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An oxonium hydrogen sulfate of 3a,6a-diphenylglycoluril

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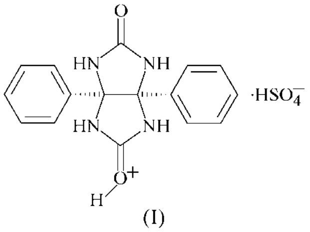
In the title compound, (5-oxo-3a,6a-diphenylperhydroimidazo[4,5-*d*]imidazol-2-ylidene)oxonium hydrogen sulfate, $C_{16}H_{15}N_4O_2^+\cdot HSO_4^-$, the asymmetric unit contains a hydrogen sulfate anion and a 3a,6a-diphenylglycoluril oxonium cation. The hydrogen sulfate anion is joined to the oxonium cation *via* a strong O—H···O hydrogen bond (H···O = 1.69 Å). The crystal packing is mainly dominated by interactions involving the hydrogen sulfate anion. The diphenylglycoluril oxonium cations also self-assemble through N—H···O hydrogen bonds, forming molecular chains along the [001] vector. Four intramolecular C—H···N hydrogen bonds are observed, having an *S*(5) motif.

Comment

Glycoluril and its derivatives, formed in the condensation reaction of two equivalents of urea with one equivalent of glyoxal (Petersen, 1973), have attracted a great deal of attention recently because of wider developments in the fields of cucurbituril chemistry (Freeman *et al.*, 1981; Kim *et al.*, 2000; Lee *et al.*, 2003), anion sensors (Kang *et al.*, 2004; Kang & Kim, 2005) and materials (Kölbel & Menger, 2001). Thus, various glycoluril derivatives have been synthesized and reported (Wu *et al.*, 2002; Burnett *et al.*, 2003). As part of this study of cucurbituril chemistry and the preparation of new cucurbiturils, we synthesized the title compound, (I). Although many crystal structures of glycoluril and its derivatives have been reported to date (Xu *et al.*, 1994; Wu *et al.*, 2002; Fettinger *et al.*, 2003, 2004; Creaven *et al.*, 2004), and and co-workers have reported the co-crystallized structure of the title organic compound with pyridine (Moon *et al.*, 2003), this is the first report of the new and interesting structure of (I).

In (I), the asymmetric unit contains a hydrogen sulfate anion and a 3a,6a-diphenylglycoluril oxonium cation (Fig. 1). Carbonyl atom O2 is protonated, forming the oxonium ion. The H atoms bonded to atoms O5 and O2 were found directly in the difference Fourier map and positioned correctly, and are not disordered over O1 or other atoms of the HSO_4 group. Geometric differences are observed between the unprotonated atom O1 and the oxonium atom O2: the C4═O2 bond of 1.279 (4) Å is significantly longer than the C3═O1 bond of 1.245 (4) Å. Furthermore, the two tetrahydroimidazole rings differ in their geometric structures (1). The C1—C2 distance of 1.624 (5) Å is similarly long to that of 1.604 (3) Å reported by Moon *et al.* (2003). The two tetrahydroimidazole rings form a dihedral angle of 65.51 (1)°.



(I)

Owing to the peculiar spatial arrangement of the crystal structure of (I), four intramolecular C—H···N hydrogen bonds (Afonin *et al.*, 2002; Moon *et al.* 2003) are formed, with the aromatic CH groups acting as donors (Table 2). These have a common motif of *S*(5) (Bernstein *et al.*, 1995), which was also found in the structures reported by Moon *et al.* (2003). The C5—C2—C1—C11 torsion angle is 13.4 (4)°, the C16—C11—C2—C1 and C12—C11—C2—C1 torsion angles are −94.1 (4) and 83.1 (4)°, respectively, and the C2—C1—C5—C6 and C2—C1—C5—C10 torsion angles are −94.0 (4) and 83.2 (4)°, respectively.

There is an intramolecular π–π interaction, as elucidated by *PLATON* (Spek, 2003), between the two phenyl ring planes, with a centroid-to-centroid distance of 4.058 (3) Å; the corresponding distance is 4.108 (2) Å in Moon's crystal structure.

