

1-{5-[2-(Trifluoromethyl)phenyl]-
1,3,4-thiadiazol-2-yl}guanidinium
chloride

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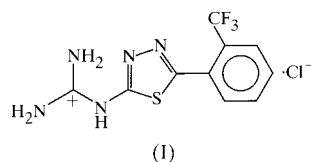
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In the title compound, $C_{10}H_9F_3N_5S^+ \cdot Cl^-$, which was developed as a potential anticonvulsant, the phenyl ring, the thiadiazole ring and the guanidinium moiety are all planar. There is a dihedral angle of $48.9(1)^\circ$ between the thiadiazole and phenyl rings which prevents steric hindrance arising from the π bonds within the former, and the trifluorophenyl moiety attached to the latter. The thiadiazole and guanidinium moieties are twisted by $12.7(2)^\circ$ with respect to each other. An extensive network of hydrogen bonds, predominantly involving the chloride ion, maintains the crystal structure.

Comment

The title compound, (I), was synthesized and supplied by Reckett and Coleman Ltd (Chapleo *et al.*, 1986), and was made as one of a series of substituted 1,3,4-thiadiazole-containing molecules being investigated as potential anticonvulsants (Stillings *et al.*, 1986; Chapleo *et al.*, 1987, 1988). A number of diverse 1,3,4-thiadiazole-containing compounds are currently being investigated by other groups for their anticonvulsant properties (Varvaresou *et al.*, 1998; Srivastava *et al.*, 1999; Srivastava & Rawat, 1999), although the title compound proved to be less efficacious than related compounds studied (Chapleo *et al.*, 1986). The title compound was also shown to possess vasodilatory properties (Turner *et al.*, 1988).



The phenyl and thiadiazole rings are both planar (Fig. 1), with root-mean-square deviations (r.m.s.d.) for their ring atoms of 0.0193 and 0.0064 Å, respectively. The two rings are not coplanar, having a dihedral angle of $48.9(1)^\circ$ between them, and S1 is $-0.729(6)$ Å, and the two N atoms N3 and N4 are 1.127(8) and 1.111(6) Å, respectively, from the phenyl ring plane. The angle between the rings prevents steric hindrance between the thiadiazole ring and the trifluoro-

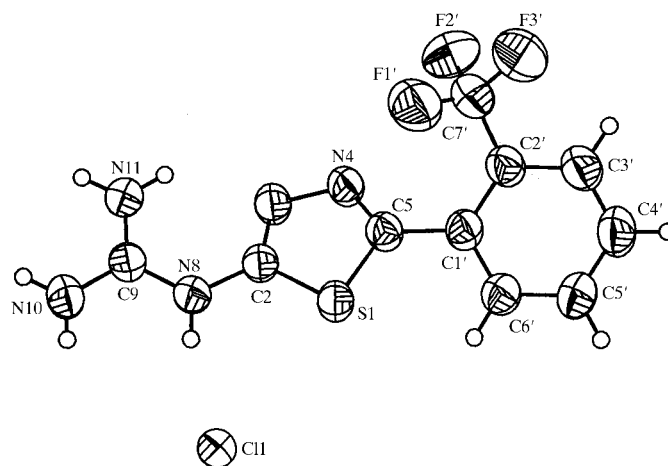


Figure 1

The asymmetric unit of (I) at 50% probability showing the numbering scheme used in the text (SNOOPI; Davies, 1983).

methyl substituent on the phenyl ring. The guanidinium group, principally the non-H atoms N8, C9, N10 and N11, is also highly planar, with an r.m.s.d. of 0.0009 Å, indicative of this being a planar carbenium ion. This group has a dihedral angle of $12.7(2)^\circ$ with respect to the thiadiazole ring.

As a result of the moieties attached to the phenyl group, the ring bonds display significant differences between their lengths. Notably, $C1'-C2'$ at 1.399(4) Å is significantly longer than both $C3'-C4'$ [1.364(6) Å] and $C4'-C5'$ [1.373(5) Å], and $C2'-C3'$ at 1.392(5) Å is also longer than $C3'-C4'$. The substituents on the phenyl ring also cause significant differences in the internal angles of the ring (Table 1). The thiadiazole moiety does not display differences in the symmetric pairs of bonds ($S1-C2/S1-C5$ and $C2-N3/C5-N4$), despite there being two different groups attached to either side of the ring. However, with the S atom in the ring, the carbon-nitrogen bonds are significantly shortened (Table 1) in comparison with those found in a comparable imidazole-like ring, being more like the mean length for such bonds as found in a furazan ring, 1.298 Å (Allen *et al.*, 1987).

