-phenothiazin-10-yl]propyl]piperazine-1,4-dium bis(2,4,6-trinitrophenolate)], $\text{C}_{21}\text{H}_{26}\text{F}_3\text{N}_2\text{S}^+\cdot 2\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$, belongs to a group of phenothiazine derivatives which exhibit tranquillizing activity. The dihedral angle between the two outer aromatic rings of the phenothiazine unit is $24.69(7)^\circ$. The crystal packing is stabilized by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and several weak $\text{C}-\text{H}\cdots\text{O}$ contacts. The molecular conformation of the trifluoperazinium cation differs significantly from that in the hydrochloride.

Received 23 February 2007
Accepted 1 March 2007

Comment

Trifluoperazine is a highly potent antipsychotic drug (approximately 20 times more potent than chlorpromazine) (Martindale, 1977). The identification and differentiation of some phenothiazine picrates have been carried out (Yung & Pernarowski, 1963) and a review on various aspects of phenothiazines has been published (Kojilo *et al.*, 2001). In a continuation of our work on phenothiazine picrates (Yathirajan *et al.*, 2007), this paper reports the formation of a salt by the interaction between 10-[3-(4-methyl-1-piperazinyl)propyl]-2-(trifluoromethyl)-10*H*-phenothiazine hydrochloride and 2,4,6-trinitrophenol in an aqueous medium.



A perspective view of the structure of (I) is shown in Fig. 1. Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 5.28, November 2006; Allen, 2002; *Mogul*, Version 1.1; Bruno *et al.*, 2004). The dihedral angle between the two aromatic rings of the phenothiazine unit is $24.69(7)^\circ$. The piperazine ring adopts a chair conformation with both substituents in equatorial positions. The crystal packing is stabilized by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and several weak $\text{C}-\text{H}\cdots\text{O}$ contacts (Table 2).

The crystal structure of trifluoperazine hydrochloride, (II), has been reported (McDowell, 1980). However, the conformation of (II) does not compare well with (I). In (II), the dihedral angle between the two outer aromatic rings of the phenothiazine unit is 38.9° . Furthermore, it is rather strange that the piperazine ring in (II) is almost planar. The torsion

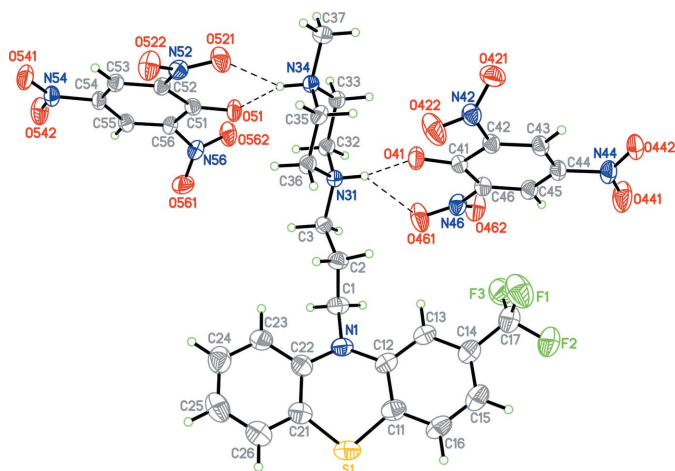


Figure 1
The molecular structure of the title compound, showing the atom numbering with displacement ellipsoids drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

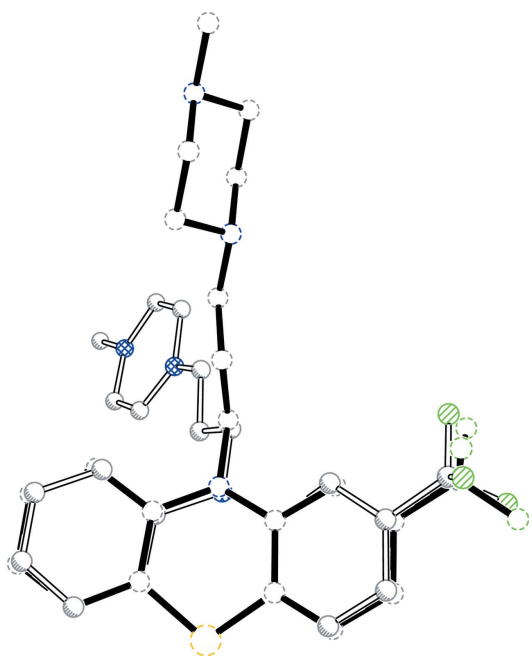


Figure 2
Least-squares fit of the trifluoperazinium cations in (I) (full bonds) and (II) (open bonds). H atoms have been omitted.

