

N,N'*-Diphenylguanidinium 8-hydroxyquinoline-5-sulfonate*P. S. Pereira Silva,^a M. Ramos Silva,^b A. Matos Beja^b and J. A. Paixão^{b*}**^aEscola Superior Agrária, Instituto Politécnico de Castelo Branco, Quinta da Senhora de Mércules, Apartado 119, 6001-909 Castelo Branco, Portugal, and ^bCEMDRX, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-516 Coimbra, Portugal

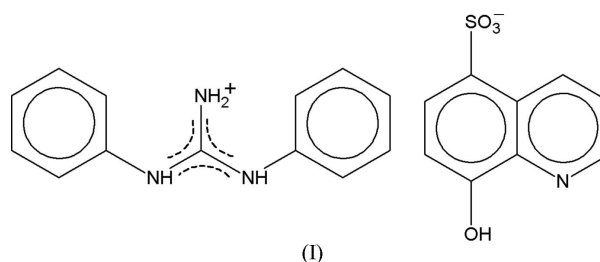
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Key indicatorsSingle-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.047
wR factor = 0.148
Data-to-parameter ratio = 17.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The cation of the title salt, $\text{C}_{13}\text{H}_{14}\text{N}_3^+ \cdot \text{C}_9\text{H}_6\text{NO}_4\text{S}^-$, is found to have a conformation with both phenyl rings lying in *syn* positions with respect to the unsubstituted N atom. The geometry of the guanidinium unit is close to that expected for a central Csp^2 atom. The anions are approximately parallel to the (010) plane. The structure is stabilized by a two-dimensional network of intermolecular hydrogen bonds.

Comment

The structure determination of the title compound, (I), was undertaken as part of a project to study the molecular conformations of diphenylguanidine salts and their optical and dielectric properties.



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 (Paixão *et al.*, 1999; Pereira Silva *et al.*, 1999, 2006). The conformation of dpg^+ is very sensitive to the counter-ion, and this effect has been studied theoretically by both *ab initio* quantum mechanical and molecular mechanics calculations (Nagy & Durant, 1996). Derivatives of 8-hydroxyquinoline (oxine) are known for their anti-amoebic, antibacterial and antifungal activities, which can be correlated to their metal-chelating ability (Banerjee & Saha, 1986). They are also well known analytical reagents. 8-Hydroxyquinoline-5-sulfonic acid exists as a zwitterion in acidic solution (Nasanen & Ekman, 1952), the proton being transferred from the sulfonic acid group to the quinoline nitrogen. Both alkyl and aryl guanidinium sulfonates have been investigated with the aim of creating materials with useful non-linear optical properties (Russel *et al.*, 1994*a,b*). The anion arises from the deprotonation of the sulfonic group, the proton being transferred to the guanidine fragment. The anions are approximately parallel to the (010) plane.

The benzene and pyridine rings of the quinoline unit are nearly coplanar, with a dihedral angle of $1.56(12)^\circ$ between them. The atoms around sulfur are arranged with the geometry of a distorted tetrahedron. The quinolinol OH group

Received 22 November 2006

Accepted 24 November 2006

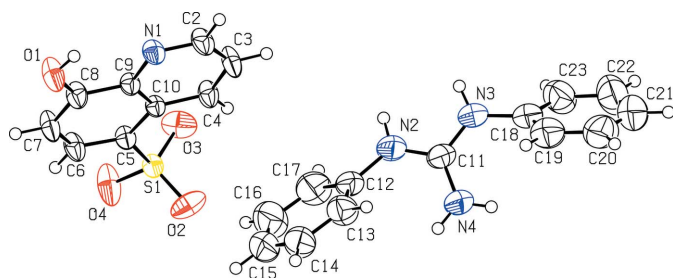


Figure 1
The asymmetric unit of (I), with the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