The bond lengths for the N atoms and the C atom of the guanidinium moiety show significant differences between them. While the $C9-N10$ and $C9-N11$ bonds are marginally different in length (Table 1), the $N8-C9$ bond is significantly

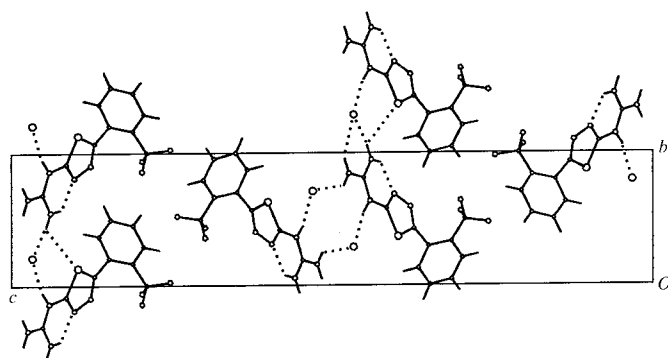


Figure 2

The packing of the unit cell of (I) viewed along the *a* axis, showing the hydrogen bonding, modified from SNOOPI (Davies, 1983).

longer than C9—N11. This difference indicates that the stabilization of the carbenium ion centred at C9 arises mainly from the N10 and N11 amino groups rather than from the N8 atom.

There are a number of hydrogen bonds that stabilize the crystal packing (Fig. 2 and Table 2). Four of the six hydrogen bonds are to the chloride ion as the acceptor. One of these four hydrogen bonds, from N11—H111, is bifurcated to the S atom of the thiadiazole ring. There is also an intramolecular hydrogen bond between N11—H112 and N3 of the thiadiazole ring. No π – π ring stacking is observed within the crystals probably as a result of the practical difficulties that would arise caused by the steric bulk of the trifluoromethyl group attached to the phenyl ring.

Experimental

Crystals were grown by slow evaporation from a 50:50 water/propan-2-ol mixture. The R_{int} values, 0.0496 for Laue class $2/m$ and 0.516 for mmm , clearly show that the crystal system is monoclinic.

Crystal data

$\text{C}_{10}\text{H}_9\text{F}_3\text{N}_5\text{S}^+\cdot\text{Cl}^-$	$D_x = 1.614 \text{ Mg m}^{-3}$
$M_r = 323.73$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 5.0864 (8) \text{ \AA}$	$\theta = 4.9\text{--}24.9^\circ$
$b = 7.315 (3) \text{ \AA}$	$\mu = 4.345 \text{ mm}^{-1}$
$c = 35.812 (9) \text{ \AA}$	$T = 296 (2) \text{ K}$
$\beta = 90.00 (2)^\circ$	Block, colourless
$V = 1332.4 (7) \text{ \AA}^3$	$0.2 \times 0.15 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 70.02^\circ$
ω – 2θ scans	$h = -6 \rightarrow 6$
4900 measured reflections	$k = -8 \rightarrow 8$
2519 independent reflections	$l = -17 \rightarrow 43$
1956 reflections with $I > 2\sigma(I)$	3 standard reflections every 200 reflections
$R_{\text{int}} = 0.050$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1023P)^2 + 0.0307P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.149$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.043$	$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
2519 reflections	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$
182 parameters	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
H atoms were constrained	Extinction coefficient: 0.0030 (6)

All H atoms were initially located in difference maps, but were then placed geometrically in riding positions and refined isotropically with U_{iso} set to $1.2U_{\text{eq}}$ of the associated atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD77* and *CADRAL* (Korber, 1982), and *CADSHL* (Cooper, 1990); program(s) used to solve structure: *SHELXL76* (Sheldrick, 1976); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SNOOPI* (Davies, 1983).

Table 1

Selected geometric parameters (\AA , $^\circ$).

S1—C2	1.715 (3)	N4—C5	1.291 (4)
S1—C5	1.726 (3)	N8—C9	1.342 (4)
C2—N3	1.299 (4)	C9—N11	1.309 (4)
C2—N8	1.382 (3)	C9—N10	1.326 (4)
N3—N4	1.386 (3)		
C2—S1—C5	86.7 (1)	C4'—C3'—C2'	121.1 (3)
N3—C2—S1	114.7 (2)	C3'—C4'—C5'	120.4 (4)
C2—N3—N4	111.8 (2)	C4'—C5'—C6'	119.1 (4)
C5—N4—N3	112.4 (2)	C1'—C6'—C5'	121.5 (3)
N4—C5—S1	114.3 (2)	N11—C9—N10	119.8 (3)
C6'—C1'—C2'	118.7 (3)	N11—C9—N8	121.5 (3)
C3'—C2'—C1'	118.9 (3)	N10—C9—N8	118.6 (3)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N8—H8 \cdots Cl1	0.86	2.25	3.092 (3)	166
N10—H101 \cdots Cl1 ⁱ	0.86	2.51	3.279 (3)	150
N10—H102 \cdots Cl1 ⁱⁱ	0.86	2.53	3.211 (3)	136
N11—H111 \cdots Cl1 ⁱ	0.86	2.57	3.327 (3)	148
N11—H111 \cdots S1 ⁱ	0.86	2.95	3.465 (3)	121
N11—H112 \cdots N3	0.86	2.06	2.711 (4)	132

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1100). Services for accessing these data are described at the back of the journal.

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