$C_{18}H_{19}NO_4S$

C4—S1—C2	88.8 (1)	N1—C5—C4	104.3 (2)
C12—N1—C5	119.1 (2)	C2'—C5—C3a'	103.4 (2)
C12—N1—C2	124.4 (2)	O1—C2'—C5	111.4 (2)
C5—N1—C2	116.4 (2)	C4'—C3a'—C6a'	101.8 (2)
C2'—O1—C6a'	111.6 (2)	C5'—C4'—C3a'	110.2 (3)
C5'—O6'—C6a'	107.5 (2)	C4'—C5'—O6'	112.9 (3)
N1—C2—S1	103.8 (2)	O6'—C6a'—C3a'	107.3 (2)

The H atoms were placed at calculated positions and refined as riding using the *SHELXL*97 (Sheldrick, 1997*a*) defaults. Examination of the structure with *PLATON* (Spek, 1995) showed that there are 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*b*). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1275). Services for accessing these data are described at the back of the journal.

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N,N'-Diphenylguanidinium dihydrogen phosphate

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Abstract

The two phenyl rings of the title compound, $C_{13}H_{14}N_3^+ \cdot H_2PO_4^-$, are oriented *anti* with respect to the unsubstituted N atom of the cation, which has approximate C_2 symmetry. Bond lengths and angles within the guanidinium moiety are close to those expected for a central Csp^2 atom. The anions form infinite $(H_2PO_4^-)_n$ chains running along the *c* axis. The amino groups of the cation interact with these chains *via* hydrogen bonds.

Comment

The structure determination of the title compound, (I), was undertaken as part of a current research project to study the structure and physical properties (optical and dielectric) of a series of diphenylguanidine (dpg) compounds. Much of the current interest in guanidine compounds and derivatives is due to their biological activity, in particular their neuroleptic and antipsychotic properties. This is the case for *N,N'*-di-*ortho*-tolylguanidine and its congeners, which are selective ligands for the haloperidol-sensitive σ receptor (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/PCP receptor [PCP is phencyclidine or *N*-(1-phenylcyclohexyl)piperidine] and these compounds have shown neuroprotective properties against glutamate-induced neuronal cell death (Olney *et al.*, 1989). Our interest in guanidine compounds is motivated by their potential applications in non-linear optics (Zyss *et al.*, 1993).

(I)
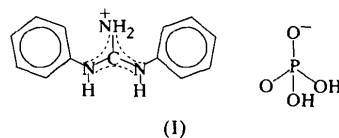
Several studies have shown that dpg is a very flexible molecule, due to the low potential barrier for rotation of the phenyl rings, and a number of different molecular conformations (*syn–syn*, *syn–anti* and *anti–anti*) have

been found both in solution (Alagona et al., 1994) and in several salts (Antolini et al., 1991; Matos Beja et al., 1998; Paixão et al., 1997, 1998a,b,c). The relative stability of the different conformers of protonated dpg in solution appears to depend on the counter-ion present, according to the ab initio and Monte Carlo calculations of Nagy & Durant (1996). Both the dipole moment and the polarizability of protonated dpg molecules depend on the orientation of the phenyl rings, which determine the optical and dielectric properties of these 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 [1.342 (2) Å] and C1—N3 [1.343 (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 C—N2 bond is shorter [1.310 (2) Å]. These three bond distances have values intermediate between the C—NH and C=N bonds in the unprotonated dpg molecule (Zakharov et al., 1980), indicating that some charge delocalization over the guanidine moiety occurs upon protonation.