angles of the six ring atoms range from -5.2 to 4.4° , and the sums of the bond angles at the two N atoms are 359.4 and 359.8° . The conformation of the methylene chain connecting the ring systems is similar in (I) and (II). The torsion angles are -167.8 (2) and -164.1 (2) $^\circ$ in (I) compared with 173.2 and -178.6° in (II). However, the conformation of the bond connecting the methylene chain to the phenothiazine unit is different in (I) [$C12-N1-C1-C2 = -85.2$ (3) $^\circ$] from that in (II) (138.0°). A least-squares comparison of the trifluoperazinium cations of (I) and (II) (r.m.s. deviation = 0.165 Å), fitting only the phenothiazine units, is shown in Fig. 2. As can be seen, the molecular conformation is significantly different in the two structures.

Experimental

Trifluoperazine dihydrochloride (0.9696 g, 0.02 M) and picric acid (0.4615 g, 0.02 M) were dissolved in water (100 ml) separately. The solutions were mixed and stirred in a beaker. The separated bright-yellow compound was washed well with distilled water, filtered off and dried in a vacuum desiccator over phosphorus pentoxide. It was observed that, regardless of the proportions in which the donor and acceptor were mixed, only the 1:2 complex was formed. The complex was recrystallized from dimethyl sulfoxide (m.p. 514 K).

Crystal data

$C_{21}H_{26}F_3N_3S^{2+} \cdot 2C_6H_2N_3O_7^-$
 $M_r = 865.72$
 Triclinic, $P\bar{1}$
 $a = 8.1472$ (7) Å
 $b = 12.5927$ (12) Å
 $c = 19.6752$ (18) Å
 $\alpha = 73.782$ (7) $^\circ$
 $\beta = 78.833$ (7) $^\circ$
 $\gamma = 73.959$ (7) $^\circ$
 $V = 1847.9$ (3) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.19$ mm⁻¹
 $T = 173$ (2) K
 $0.23 \times 0.20 \times 0.19$ mm

Data collection

Stoe IPDSII two-circle diffractometer
 Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)
 $T_{min} = 0.969$, $T_{max} = 0.976$
 19064 measured reflections
 6895 independent reflections
 5091 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.078$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.149$
 $S = 1.01$
 6895 reflections
 550 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.34$ e Å⁻³
 $\Delta\rho_{min} = -0.42$ e Å⁻³

Table 1

Selected torsion angles ($^\circ$).

N1—C1—C2—C3	-167.8 (2)	C32—C33—N34—C35	55.9 (2)
C1—C2—C3—N31	-164.1 (2)	C33—N34—C35—C36	-56.8 (2)
C36—N31—C32—C33	55.6 (2)	C32—N31—C36—C35	-57.6 (2)
N31—C32—C33—N34	-55.6 (2)	N34—C35—C36—N31	58.5 (2)

Table 2

Hydrogen-bond geometry (Å, $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N31—H31 \cdots O41	0.92 (4)	1.79 (4)	2.666 (3)	160 (3)
N31—H31 \cdots O461	0.92 (4)	2.46 (3)	3.041 (3)	122 (3)
N34—H34 \cdots O51	0.96 (3)	1.77 (3)	2.683 (2)	157 (2)
N34—H34 \cdots O521	0.96 (3)	2.33 (3)	2.918 (3)	118.8 (18)
C16—H16 \cdots O442 ⁱ	0.95	2.39	3.147 (3)	136
C32—H32A \cdots O51	0.99	2.34	3.060 (3)	129
C35—H35B \cdots O41	0.99	2.41	3.132 (3)	129
C36—H36B \cdots O442 ⁱⁱ	0.99	2.45	3.318 (3)	146
C55—H55 \cdots O522 ⁱⁱⁱ	0.95	2.40	3.269 (3)	151

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

H atoms were found in a difference map. The H atoms bonded to nitrogen were freely refined and all other H atoms were refined using

a riding model, with C—H = 0.95–0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

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* and *PLATON* (Spek, 2003).

MAA thanks the University of Mysore for Research facilities.

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