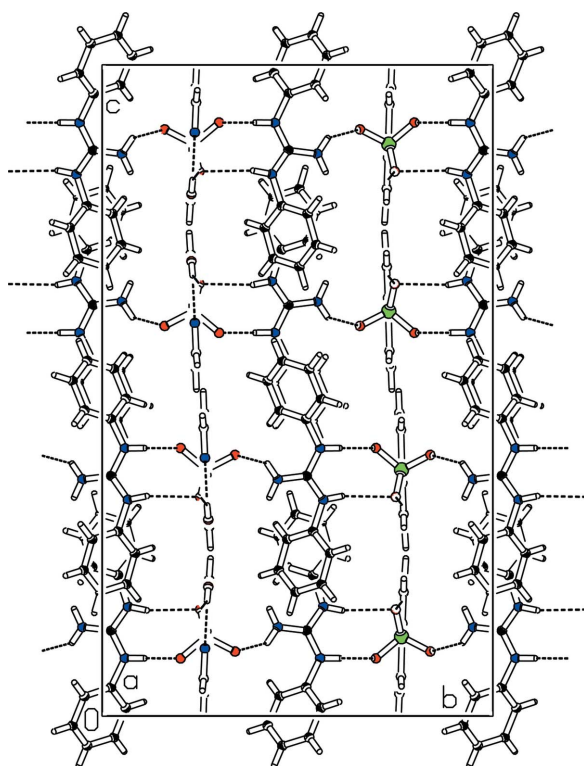


Figure 2
A projection of the crystal structure down the *a* axis. Hydrogen bonds are shown as dashed lines.

is not deprotonated and participates in two hydrogen bonds, one with a symmetry-related O atom of the sulfonic acid group (O1—H1...O4ⁱ; see Table 2 for symmetry codes) and the other an intramolecular bond with the quinoline N atom leading to a hydrogen-bonded ring. Atoms C4 and C6 are also involved in intramolecular hydrogen bonding, with atoms O3 and O4 of the sulfonate group (Table 1), forming rings on both sides of the S—C bond. The central guanidinium fragment of the cation is planar and the geometry is close to that expected for a central *Csp*² atom. The bond lengths C11—N2 [1.324 (4) Å] and C11—N3 [1.334 (4) Å] are within the range expected for a delocalized C=N bond, while the C11—N4 bond length is slightly shorter [1.317 (4) Å]. The phenyl rings have a *syn-syn* conformation with respect to the unsubstituted N atom. The

dihedral angle between the two phenyl rings is 25.6 (2)°, and the dihedral angles between the ring planes and the plane defined by the central guanidinium fragment are 52.8 (2)° (C12—C17) and 55.2 (2)° (C18—C23).

There are infinite chains of anions running along [100], assembled *via* O1—H1...O4ⁱ interactions (Table 1). The anions are linked *via* sulfonate and hydroxyl acceptors in the *b*-axis direction by guanidinium fragments.

Experimental

8-Hydroxyquinoline-5-sulfonic acid hydrate (Aldrich, 98%, 1 mmol) was added to diphenylguanidine (Aldrich, 97%, 1 mmol) in a water-ethanol (1/1) solution (100 ml). The solution was slowly warmed and then left to evaporate under ambient conditions. After a few days, small colourless transparent single crystals were deposited.

Crystal data

$C_{13}H_{14}N_3^+ \cdot C_9H_6NO_4S^-$	$Z = 8$
$M_r = 436.48$	$D_x = 1.387 \text{ Mg m}^{-3}$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 8.797 (2) \text{ \AA}$	$\mu = 0.19 \text{ mm}^{-1}$
$b = 16.880 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 28.145 (4) \text{ \AA}$	Parallelepiped, colourless
$V = 4179.6 (12) \text{ \AA}^3$	$0.39 \times 0.37 \times 0.17 \text{ mm}$

Data collection

Enraf-Nonius CAD-4 diffractometer	4800 independent reflections
ω - 2θ scans	2976 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$R_{\text{int}} = 0.018$
$T_{\text{min}} = 0.942$, $T_{\text{max}} = 0.964$	$\theta_{\text{max}} = 27.5^\circ$
7311 measured reflections	3 standard reflections
	frequency: 180 min
	intensity decay: 1.6%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.148$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.69 \text{ e \AA}^{-3}$
4800 reflections	$\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$
282 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0009 (2)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1...O4 ⁱ	0.82	1.99	2.691 (2)	143
O1—H1...N1	0.82	2.22	2.686 (3)	116
N2—H2A...O3 ⁱⁱ	0.86	2.01	2.806 (3)	153
N3—H3A...O4 ⁱⁱⁱ	0.86	2.32	3.145 (4)	160
N4—H4A...O2 ⁱⁱⁱ	0.86	2.22	2.891 (3)	135
C4—H4...O3	0.93	2.56	3.102 (3)	117
C6—H6...O4	0.93	2.39	2.815 (3)	107

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

The H atoms were located in a difference Fourier synthesis, placed at calculated positions and refined as riding using *SHELXL97* (Sheldrick, 1997) defaults [$C-H = 0.93 \text{ \AA}$, $N-H = 0.86 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C, N)$; $O-H = 0.82 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$].

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: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

This work was supported by Fundação para a Ciência e a Tecnologia (FCT), under project POCI/FIS/58309/2004.

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