The conformation of the cation in (I) is such that the two phenyl rings are both oriented anti to the unsubstituted N2 atom. This conformation is less common in dpg salts than the syn–anti (Antolini et al., 1991; Paixão et al., 1998a) and syn–syn conformations (Paixão et al., 1997, 1998b,c). Indeed, the only occurrence that has been reported so far of an anti–anti dpg+ cation is in bis(dpg) sulfate monohydrate (Matos Beja et al., 1998), where one of the two symmetry-independent cations has a similar conformation to the present case.
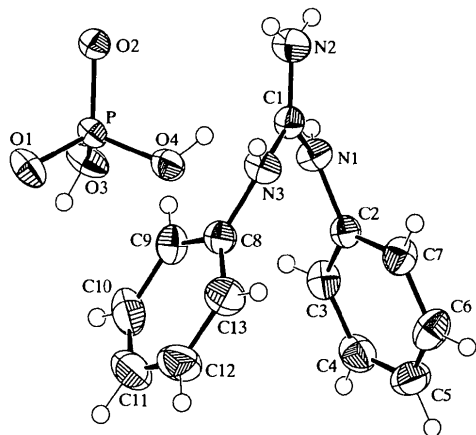

Fig. 1. ORTEPII (Johnson, 1976) plot of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

The dihedral angle between the ring planes is 49.47 (7)°. The C2–C7 ring makes an angle of 65.64 (7)° with the least-squares plane of the guanidinium CN_3 group, while the corresponding angle for

the C8–C13 ring is 60.27 (6)°. Ab initio calculations for the free cation reported by Nagy & Durant (1996) determined that the equilibrium geometry of the anti–anti conformer has C2 symmetry around the C1—N2 bond, with torsion angles φ_1 = C2—N1—C1—N2 = φ_2 = C8—N3—C1—N1 = 156.9° and φ_3 = C7—C2—N1—C1 = φ_4 = C9—C8—N3—C1 = −67.5°. In the dihydrogen phosphate salt, (I), these angles are φ_1 = 151.67 (16), φ_2 = 144.91 (16), φ_3 = −46.9 (2) and φ_4 = −33.7 (2)°, which shows that the cation retains approximate C_2 symmetry in the dihydrogen phosphate salt.

The geometry of the anion is that of a slightly distorted tetrahedron [O—P—O angles: 106.40 (7)–110.25 (7)°; P—O distances: 1.5056 (11)–1.5661 (13) Å]. Inspection of the bond distances shows the presence of two short and two long P—O bonds, the longer bonds corresponding, as expected, to the P—OH groups. This, and the objective localization of the H atoms on a difference Fourier map, confirms the full transfer of one proton from the orthophosphoric acid to the dpg molecule.

In addition to purely electrostatic interactions, the crystalline structure of (I) is stabilized by an extended hydrogen-bond network. The anions are linked together by rather strong hydrogen bonds to form infinite chains running along the c axis. In these hydrogen bonds, each
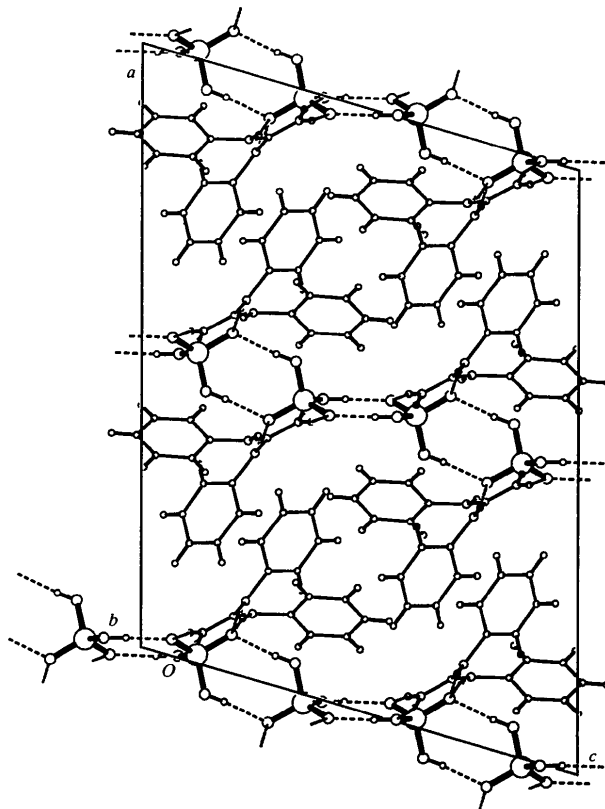

Fig. 2. The packing diagram for (I) viewed along the b axis, showing the hydrogen-bonding scheme as dashed lines.

