ORGANIC COMPOUNDS

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N,*N*′-Diphenylguanidinium hydrogen (+)-L-tartrate monohydrate

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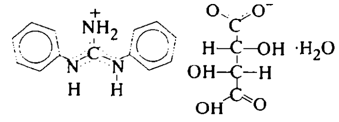
Abstract

The cation of the title compound, $C_{13}H_{14}N_3^+\cdot C_4H_5O_6^-\cdot H_2O$, has a central guanidinium fragment with a planar geometry, as expected for sp^2 hybridization at the C atom. The conformation of the phenyl rings is *syn–syn* with respect to the unsubstituted N atom, but the overall conformation of the cation is far from the C_{2v} symmetry predicted by *ab initio* calculations for the isolated ion. A broad range of hydrogen-bond interactions contributes to packing cohesion, the strongest of these linking the anions head-to-tail.

Comment

The synthesis of new materials with interesting nonlinear optical properties, by encapsulation of guanidinium cations between hydrogen L-tartrate anions, has been shown to be a potential route for the crystal engineering of materials with enhanced second-order nonlinear optical properties (Zyss *et al.*, 1993).

Much of the interest in diphenylguanidine compounds has been prompted by the biological and therapeutic properties of some diarylguanidines, which were found to be highly active as antagonists at σ receptor sites (Weber *et al.*, 1986; Largent *et al.*, 1987) and at the ion channel associated with the *N*-methyl-D-aspartate/*N*-(1-phenylcyclohexyl)piperidine receptor (Olney *et al.*, 1989). The *N*,*N*′-diphenylguanidinium cation (dpg$^+$) has been found to adopt different conformations both in aqueous solution (Alagona *et al.*, 1994) and in several salts (Antolini *et al.*, 1991; Paixão *et al.*, 1997; 1998*a*,*b*,*c*; Matos Beja *et al.*, 1998). The conformation of dpg$^+$ is very sensitive to the counter-ion, and this effect has been the subject of *ab initio* quantum mechanical and molecular mechanics calculations (Nagy & Durant, 1996). Stabilization of a particular conformation depends critically on intermolecular interactions with the solvent, since the energetic cost of rotation of the phenyl rings is much lower than typical solvation energies. The dpg$^+$ cation has a large potential for hydrogen bonding *via* the NH and NH$_2$ groups and the dipole moments for the *syn–syn*, *syn–anti* and *anti–anti* conformations are quite different, which indicates a delicate energetic balance. If the *anti–anti* conformation could be stabilized by a counter-ion such as hydrogen (+)-L-tartrate, we would expect the *N*,*N*′-diphenylguanidinium cation to be polarizable and noncentrosymmetric. With this in mind, we have synthesized the title compound, (I), and here we report its crystal structure, as determined by single-crystal X-ray diffraction, and its optical properties.



(I)

The geometry of the guanidinium group in (I) is close to that expected for a central Csp^2 atom. The N1—C1 [1.330 (3) Å] and N3—C1 [1.332 (3) Å] bond lengths are close to the expected value for a delocalized C$\overset{...}{=}$N double bond [1.339 (5) Å] and compare well with the average values for the guanidinium cation [1.321 and 1.328 Å for unsubstituted and substituted species, respectively (Allen *et al.*, 1987)]. The N2—C1 bond length [1.314 (3) Å] is somewhat shorter, but still larger than the value expected for a Csp^2=N bond (1.295 Å), indicating that some charge delocalization occurs within the guanidine fragment.

The N1—C2 [1.418 (3) Å] and N3—C8 [1.419 (3) Å] bond lengths compare closely with the values found in diphenylguanidine (Zakharov *et al.*, 1980), diphenylformazane (Omel'chenko *et al.*, 1974) and other di-

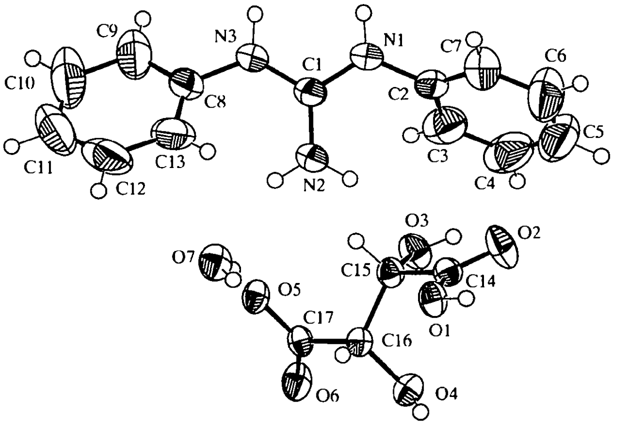


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% level and H atoms are shown as spheres of an arbitrary radius.

phenylguanidinium salts (Antolini *et al.*, 1991; Paixão *et al.*, 1997, 1998*a*,*b*,*c*; Matos Beja *et al.*, 1998).

