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

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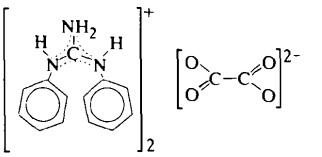
## Abstract

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 $\sigma$ 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 $CH_3COO^-$. 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-

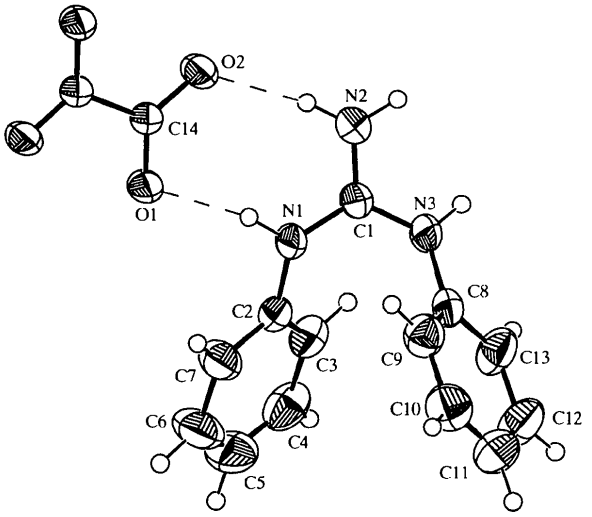



Fig. 1. An *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% level and H atoms are shown as circles of an arbitrary radius.

lations at the MP2/6-31G*//HF/4-31G level (Nagy & Durant, 1996). Although the results of such calculations cannot easily be extrapolated from solution to the solid, where packing effects are important, it appears that the *anti–anti* conformation occurs less frequently in $dpg^+$ salts than the *syn–syn* and *syn–anti* conformations. The only two further occurrences of an *anti–anti* conformation reported so far are in bis($dpg^+$) sulfate monohydrate (Matos Beja *et al.*, 1998) and in $dpg^+$-dihydrogenphosphate (Pereira Silva *et al.*, 1999).

The dihedral angle between the ring planes in (I) is 53.37 (8)°. The C2–C7 ring makes an angle of 50.85 (8)° with the least-squares plane of the guanidinium $CN_3$ group; the corresponding angle for the C8–C13 ring is 59.42 (9)°. *Ab initio* calculations for the free cation reported by Nagy & Durant (1996) determined that the equilibrium geometry of the *anti–anti* conformer has $C_2$ symmetry (binary axis parallel to the C1—N2 bond), with torsion angles $\varphi_1$ = C2—N1—C1—N2 = $\varphi_2$ = C8—N3—C1—N2 = 156.9 and $\varphi_3$ = C3—C2—N1—C1 = $\varphi_4$ = C9—C8—N3—C1 = −67.5°. In the present compound, these angles are $\varphi_1$ = 151.2 (2), $\varphi_2$ = 149.9 (2), $\varphi_3$ = −29.0 (2) and $\varphi_4$ = −38.1 (3)°, which shows that the cation retains only an approximate $C_2$ symmetry in the oxalate salt.

The anion in (I) is located at an inversion centre. The C=O bond lengths are similar, which is expected since the two carboxylate O atoms are involved in hydrogen bonds of approximately equal strength. The longer than usual $Csp^2$—$Csp^2$ bond length [1.554 (3) Å] in the oxalate anion is in good agreement with the average tabulated value for a number of oxalate salts (Allen *et al.*, 1987).

The anions and cations are interconnected in a two-dimensional hydrogen-bond network which extends in the (100) plane, as shown in Fig. 2. Each O atom of the anion accepts two protons donated by the NH and $NH_2$ groups of the neighbouring cations. All amino H atoms of the guanidine moiety participate in hydrogen-bonding, which is the situation typically found in $dpg^+$ salts but not in the unprotonated molecule in the free base (Zakharov *et al.*, 1980; Paixão *et al.*, 1999). Details of the hydrogen bonds are given in Table 2.

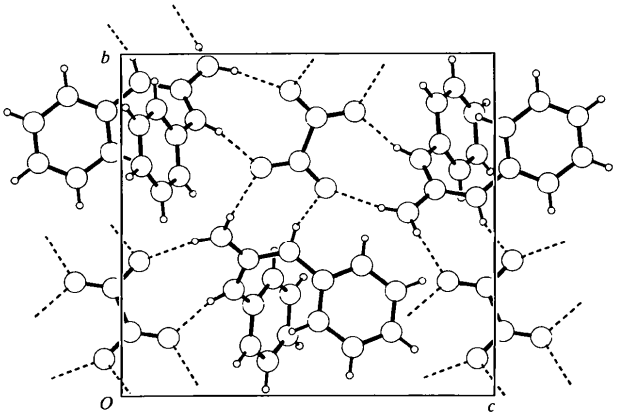



Fig. 2. The packing diagram for (I) projected along the *a* axis, showing the hydrogen-bonding scheme as dashed lines.