$C_{13}H_{14}N_3^+ \cdot H_2PO_4^-$

of the non-hydroxy atoms, O1 and O2, is an acceptor from a hydroxyl group of a neighbouring anion. Similar polymeric $(H_2PO_4^-)_n$ macro-anions are found in other dihydrogen phosphate salts (Averbuch-Pouchot, 1993). As is usually found in dpg salts, full capability for hydrogen bonding of the cation is achieved. Indeed, each H atom of the NH and NH_2 groups is shared in moderately strong hydrogen bonds with the O atoms of the dihydrogen phosphate chains. Further details of the hydrogen bonds are given in Table 2. In addition to these, it is worth mentioning a possible interaction between atom H7 and the π cloud of the C2–C7 phenyl ring of a neighbouring cation [H7$\cdots Cg^i$ = 2.84 Å; Cg is the ring centroid; symmetry code: (i) $\frac{1}{2} - x$, $\frac{1}{2}$ y, $\frac{1}{2} - z$].

Experimental

The title compound was prepared by neutralizing an ethanolic solution of N,N'-diphenylguanidine (98%, Aldrich) with ortho-phosphoric acid in equimolar proportions. Colourless prismatic single crystals of (I) grew from the solution by slow evaporation over a period of a few days. One small crystal was selected and used for the X-ray analysis.

Crystal data

$C_{13}H_{14}N_3^+ \cdot H_2PO_4^-$	Mo $K\alpha$ radiation
$M_r = 309.26$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 22.8032\,(10)$ Å	$\theta = 9.80$–$13.91°$
$b = 7.639\,(2)$ Å	$\mu = 0.214$ mm^{-1}
$c = 16.986\,(2)$ Å	$T = 293\,(2)$ K
$\beta = 106.290\,(10)°$	Prism
$V = 2839.9\,(8)$ Å^3	$0.40 \times 0.32 \times 0.25$ mm
$Z = 8$	Colourless
$D_x = 1.447$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.015$
diffractometer	$\theta_{max} = 24.94°$
Profile data from $\omega/2\theta$ scans	$h = -26 \rightarrow 25$
Absorption correction: none	$k = -7 \rightarrow 9$
4003 measured reflections	$l = 0 \rightarrow 20$
2472 independent reflections	3 standard reflections
2010 reflections with	frequency: 180 min
$I > 2\sigma(I)$	intensity decay: 1.8%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.166$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.027$	$\Delta\rho_{min} = -0.272$ e Å^{-3}
$wR(F^2) = 0.080$	Extinction correction:
$S = 1.035$	SHELXL97 (Sheldrick,
2472 reflections	1997)
209 parameters	Extinction coefficient:
H atoms: see below	0.0021 (3)
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2$	Scattering factors from
$+ 1.8180P]$	*International Tables for*
where $P = (F_o^2 + 2F_c^2)/3$	*Crystallography* (Vol. C)
$(\Delta/\sigma)_{max} = 0.001$	

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

P—O2	1.5056 (11)	N1—C2	1.427 (2)
P—O1	1.5081 (12)	N2—C1	1.310 (2)
P—O3	1.5522 (13)	N3—C1	1.343 (2)
P—O4	1.5661 (13)	N3—C8	1.433 (2)
N1—C1	1.342 (2)		
N2—C1—N1	119.52 (15)	N1—C1—N3	120.30 (15)
N2—C1—N3	120.18 (15)		
C2—N1—C1—N2	151.67 (16)	C1—N1—C2—C7	−46.9 (2)
C8—N3—C1—N2	144.91 (16)	C1—N3—C8—C9	−33.7 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O1^i	0.83 (2)	1.73 (2)	2.5564 (17)	172 (2)
O4—H4$\cdots$O2^{ii}	0.82 (2)	1.85 (2)	2.6682 (17)	174 (2)
N1—H1$\cdots$O2	0.854 (19)	2.12 (2)	2.9715 (19)	171.2 (18)
N2—H2B$\cdots$O1	0.89 (2)	1.95 (2)	2.825 (2)	166.5 (19)
N2—H2A$\cdots$O3^{iii}	0.80 (2)	2.16 (2)	2.926 (2)	160 (2)
N3—H3A$\cdots$O2^{iii}	0.86 (2)	2.11 (2)	2.953 (2)	164.6 (18)

