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N,*N*′,*N*‴-Triphenylguanidinium nitrate

P. S. Pereira Silva,[a]* J. A. Paixão,[b] M. Ramos Silva[b] and A. Matos Beja[b]

[a]Escola Superior Agrária, Instituto Politécnico de Castelo Branco, Quinta da Senhora de Mércules, Apartado 119, 6001-909 Castelo Branco, Portugal, and [b]CEMDRX, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-516 Coimbra, Portugal

Correspondence e-mail: psidonio@esa.ipcb.pt

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.054
wR factor = 0.165
Data-to-parameter ratio = 14.3

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

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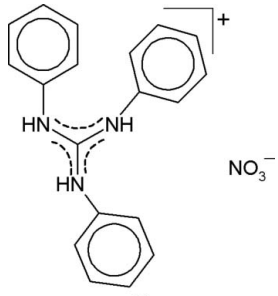
The title salt, $C_{19}H_{18}N_3^+\cdot NO_3^-$, has two symmetry-independent cations and two symmetry-independent anions in the asymmetric unit, with almost identical geometries. Bond lengths and angles within the guanidinium unit are close to those expected for a Csp^2 atom. Intermolecular hydrogen bonds link anions and cations, forming chains that run along the *c* axis.

Comment

The structure determination of the title compound, (I), was undertaken as part of an ongoing research project aimed at studying the structural and optical properties of a series of triphenylguanidine (tpg) salts. Triphenylguanidine compounds are regarded as potentially interesting for quadratic nonlinear optical (NLO) applications since it was shown experimentally that molecules with octupolar charge distributions have NLO properties that may compare favourably to those of their dipolar counterparts (Verbiest *et al.*, 1994).



(I)

There are two symmetry-independent cations, *A* and *B*, and two symmetry-independent anions, *C* and *D*, in the asymmetric unit, with similar geometries. 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 [*A* 1.339 (3), *B* 1.339 (3) Å], N2—C1 [*A* 1.327 (3), *B* 1.333 (3) Å] and N3—C1 [*A* 1.325 (3), *B* 1.322 (3) Å] are within the range expected for a delocalized C⋯N bond.

The dihedral angles between the ring planes and the plane defined by the central guanidinium fragment are 45.98 (14) (C2–C7, *A*), 48.31 (14) (C2–C7, *B*), 55.56 (15) (C8–C13, *A*), 52.80 (16) (C8–C13, *B*), 42.05 (15) (C14–C19, *A*) and 41.05 (15)° (C14–C19, *B*). There are only two tpg salts reported in the literature, the acetate and trichloroacetate salts (Kemme *et al.*, 1988). The corresponding angles for tpg^+ acetate (two cations) and tpg^+ trichloroacetate are 69.7 (4), 70.2 (3), 32.6 (3), 47.5 (3), 50.9 (3) and 57.4 (3)° for the two symmetry-independent cations (acetate) and 50.3 (6), 59.0 (6)

and 61.9 (7)° (trichloroacetate). The variability of these values reveals the flexibility of tpg$^+$.

Regarding the geometry of the nitrate anion, there is a slight asymmetry in the N—O bond lengths; the N4—O3 bond is longer [*A* 1.248 (3) Å and *B* 1.246 (3) Å] than the other two [N4—O1: *A*1.236 (3) Å and *B* 1.240 (3) Å; N4—O2: *A* 1.233 (3) Å and *B* 1.232 (3) Å] This probably reflects the fact that atom O3 is involved in two hydrogen bonds. The anions and cations are linked into infinite chains running parallel to the *c* axis, *via* hydrogen bonds involving the NH groups and the O atoms of the anion. Atom O3 is an acceptor of two H atoms and the other O atoms accept an H atom each. There is, in addition, a short intramolecular contact between atoms C3*A* and N3*A*.

Experimental

The title compound was synthesized by reaction of tpg (Aldrich) (0.01 g, 0.035 mmol) with an excess of nitric acid (Pronolab, 65%, 5 ml) in methanol (Pronolab, 99%, 50 ml). Crystals of (I) grew from the solution by slow evaporation over a period of a few days.