Due to the low potential barrier for rotation about the C—N bonds, the dihedral angle between the phenyl rings can vary substantially in diphenylguanidine compounds. While in both the free base (Zakharov *et al.*, 1980) and in dpg$^+$ *m*-chloroselenate (Antolini *et al.*, 1991), one of the phenyl rings lies *syn* and the other *anti* to the unsubstituted N atom (N2), in the present case both rings lie *syn* to N2. A similar *syn–syn* conformation of the phenyl rings was found in dpg$^+$ hydrogenselenite monohydrate (Paixão *et al.*, 1997), dpg$^+$ nitrate (Paixão *et al.*, 1998*a*) and dpg$^+$ trifluoroacetate (Paixão *et al.*, 1998*b*). The angle between the least-squares planes of the two phenyl rings is 84.97 (10)°, which is close to the value of 88.21 (10)° observed in the hydrogen selenite salt, but larger than the corresponding values observed in both the nitrate [81.49 (11)°] and trifluoroacetate [70.53 (10)°] salts. The dihedral angles between the central planar guanidine CN_3 fragment and the phenyl rings are 56.67 (11)° [C2–C7] and 44.02 (14)° [C8–C13]. These values are far from the 90° angle corresponding to the ideal C_{2v} symmetry predicted for this cation in the gas phase by *ab initio* calculations (Alagona *et al.*, 1994).

As is usually found, the carboxyl and carboxylate groups in (I) have a *trans* conformation about the central C15—C16 bond [C14—C15—C16—C17 −177.39 (15)°]. In previous structure analyses of hydrogen (+)-tartrate salts, this enantiomer gives a negative torsion angle for the two hydroxyl groups down the C15—C16 bond vector, which provides an easy check on the configuration and allows a comparison between conformational differences in tartrate moieties. The O3—C15—C16—O4 torsion angle is −62.70 (18)° in (I), compared with −58.1° for (+)-tartaric acid (Okaya *et al.*, 1966). For the alkali metal hydrogen (+)-tartrate salts, this torsion angle ranges from −69.7 to −68.2°.

The bond lengths and angles of the hydrogen tartrate moiety are within the expected ranges. It is noteworthy that in the geometry of the carboxyl and carboxylate groups, the bond lengths in the carboxyl group are very close to those of the carboxylate group. The undissociated H atom was found close to O1 in a difference Fourier map, but the proton participates in a moderately strong hydrogen bond between atoms O1 and O5 of two neighbouring ions, which explains the similar lengths of the C17—O5 and C14—O1 bonds.

Previous structural studies of tartrate and hydrogen tartrate salts have shown that the carboxylate groups tend to be coplanar with their vicinal Cα—OH group. However, in a few cases, significant rotation of the carboxyl group away from the C—Cα—OH group has been noted. In (−)-1-phenylethylammonium hydrogen (+)-tartrate (Molins *et al.*, 1989), a rotation of 30.8° has been reported, while in anhydrous ethylenediamine (+)-tartrate (Pérez, 1976), a rotation of 20° was attributed to the influence of the hydrogen bonds between the carboxyl O atoms and the cation. In the present case, the carboxyl and carboxylate groups are rotated from the C—Cα—OH planes by 9.4 (1) and 3.92 (9)°, respectively, and both of these values are within the range of 0–10° that covers most of the reported data. The angle between the least-squares planes of the two α-hydroxycarboxyl groups (O1,O2,C14,C15,O3 and O5,O6,C17,C16,O4) is 74.86 (9)°, which is larger than the value of 56.5° in the parent (+)-tartaric acid (Okaya *et al.*, 1966), but close to the value of 76.5 (2)° found in sodium hydrogen (+)-tartrate (Bott *et al.*, 1993).