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

All H atoms could be located in a difference Fourier map at an intermediate stage of the refinement. The coordinates of the H atoms bonded to O or N were freely refined with an isotropic displacement parameter $U_{eq}(H) = 1.5U_{eq}(O)$ or $U_{eq}(H) = 1.2U_{eq}(N)$. The H atoms of the phenyl rings were placed at calculated positions and refined as riding using the SHELXL97 (Sheldrick, 1997) defaults of C_{aryl}—H = 0.93 Å and $U_{eq}(H) = 1.2U_{eq}$ of the parent atom. 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. Program(s) used to refine structure: SHELXL97. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL97.

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3,12-Diaza-6,9-diazoniadispiro[5.2.5.2]hexadecane dichloride from X-ray powder data

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Abstract

The crystal structure of the title compound, $C_{12}H_{26}N_4^{2+} \cdot 2Cl^-$, was determined from X-ray laboratory powder data. All three rings adopt a chair conformation. Hydrogen bonds involving NH groups are absent from this structure.

Comment

The title compound, (I), is an important precursor of some anticancer agents, e.g. prospidine (Mikhalev et

al., 1972), acting as dihydrofolate reductase inhibitors (Makarov, 1996). Recently, derivatives of (I) were also found to exhibit antiviral properties (Makarov et al., 1999). The title compound is hygroscopic and forms several phases with different water content. The present powder diffraction study was carried out in order to determine the structure of anhydrous 3,12-diaza-6,9-diazoniadispiro[5.2.5.2]hexadecane dichloride, since we failed to obtain single crystals.
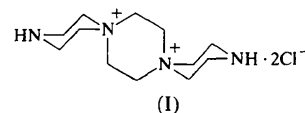
As in the structure of 3,12-bis(2-hydroxy-3-chloropropyl)-3,6,9,12-tetraazoniadispiro[5.2.5.2]hexadecane tetrachloride (Karapetyan et al., 1981), the cation of (I) occupies a special position at the inversion centre, and therefore has a *transoid* conformation relative to the central piperazinium ring. The bond lengths and angles are within the normally expected ranges. All three rings adopt chair conformations, with torsion angles within the range 52–61° (Table 2).

The crystal packing in (I) is illustrated in Fig. 1. The chloride anion makes nine Cl···H contacts shorter than 3.0 Å, the shortest being Cl···H72 (2.57 Å). The imino H atom was placed in the axial position because such an
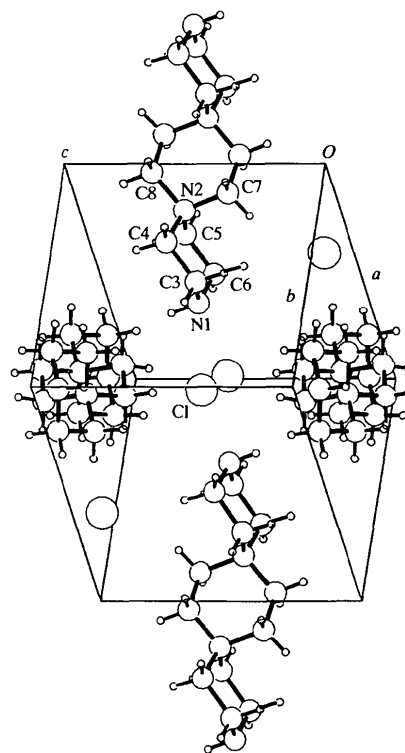

Fig. 1. Packing diagram of (I), showing the atom-numbering scheme.