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1,3-Diphenylguanidinium Trifluoroacetate

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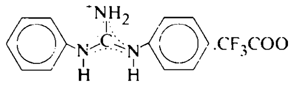
Abstract

The two phenyl rings of the title compound, $C_{13}H_{14}N_3^+.CF_3CO_2^-$, assume a *syn* conformation with respect to the unsubstituted N atom of the cation. Bond lengths and angles within the guanidinium moiety are close to those expected for a central C_{sp^2} atom, accounting for some charge delocalization between the three C—N bonds. The structure is stabilized by a two-dimensional network of intermolecular hydrogen bonds, where the carboxylate O atoms of the anions are acceptors from the N—H groups of the diphenylguanidinium cations.

Comment

Guanidine compounds and their salts continue to attract interest because of their biological and pharmaceutical (*e.g.* neuroleptic and antipsychotic) activities. *N*,*N*′-Di-*o*-tolylguanidine and its congeners are selective ligands for the haloperidol-sensitive σ receptor (Weber *et al.*, 1986; Largent *et al.*, 1987; Largent *et al.*, 1988). Certain *N*,*N*′-diarylguanidines are potent ligands for the *N*-methyl-D-aspartate/PCP receptor, and such compounds have neuroprotective properties against glutamate-induced neuronal cell death (Olney *et al.*, 1989). In addition, guanidine compounds are regarded as potentially interesting for non-linear optical applications (Zyss *et al.*, 1993). The structure determination of the title compound, (I), was undertaken as part of a current research project to study the structural, optical and dielectric properties of a series of diphenylguanidine (dpg) compounds.



(I)

The CN_3 fragment of the guanidinium group has the planar geometry expected for a central C_{sp^2} atom. The C1—N1 [1.329 (3) Å] and C1—N3 [1.334 (3) Å] bond lengths are comparable with literature averages for substituted and unsubstituted guanidinium cations (1.321 and 1.328 Å, respectively; Allen *et al.*, 1987), while the C1—N2 bond length [1.318 (3) Å] is slightly shorter. These values are larger than the mean value of a C_{sp^2}=N bond [1.295 Å], indicating that some charge delocalization occurs within the guanidinium fragment. With regard to the bond angles in the guanidinium group, there are small deviations from the ideal value of 120°, the angle opposite to the unsubstituted N atom being significantly smaller than the other two.

Both phenyl rings lie *syn* to the unsubstituted N2 atom, the dihedral angle between the planes of the phenyl rings being 70.53 (10)°. This conformation is similar to that of dpg$^+$ hydrogenselenite monohydrate (Paixão *et al.*, 1997), but different from the *syn-anti* conformation found in the molecular crystal of the free base (Zakharov *et al.*, 1980), as well as in dpg$^+$ *m*-chlorobenzeneseleninate (Antolini *et al.*, 1991) and dpg$^+$ perchlorate (Paixão *et al.*, 1998). These differences in conformation arise from the low value of the barrier of rotation of the phenyl rings, as can be shown by comparing the dihedral angles between the ring planes and the plane defined by the central guanidine fragment. In the present compound, these angles are 62.86 (11) (C2–C7) and 53.54 (8)° (C8–C13), and may be compared with the corresponding values in dpg$^+$ hydrogenselenite monohydrate [45.74 (13) and 48.35 (15)°; Paixão *et al.*, 1997], dpg$^+$ perchlorate [69.00 (13) and 79.26 (15)°; Paixão *et al.*, 1998] and dpg$^+$ *m*-chlorobenzeneseleninate [119.1 and 138.0°; Antolini *et al.*, 1991].

The geometry of the anion is unexceptional. The bond lengths in the carboxylate group are equal within estimated uncertainty and have a value compatible with a full proton transfer to the dpg molecule. As the F atoms are not involved in strong hydrogen bonds (see below), one might expect some degree of rotational disorder of the CF_3 group, however, the refinement shows that the position of this group is well defined in a single minimum, with reasonable displacement parameters for the F atoms.

The anions and cations interact strongly *via* hydrogen bonds. Each N—H group of the cation is a donor towards the bare O atoms of the carboxylate group of the anion, forming an infinite two-dimensional hydrogen-bond network extended in the (100) plane. An inspection of the intermolecular distances shows that the F atoms are not involved in strong hydrogen bonds, the closest short contacts being N2···F1 [3.305 (4) Å] and C10···F2^{i} [3.285 (4) Å; symmetry code: (i) $1-x$, $-y$, $-z$].

