Acta Crystallographica Section E
**Structure Reports**
**Online**
ISSN 1600-5368

# $N,N',N''$-Triphenylguanidinium trifluoroacetate

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Received 18 December 2006
Accepted 22 December 2006

In the title salt, $C_{19}H_{18}N_3^+\cdot C_2F_3O_2^-$, the anion exhibits rotational disorder of the $CF_3$ group. The structure is stabilized by hydrogen bonds where the O atoms of the anion are acceptors from the NH guanidinium groups, forming infinite chains that run along the [001] direction.

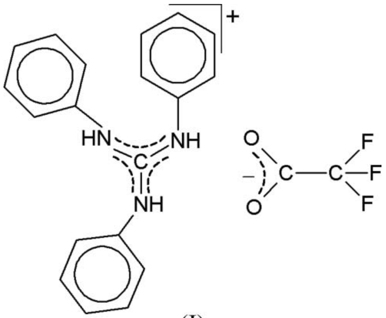
**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.009 Å
Disorder in solvent or counterion
$R$ factor = 0.073
$wR$ factor = 0.247
Data-to-parameter ratio = 13.4

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

## Comment

Guanidine compounds and their salts continue to attract attention due to their biological and pharmaceutical activities (Olney *et al.*, 1989). Triphenylguanidine compounds are regarded as potentially interesting for quadratic nonlinear optical (NLO) applications since it was shown experimentally that octupolar molecules have NLO properties that may compare favourably to those of their dipolar counterparts (Verbiest *et al.*, 1994). Trifluoroacetic acid is a very strong carboxylic acid because of the charge-withdrawing effect of the F atoms on the $\alpha$-C atom [dissociation constant, $K$ = 0.66 mol dm$^{-3}$ (Strehlow & Hildebrandt, 1990)]. Crystalline trifluoroacetic acid tetrahydrate exhibits phase transitions at low temperature, both for undeuterated and deuterated forms (Mootz & Schilling, 1992). Motivated by the interesting physical properties of this acid, we have engaged in the study of trifluoroacetate salts, searching for compounds displaying phase transitions and superstructures (Paixão *et al.*, 1998; Rodrigues *et al.*, 2000, 2001*a*,*b*, 2002; Silva *et al.*, 2003), and synthesized the title compound, (I).



(I)

The $CN_3$ fragment of the guanidinium group in (I) is planar, as expected for $sp^2$-hybridization of the central C atom. The bond lengths N1—C1 [1.329 (6) Å], N2—C1 [1.346 (6) Å] and N3—C1[1.334 (6) Å] are within the range expected for a delocalized C$\cdots$N bond. The dihedral angles between the ring planes and the plane defined by the central guanidinium fragment are 53.4 (3) (C2–C7), 54.4 (3) (C8–C13) and 56.2 (3)° (C14–C19). The corresponding angles for other triphenylguanidinium salts reported in the literature are

doi:10.1107/S1600536806055899

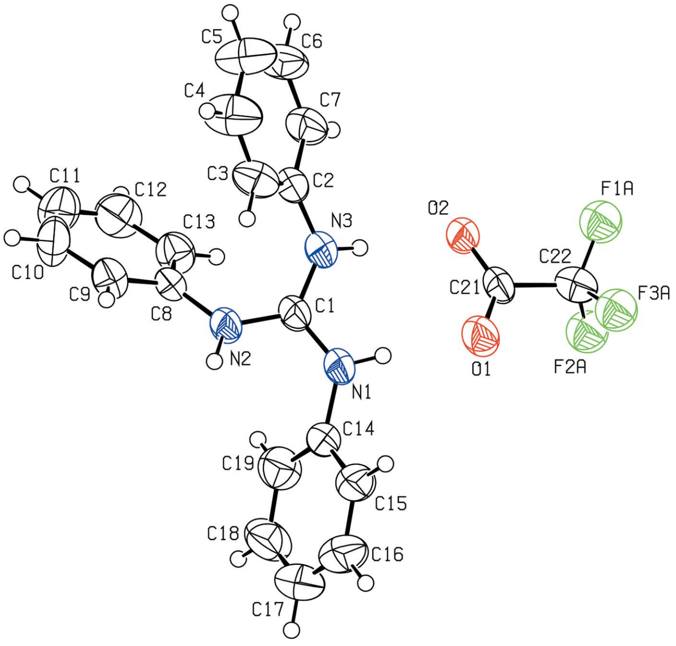


**Figure 1**
The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level. For clarity, only the major disorder component is shown.