## Experimental

The title compound was prepared by neutralizing an ethanolic solution of *N,N'*-diphenylguanidine (98%, Aldrich) with oxalic acid (98%, Aldrich) in a 2:1 molar ratio. Crystals of (I) grew from the solution by slow evaporation over a period of a few weeks, and one small crystal was selected and used for the X-ray analysis.

*Crystal data*

$2C_{13}H_{14}N_3^+ \cdot C_2O_4^{2-}$
$M_r$ = 512.56
Monoclinic
$C2/c$
$a$ = 19.784 (9) Å
$b$ = 11.101 (9) Å
$c$ = 12.384 (4) Å
$\beta$ = 106.59 (2)°
$V$ = 2607 (3) Å$^3$
$Z$ = 4
$D_x$ = 1.306 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 10.20–15.38°
$\mu$ = 0.090 mm$^{-1}$
$T$ = 293 (2) K
Prism
0.25 × 0.25 × 0.13 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
2918 measured reflections
2682 independent reflections
1688 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.017
$\theta_{max}$ = 27.5°
$h = -25 \rightarrow 22$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 180 min
intensity decay: 5.8%

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $R[F^2 > 2\sigma(F^2)] = 0.035$ | $\Delta\rho_{max} = 0.162$ e Å$^{-3}$ |
| $wR(F^2) = 0.095$ | $\Delta\rho_{min} = -0.136$ e Å$^{-3}$ |
| $S = 1.017$ | Extinction correction: *SHELXL97* (Sheldrick, 1997) |
| 2682 reflections | Extinction coefficient: 0.0038 (4) |
| 215 parameters | Scattering factors from *International Tables for Crystallography* (Vol. C) |
| Only coordinates of H atoms refined | |
| $w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.9201P]$ where $P = (F_o^2 + 2F_c^2)/3$ | |

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

| | | | |
|---|---|---|---|
| C1—N2 | 1.314 (2) | N1—C2 | 1.425 (2) |
| C1—N1 | 1.333 (2) | N3—C8 | 1.416 (2) |
| C1—N3 | 1.341 (2) | | |
| N2—C1—N1 | 119.38 (15) | C1—N1—C2 | 126.88 (14) |
| N2—C1—N3 | 118.72 (14) | C1—N3—C8 | 125.69 (13) |
| N1—C1—N3 | 121.90 (14) | | |
| N2—C1—N1—C2 | 151.2 (2) | C1—N1—C2—C3 | −29.0 (2) |
| N2—C1—N3—C8 | 149.9 (2) | C1—N3—C8—C9 | −38.1 (3) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O1 | 0.876 (19) | 1.894 (19) | 2.753 (2) | 166.2 (16) |
| N2—H2*A*···O2 | 0.90 (2) | 2.03 (2) | 2.906 (2) | 166.3 (17) |
| N2—H2*B*···O1$^{i}$ | 0.889 (19) | 2.03 (2) | 2.885 (2) | 162.2 (17) |
| N3—H3···O2$^{ii}$ | 0.884 (19) | 1.937 (19) | 2.776 (2) | 158.0 (17) |

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

All H atoms were clearly seen in a difference Fourier map at an intermediate stage of the refinement. The coordinates of the H atoms were freely refined with an isotropic displacement parameter $U(H) = 1.2U_{eq}$ of the parent atom. The data collection was complete up to 25°, but only a partial shell up to 27.5° was measured because the crystal fell off the mounting pin before the end of the data collection. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no 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: *SHELXS97* (Sheldrick, 1990). 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1285). Services for accessing these data are described at the back of the journal.

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# 4-(*N*-Methylnitramino)pyridine 1-oxide

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## Abstract

In the title compound, $C_6H_7N_3O_3$, the $NNO_2$ group is twisted *ca* 59° from the planar pyridine ring. The nitramino group is almost planar, with the N7 atom diverging 0.15 Å from the C4–N8–C11 plane. The lone pair on N7 is included into the *N*-nitro group $\pi$-electron system resulting in two independent sets of multicenter