The anions and cations in (I) are held together by an intricate network of hydrogen bonds. The full potential for hydrogen bonding of both the anion and cation is realised in this structure. The strongest hydrogen bond links the carboxyl and carboxylate groups of two neighbouring hydrogen tartrate molecules in a head-to-tail fashion. Each N atom of the guanidinium moiety shares its proton with one of the O atoms of the anion, forming moderately strong hydrogen bonds. The water molecule forms hydrogen bonds exclusively with the anion.

Second harmonic generation measurements relative to crystalline (+)-L-tartaric acid were performed on polycrystalline samples of (I), using a powder technique known as the Kurtz test (Kurtz & Perry, 1968). The 1064 nm line of a Nd–YAG laser was used and samples had an average crystallite size in the range 90–180 μm. It was found that the second harmonic signal was not significantly enhanced in the dpg$^+$ salt compared with that for the parent (+)-L-tartaric acid. The reason for this behaviour might lie in an unfavourable *syn–syn* conformation of the phenyl rings.

Experimental

The title compound was prepared by mixing equimolar portions of *N*,*N*′-diphenylguanidine (97%, Aldrich) and (+)-L-tartaric acid (99%, Sigma) in a 1:1 solution of ethanol and water. Slow evaporation of the solvent enabled good quality colourless single crystals of tabular habit to grow from the saturated solution.

Crystal data

$C_{13}H_{14}N_3^+ \cdot C_4H_5O_6^- \cdot H_2O$
$M_r = 379.37$
Orthorhombic
$P2_12_12_1$
$a = 7.066\ (3)$ Å
$b = 14.723\ (8)$ Å
$c = 18.219\ (6)$ Å
$V = 1895.4\ (14)$ Å^3
$Z = 4$
$D_x = 1.329$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.29–16.33°$
$\mu = 0.104$ mm^{-1}
$T = 293\ (2)$ K
Block
0.46 × 0.24 × 0.24 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
4207 measured reflections
3311 independent reflections
2860 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.009$
$\theta_{\rm max} = 24.98°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 180 min
intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.084$
$S = 1.057$
3311 reflections
254 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 0.4536P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0137 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C1	1.330 (3)	C14—O2	1.213 (2)
N1—C2	1.418 (3)	C14—O1	1.289 (2)
N2—C1	1.314 (3)	C17—O6	1.230 (2)
N3—C1	1.332 (3)	C17—O5	1.276 (2)
N3—C8	1.419 (3)		
N2—C1—N1	120.6 (2)	N1—C1—N3	117.6 (2)
N2—C1—N3	121.8 (2)		
C2—N1—C1—N2	−8.0 (4)	C1—N1—C2—C7	128.7 (3)
C8—N3—C1—N2	−8.0 (4)	C1—N3—C8—C9	142.8 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O5$^{\rm i}$	0.82	1.67	2.4819 (19)	170.8
N1—H1···O6$^{\rm ii}$	0.86	2.01	2.828 (3)	158.3
N2—H2*A*···O3	0.86	2.09	2.866 (3)	149.2
N2—H2*B*···O2$^{\rm iii}$	0.86	2.32	2.885 (3)	123.7
N3—H3···O4$^{\rm ii}$	0.86	1.97	2.782 (2)	156.7
O3—H3*B*···O2	0.82	2.13	2.622 (2)	118.0
O4—H4*A*···O7$^{\rm i}$	0.82	1.86	2.682 (2)	176.1
O7—H7*B*···O5$^{\rm iv}$	0.86 (3)	1.99 (3)	2.831 (2)	169 (3)
O7—H7*A*···O6	0.81 (3)	2.11 (3)	2.911 (2)	174 (3)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $x - 1, y, z$; (iv) $x - \frac{1}{2}, \frac{3}{2} - y, 2 - z$.

Because of the weak anomalous scattering at the Mo wavelength, the absolute structure could not be determined from the X-ray data, and so to fix the enantiomorph the known *R*,*R* configuration was assigned to the hydrogen (+)-L-tartrate anion. The structure was solved by direct methods. The H atoms were placed at calculated positions and refined as riding using the *SHELXL*97 (Sheldrick, 1997) defaults, except for those of the water molecule, which were determined from a difference Fourier synthesis and refined with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$. There is a relatively wide distribution of bond lengths within the phenyl rings, C4—C5 and C11—C12 being particularly short. Inspection of the anisotropic displacement parameters shows some relatively high values for the *para* C atoms, C5 and C11. Taken together, these observations suggest there may be a small degree of disorder affecting these rings, but it was not possible to develop a model for static disorder. Analysis of the crystal structure with *PLATON* (Spek, 1995) showed that there are no additional solvent-accessible voids in the crystal lattice.