The geometric parameters of the hydrogen sulfate anion in (I) are consistent with those reported by Hemamalini *et al.*

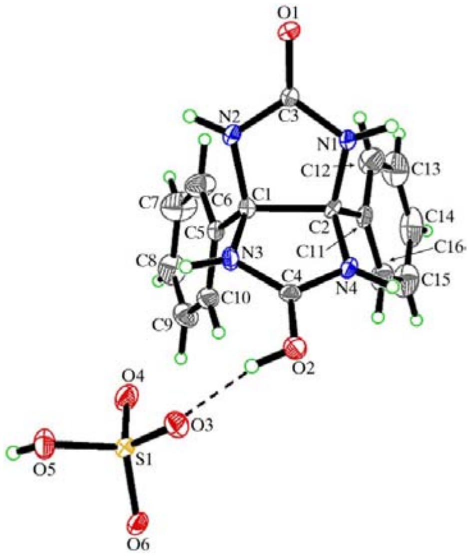


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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(2005). The O—S—O bond angles of the sulfate group, in the range 103.46 (16)–113.15 (17)°, indicate a distorted tetrahedron. The HSO_4^- anion is anchored to the diphenylglycoluril oxonium cation by a strong O—H···O hydrogen bond, indicated by the H···O distance of 1.69 Å, with an O—H···O angle of 165°. As well as this strong interaction, the hydrogen sulfate anion is hydrogen bonded to five diphenylglycoluril molecules *via* O—H···O, N—H···O and C—H···O interactions (Fig. 2 and Table 2). These interactions involving the hydrogen sulfate anion dominate the crystal packing of (I) in a way that is distinctly different from the packing of glycoluril and its derivatives published previously, where hydrogen-bonded tapes were formed (Xu *et al.*, 1994; Wu *et al.*, 2002; Moon *et al.*, 2003). In addition, there is also an N3—H3···O1 hydrogen bond, with atom N3 of one glycoluril moiety as donor and carbonyl atom O1 of the other glycoluril moiety as acceptor, which links the molecules of (I) into an infinite one-dimensional chain along the [001] vector. All these interactions form a network of hydrogen-bonded hydrophilic zones, separating hydrophobic zones composed of the phenyl groups, similar to the structure described by Moon (Fig. 3).

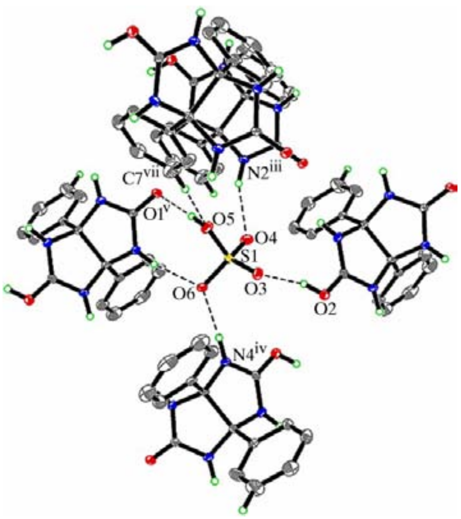

Figure 2
The hydrogen sulfate anion of (I) and its surroundings. Hydrogen-bonding interactions are indicated by dotted lines. Only atoms involved in the hydrogen bonds are labelled. The symmetry codes are as in Table 2, with the addition of (vii) $x-1, \frac{1}{2}-y, \frac{1}{2}+z$.

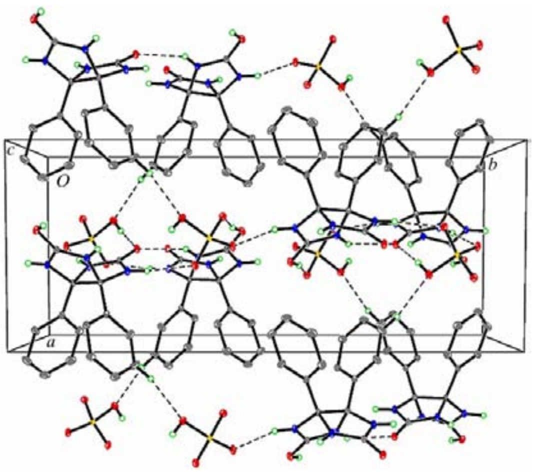

Figure 3
A packing diagram for (I), viewed down the *c* axis.

In conclusion, we have obtained an interesting crystal structure of diphenylglycoluril hydrogen sulfate oxonium from its sulfuric acid solution. X-ray analysis demonstrates that the crystal adopts a different packing from the extensive hydrogen-bonding networks reported previously, a result of the presence of the hydrogen sulfate anion.

Experimental

Compound (I) (100 mg) was dissolved in aqueous H_2SO_4 (1 *M*, 1 ml). The solution was allowed to evaporate slowly at room temperature for one week. Colourless crystals of (I) suitable for X-ray crystallographic analysis were collected.