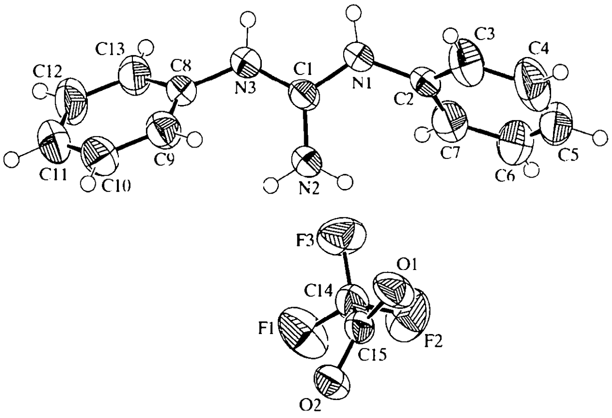


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

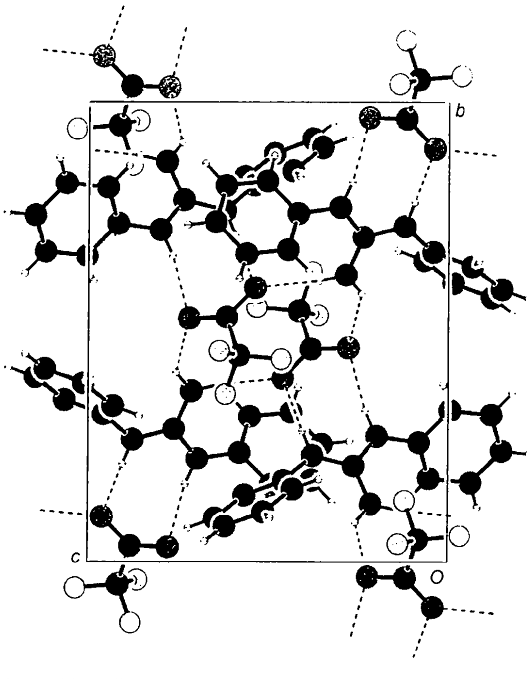


Fig. 2. Packing diagram showing the hydrogen-bonding scheme as dashed lines.

Experimental

The title compound was prepared by neutralizing an aqueous solution of *N*,*N*′-diphenylguanidine (98%, Aldrich) with trifluoroacetic acid (99%, Riedel-de-Haën). A clear transparent block-shaped single crystal (3.0 × 0.2 × 0.2 mm) grew from slow evaporation of the solution over a period of a few weeks and from which a small piece was cut and used for the X-ray analysis.

Crystal data

$C_{13}H_{14}N_3^+.C_2F_3O_2^-$
$M_r = 325.29$
Monoclinic
$P2_1/c$
$a = 10.153\,(2)$ Å
$b = 13.824\,(3)$ Å
$c = 11.673\,(3)$ Å
$\beta = 110.14\,(2)°$
$V = 1538.2\,(6)$ Å^3
$Z = 4$
$D_x = 1.405$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.11–15.85°$
$\mu = 0.120$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.41 × 0.18 × 0.13 mm
Clear, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: none
4821 measured reflections
2684 independent reflections
1529 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.054$
$\theta_{\rm max} = 25°$
$h = -11 \rightarrow 12$
$k = 0 \rightarrow 16$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 180 min
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.123$
$S = 0.987$
2684 reflections
209 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.4856P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.000$
$\Delta\rho_{\rm max} = 0.270$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.204$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0131 (17)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C15	1.240 (3)	N2—C1	1.318 (3)
O2—C15	1.242 (3)	N3—C1	1.334 (3)
N1—C1	1.329 (3)	N3—C8	1.421 (3)
N1—C2	1.425 (3)		
N2—C1—N1	121.8 (2)	C3—C2—N1	119.1 (3)
N2—C1—N3	121.3 (2)	C9—C8—N3	122.3 (2)
N1—C1—N3	116.9 (2)	C13—C8—N3	118.2 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.86	2.01	2.864 (3)	170.9
N2—H2*A*···O1	0.86	2.43	3.111 (3)	136.6
N2—H2*B*···O2^{ii}	0.86	2.10	2.852 (3)	145.5
N3—H3*B*···O1^{i}	0.86	1.97	2.813 (3)	167.3

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

The H atoms of the organic moiety were placed at calculated positions and refined as riding using *SHELXL*97 (Sheldrick, 1997) defaults [C_{aryl}—H = 0.93, N—H = 0.86 Å and $U(H)_{eq}$ = $1.2U_{eq}$ of the parent atom]. A planar-trigonal geometry was assumed for the N—H bonds. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there were no solvent-accessible voids in the crystal lattice. All calculations were performed on a Pentium 150 MHz PC running LINUX.

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: *SHELXS*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1182). Services for accessing these data are described at the back of the journal.

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(*S*,*S*)-*trans*-2,3-Tetralindiol

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Abstract

Enantiomerically pure *trans*-2,3-tetralindiol [(*R*,*R*)- or (*S*,*S*)-*trans*-1,2,3,4-tetrahydro-2,3-naphthalenediol, $C_{10}H_{12}O_2$] crystallizes in a layered structure, with two independent molecules in the asymmetric unit and an unbalanced arrangement of hydrogen bonds. The hydroxyl groups of one molecule form normal, if somewhat long, hydrogen bonds, but one of the O atoms in the other molecule accepts two protons while the second accepts none. The four O···O distances range from 2.817 (3) to 2.921 (3) Å.

Comment

Brianso (1976) reported the melting points of the resolved enantiomers of *trans*-2,3-tetralindiol to be 436 K, and the eutectic temperature of the racemic phase with one of the enantiomerically pure phases to be 403 K. This eutectic temperature is only 5 K lower than the melting point of the racemic material (T_{fus} 408–409 K; Verkade *et al.*, 1928). Crystals of *rac*-*trans*-2,3-tetralindiol are therefore only marginally more stable than the crystals of the pure enantiomers. Since crystals of racemic compounds are usually considerably more stable than crystals of the corresponding enantiomerically pure materials (Jacques *et al.*, 1981; Brock *et al.*, 1991), we decided to investigate.

The structure of the enantiomerically pure isomer, (I), has been published previously (Brianso, 1976), but its precision is so low (R = 0.13; structure said to be disordered) that its accuracy was in doubt. The structure of the racemic compound is unknown. We had no difficulties obtaining high-quality crystals of the enantiomerically pure material (recrystallization from toluene), but were unable to obtain suitable crystals of the racemic compound. The latter grew, from the many

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