Crystal data

$C_{19}H_{18}N_3^+\cdot NO_3^-$
M_r = 350.37
Triclinic, $P\overline{1}$
a = 9.783 (3) Å
b = 13.849 (3) Å
c = 14.237 (3) Å
α = 76.285 (13)°
β = 89.264 (12)°
γ = 75.609 (12)°
V = 1812.8 (8) Å^3
Z = 4
D_x = 1.284 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 (2) K
Thin square plate, clear pale yellow
0.49 × 0.44 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
11545 measured reflections
6704 independent reflections
3901 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.5°
3 standard reflections
frequency: 180 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.165
S = 1.03
6704 reflections
469 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0881P)^2 + 0.2511P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1*A*—H1*A*···O1*C*^{i}	0.86	2.02	2.841 (3)	160
N1*B*—H1*B*···O1*D*	0.86	2.00	2.837 (3)	164
N2*A*—H2*A*···O3*C*^{i}	0.86	1.94	2.790 (3)	172
N2*B*—H2*B*···O3*D*	0.86	1.94	2.792 (3)	173
N3*A*—H3*A*···O2*D*^{ii}	0.86	2.04	2.893 (3)	174
N3*A*—H3*A*···O3*D*^{ii}	0.86	2.57	3.139 (3)	124
N3*B*—H3*B*···O2*C*^{ii}	0.86	2.05	2.907 (3)	172
N3*B*—H3*B*···O3*C*^{ii}	0.86	2.58	3.163 (3)	126
C3*A*—H31*A*···N3*A*	0.93	2.61	3.071 (3)	111

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

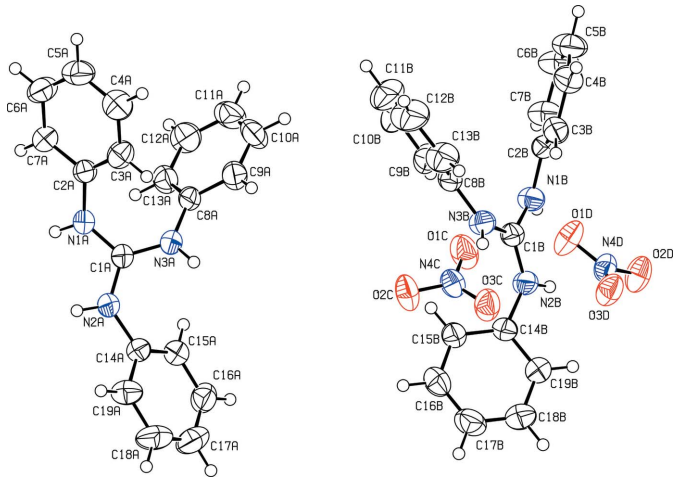


Figure 1
The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

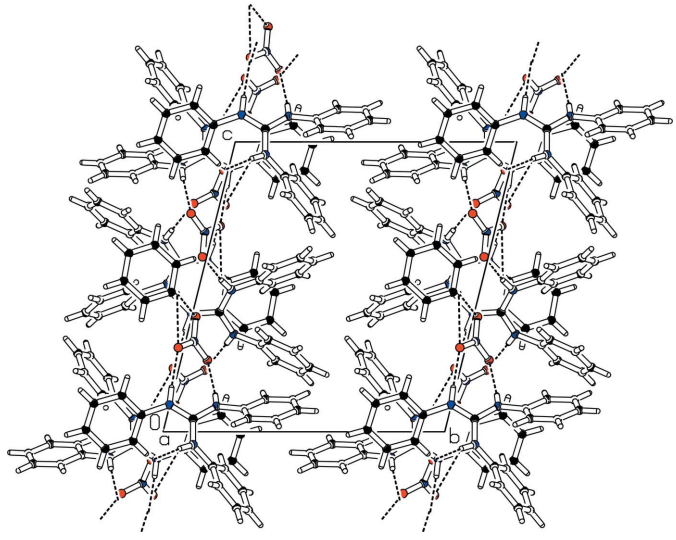


Figure 2
Packing diagram, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

H atoms were placed at calculated positions and refined as riding on their parent atoms with C—H = 0.93 Å, N—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(C,N).

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: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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