Crystal data

$C_{16}H_{15}N_4O_2^+\cdot HSO_4^-$
$M_r = 392.39$
Monoclinic, $P2_1/c$
$a = 8.4695$ (18) Å
$b = 20.686$ (4) Å
$c = 10.269$ (2) Å
$\beta = 93.655$ (3)°
$V = 1795.5$ (7) Å^3
$Z = 4$
$D_x = 1.452$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7302 reflections
$\theta = 2.4$–26.9°
$\mu = 0.22$ mm^{-1}
$T = 203$ (2) K
Block, colourless
0.50 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.897$, $T_{max} = 0.978$
7302 measured reflections
3160 independent reflections
2888 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 25.0$°
$h = -5 \rightarrow 10$
$k = -23 \rightarrow 24$
$l = -12 \rightarrow 12$

Table 1
Selected geometric parameters (Å, °).

S1—O4	1.435 (3)	N2—C1	1.442 (5)
S1—O6	1.451 (3)	N1—C3	1.337 (4)
S1—O3	1.455 (3)	N1—C2	1.441 (5)
S1—O5	1.542 (3)	N3—C4	1.327 (4)
O1—C3	1.245 (4)	N3—C1	1.465 (5)
O2—C4	1.279 (4)	C1—C5	1.509 (5)
N4—C4	1.319 (5)	C1—C2	1.624 (5)
N4—C2	1.439 (4)	C11—C2	1.511 (5)
N2—C3	1.340 (4)		
O3—S1—O5	103.46 (16)	C12—C11—C2	119.4 (4)
O4—S1—O3	113.15 (17)	C6—C5—C1	120.4 (4)
O4—S1—O5	107.98 (16)	C10—C5—C1	120.7 (3)
O4—S1—O6	112.89 (18)	O1—C3—N1	126.2 (3)
O6—S1—O3	111.29 (16)	O1—C3—N2	124.8 (3)
O6—S1—O5	107.42 (16)	N1—C3—N2	109.0 (3)
N2—C1—C5	114.2 (3)	N4—C2—N1	111.7 (3)
N3—C1—C5	111.3 (3)	N4—C2—C11	113.1 (3)
C5—C1—C2	115.8 (3)	N1—C2—C11	113.4 (3)
O2—C4—N4	120.4 (3)	N4—C2—C1	101.7 (3)
O2—C4—N3	127.5 (3)	N1—C2—C1	100.2 (3)
C16—C11—C2	122.0 (4)	C11—C2—C1	115.5 (3)
C2—C1—C5—C6	−94.0 (4)	N3—C1—C2—N4	10.5 (3)
C2—C1—C5—C10	82.3 (4)	N2—C1—C2—N1	11.6 (3)
C16—C11—C2—C1	−94.1 (4)	C5—C1—C2—C11	13.4 (4)
C12—C11—C2—C1	83.1 (4)		

Huo *et al.* · $C_{16}H_{15}N_4O_2^+\cdot HSO_4^-$ **o501**

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6$\cdots$N2	0.94	2.50	2.838 (6)	101
C10—H10$\cdots$N3	0.94	2.52	2.839 (5)	100
C12—H12$\cdots$N1	0.94	2.54	2.851 (6)	100
C16—H16$\cdots$N4	0.94	2.52	2.849 (6)	101
N1—H1$\cdots$O6$^{\rm i}$	0.87	2.01	2.869 (4)	169
N2—H2$\cdots$O4$^{\rm ii}$	0.87	2.05	2.874 (4)	158
N3—H3$\cdots$O1$^{\rm iii}$	0.87	2.19	2.910 (4)	140
N4—H4$\cdots$O6$^{\rm iv}$	0.87	1.96	2.806 (4)	162
O5—H5$\cdots$O1$^{\rm v}$	0.83	1.71	2.538 (4)	172
C7—H7$\cdots$O5$^{\rm vi}$	0.94	2.32	3.244 (6)	166
O2—H2$A\cdots$O3	0.83	1.69	2.495 (4)	165

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.077$
$wR(F^2) = 0.149$
$S = 1.28$
3160 reflections
250 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 2.3309P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

All H atoms were located in a difference Fourier synthesis and fixed on their parent atoms, with $U_{\rm iso}$(H) values set at $1.5U_{\rm eq}$(O) and $1.2U_{\rm eq}$(N,C) for the other H atoms; C—H distances were fixed in the range 0.93–0.99 Å, O—H distances were fixed at 0.83 Å and N—H distances were fixed at 0.87 Å. The R factor of 0.077 may be due to random protonation of the diphenylglycoluril by the hydrogen sulfate to form the oxonium ion.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1059). Services for accessing these data are described at the back of the journal.

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