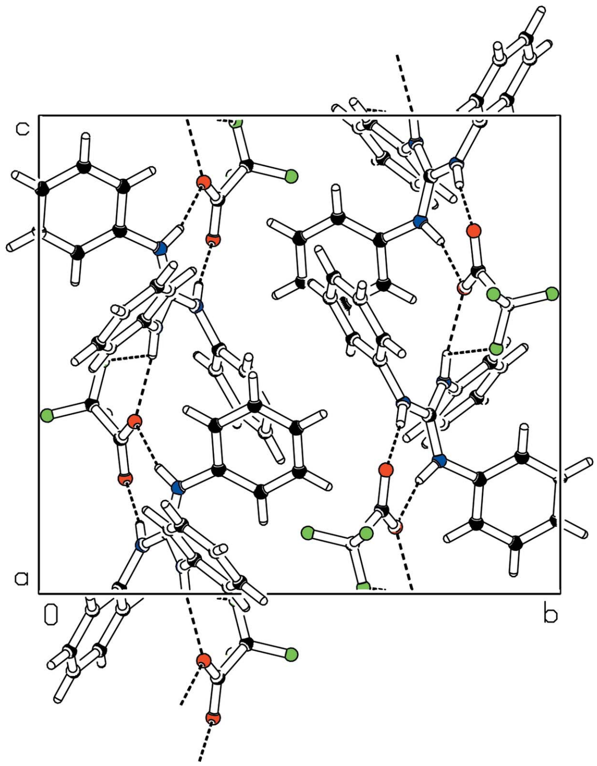


**Figure 2**
Packing diagram, viewed down the *a* axis, with the hydrogen bonds shown as dashed lines. For clarity only the major disorder component is shown.

within the range 32.6 (3)–70.2 (3)° (Kemme *et al.*, 1988; Klement *et al.*, 1995; Pereira Silva *et al.*, 2006). The variability of these values reveals the flexibility of triphenylguanidinium.

The bond lengths in the carboxylate group of the anion are compatible with a full proton transfer to the triphenylguanidine molecule [1.231 (6) and 1.237 (6) Å]. The C21—C22 bond length of 1.552 (8) Å is longer than the average value for a C$sp^3$–C$sp^2$ bond (Allen *et al.*, 1987), but is within the normal range of values found in trifluoroacetic acid and trifluoroacetate compounds (Gleghorn & Small, 1995). The $CF_3$ group is disordered over three positions with an occupancy ratio of 0.506 (4):0.314 (10):0.179 (10), a feature that is in agreement with the absence of any hydrogen-bonding interactions with F atoms. Intermolecular hydrogen bonds link the anions and cations. Chains running parallel to the *c* axis are assembled *via* hydrogen bonds involving the NH groups and O atoms of the carboxylate group. O1 accepts one H atom while O2 is an acceptor of two H atoms.

## Experimental

Trifluoroacetic acid (Riedel-de-Haën, 98%, 0.035 mmol) was added to triphenylguanidine (Aldrich, 0.035 mmol) in a water/ethanol (1:1) solution (30 ml). The solution was slowly warmed and then left to evaporate under ambient conditions. After a few days, small, colourless and transparent single crystals were deposited.

*Crystal data*

$C_{19}H_{18}N_3^+\cdot C_2F_3O_2^-$
$M_r = 401.38$
Monoclinic, $P2_1/c$
$a = 9.9905$ (8) Å
$b = 14.9348$ (13) Å
$c = 14.1194$ (10) Å
$\beta = 104.052$ (9)°
$V = 2043.7$ (3) Å$^3$
$Z = 4$
$D_x = 1.305$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm$^{-1}$
$T = 293$ (2) K
Block, colourless
0.29 × 0.20 × 0.12 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–$2\theta$ scans
Absorption correction: none
7224 measured reflections
3601 independent reflections
1507 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.086$
$\theta_{\rm max} = 25.0$°
3 standard reflections frequency: 180 min intensity decay: 2%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.073$
$wR(F^2) = 0.247$
$S = 1.03$
3601 reflections
268 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1036P)^2 + 1.7521P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.006$
$\Delta\rho_{\rm max} = 0.57$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.45$ e Å$^{-3}$

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O1 | 0.86 | 1.90 | 2.756 (5) | 173 |
| N2—H2···O2$^{\rm i}$ | 0.86 | 1.99 | 2.833 (5) | 165 |
| N3—H3···O2 | 0.86 | 2.00 | 2.806 (5) | 156 |

Symmetry code: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

The H atoms were located in a difference Fourier synthesis, placed at calculated positions and refined as riding [C—H = 0.93 Å, N—H =

0.86 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C,N})$]. DFT calculations performed with the computer program *GAMESS* (Schmidt *et al.*, 1993) have shown that the rotation energy barrier of the $CF_3$ group is low (of the order of 1.31 kJ mol$^{-1}$) so a continuous distribution of the F electrons would be more realistic. We have chosen to model the disorder as three $CF_3$ groups sharing a common C atom, subject to C—F = 1.29 (1) Å. The F atoms were restrained to lie approximately in the same plane. All F atoms were refined isotropically and with equal displacement parameters for each atom in a group. The conformation with highest occupancy coincides with the optimized geometry calculated within the DFT scheme, using the B3LYP exchange correlation potential (Becke 1993; Stephens *et al.*, 1994) and a 6–311G* Gaussian basis set.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *SDP*-Plus (Frenz, 1985); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

This work was supported by Fundação para a Ciência e a Tecnologia (FCT), under project POCI/FIS/58309/2004.

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