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, 1990). 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: BM1310). Services for accessing these data are described at the back of the journal.

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Bis(*N*,*N*′-diphenylguanidinium) oxalate

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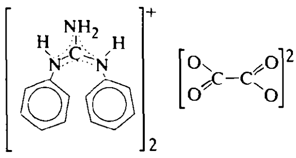
Abstract

In the title compound, $2C_{13}H_{14}N_3^+\cdot C_2O_4^{2-}$, the anion is at an inversion centre. The cation has approximate C_2 symmetry, with the two phenyl rings oriented *anti* with respect to the unsubstituted N atom. Bond lengths and angles within the guanidinium moiety are close to those expected for a central C*sp*^{2} atom with a small charge delocalization between the three C—N bonds. The anions and cations are interconnected by a two-dimensional hydrogen-bonding network extended in the (100) plane.

Comment

Physicochemical studies of diarylguanidines are important, since they are of biological and therapeutic interest, particularly in the light of the neuroleptic and antipsychotic properties of some of these compounds. For instance, *N*,*N*′-di-*ortho*-tolylguanidine is highly active as antagonist at the haloperidol-sensitive σ receptor sites (Weber *et al.*, 1986; Largent *et al.*, 1987). It is also well known that certain *N*,*N*′-diarylguanidines are potent ligands for the *N*-methyl-D-aspartate/*N*-(1-phenylcyclohexyl)piperidine (NMDA/PCP) receptor and have neuroprotective properties against glutamate-induced neuronal cell death (Olney *et al.*, 1989) and therapeutic value in the treatment of the neurodegenerative symptoms of stroke or heart attack (Choi, 1988).

Our interest is focused on the physical properties of guanidine compounds, which are regarded as potentially interesting for non-linear optics applications (Zyss *et al.*, 1993). The structure determination of the title compound, (I), was undertaken as part of an on-going research project aimed at studying the structural and physical properties (optical and dielectric) of a series of diphenylguanidine (dpg) compounds.



(I)

Several studies have shown that dpg is a very flexible molecule, due to the low potential barrier for rotation of the phenyl rings, and a number of different molecular conformations (*syn–syn*, *syn–anti* and *anti–anti*) have been found both in solution (Alagona *et al.*, 1994) and in several salts (Antolini *et al.*, 1991; Paixão *et al.*, 1997, 1998*a*,*b*,*c*; Matos Beja *et al.*, 1998; Pereira Silva *et al.*, 1999). There is both experimental and theoretical evidence that the relative proportions of the different conformers in solution depend on the counter-ion of the protonated molecule (Alagona *et al.*, 1994; Nagy & Durant, 1996), a subject that clearly has important consequences for the biological activity of guanidine derivatives, which are generally protonated at physiological pH. Also, both the dipole moment and the polarizability of protonated dpg molecules depend on the orientation of the phenyl rings. Therefore, accurate structural studies are needed for a detailed understanding of the optical and dielectric properties of dpg compounds.

The CN$_3$ fragment of the guanidinium group in (I) is planar, as expected for *sp*^{2} hybridization of the central C atom. The C1—N1 [1.333 (2) Å] and C1—N3 [1.341 (2) Å] bond lengths are slightly longer than the reported average values for unsubstituted and substituted guanidinium salts [1.321 and 1.328 Å, respectively (Allen *et al.*, 1987)], while the C1—N2 bond is shorter [1.314 (2) Å]. These three bond distances have values intermediate between the C—NH and C═N bonds in the unprotonated dpg molecule, which may be explained by a small charge delocalization on the guanidine moiety upon protonation.

Both phenyl rings are oriented *anti* to the terminal unsubstituted N2 atom. Quantum-mechanical calculations performed at the MP2/4-31G//HF/4-31G level by Alagona *et al.* (1994) show that the *anti–anti* conformation of dpg$^+$ has a higher energy than both the *syn–anti* and *syn–syn* conformations *in vacuo*. However, when the effect of the counter-ion of the protonated molecule is included in similar calculations performed within the SCRF (Self-Consistent Reaction Field) continuum model, the energy difference is significantly reduced, but not cancelled, by the solvation energy of common counter-ions like Cl$^-$ and CH$_3$COO$^-$. Similar conclusions have been obtained from Monte Carlo simulations based on the relative free energies of the three conformers from more precise *ab initio* calcu-