

## Bis(phenylguanidinium) carbonate monohydrate

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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$ 

R factor = 0.041

wR factor = 0.126

Data-to-parameter ratio = 18.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $2 \text{ C}_6\text{H}_5\text{NHC}(\text{NH}_2)_2^+ \cdot \text{CO}_3^{2-} \cdot \text{H}_2\text{O}$ , the phenylguanidinium cations and carbonate anions are arranged to form planes parallel to *bc*. The water molecules are located between these planes. A three-dimensional network of hydrogen bonds is observed in the crystal and H atoms of the guanidinium cations and water molecules are involved. The phenylguanidinium cations show a conformation different from that observed in other guanidyl derivatives.

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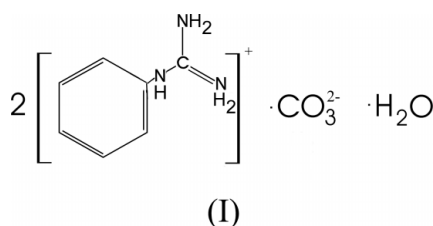
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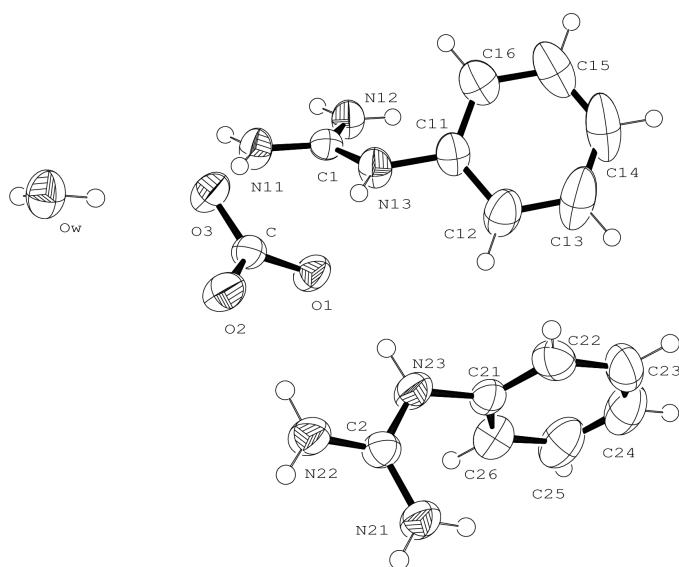
Contribution No. 1 to the 'Molecular and crystal, engineering of some octupolar cations'.

## Comment

In the title compound, (I), there are two independent phenylguanidinium cations, Phg1 and Phg2 (Fig. 1). They have different geometry in spite of the similar positioning of the phenyl and guanidine moieties. The torsion angles C1—N13—C11—C16 and C2—N23—C21—C26 are, respectively, 54.4 (2) and 79.7 (2)°. Similar conformational non-equivalence is observed in arginine glutamate hydrate (Bhat & Vijayan, 1977), arginine dihydrate (Lehmann *et al.*, 1973) and L-arginine hydrogen squarate (Angelova *et al.*, 1996).



The phenyl groups of Phg1 are situated facing one another and form hydrophobic layers parallel to *bc* (Fig. 2). The Phg2 molecules and carbonate anions are located on both sides of the layers. The water molecules are situated between these layers. H atoms of the guanidinium groups and water molecules take part in an extensive network of hydrogen bonds, connecting the layers in the *c* direction. The observed different conformations of the two cations are due to the different hydrogen-bonding systems involving atoms N12 and N21, because the only conformational freedom of the phenylguanidinium cation is rotation about the N(guan)—C(phen) bond. The first guanidiny group is hydrogen bonded to a carbonate O atom and interacts with the adjacent phenyl ring. The second one is bound to the water molecule in two different equivalent positions. To the best of our knowledge, only one compound, apart from the title compound, containing the phenylguanidinium cation, has been characterized by X-ray diffraction, *viz.* bisphenylguanidinium squarate (Kolev *et al.*, 1997). The conformation of the phenylguanidinium cation in the latter structure is different



**Figure 1**  
The independent entities of the title compound with atom labels and 50% probability ellipsoids for non-H atoms.

with respect to Phg1 and Phg2 and the C3–N3–C4–C5 torsion angle is  $43.14^\circ$ . We can conclude that the conformation of the cation is very sensitive to the environment.

The IR spectrum in the solid state (KBr pellet) confirms that the phenylguanidine exists as a cation. We assign the strong sharp bands at  $3435\text{ cm}^{-1}$  to the asymmetric stretching vibration of the water molecule. There are six strong broad bands between  $3390\text{--}2750\text{ cm}^{-1}$ . They are assigned to the stretching N–H vibrations, connected with N–H $\cdots$ O hydrogen bonds.

## Experimental

The title compound is commercially available as powder (EGA Chemie, Germany). The crystals obtained after recrystallization from water–methanol solution have a melting point of  $415\text{--}417\text{ K}$ , higher than that of the crude product,  $413\text{--}415\text{ K}$ . In both cases, the product melts with decomposition. Colorless crystals suitable for X-ray single-crystal analysis were grown from solution in doubly-distilled water at room temperature. The compound was characterized by elemental analysis and spectroscopic methods.

### Crystal data

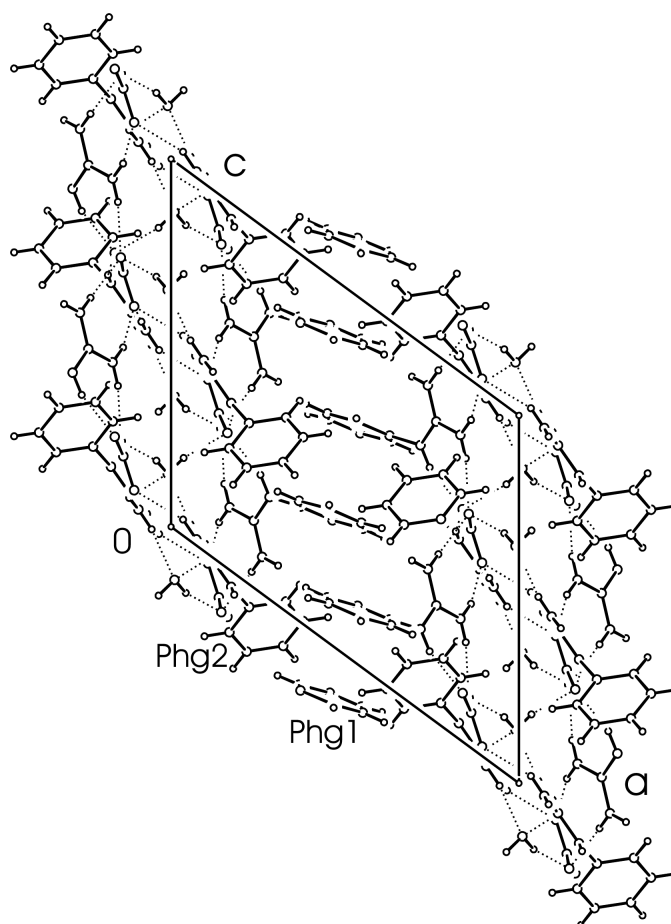
$2\text{C}_7\text{H}_{10}\text{N}_3^+\cdot\text{CO}_3^{2-}\cdot\text{H}_2\text{O}$   
 $M_r = 350.39$   
 Monoclinic,  $P2_1/c$   
 $a = 15.527(3)\text{ \AA}$   
 $b = 10.648(5)\text{ \AA}$   
 $c = 13.081(5)\text{ \AA}$   
 $\beta = 125.98(2)^\circ$   
 $V = 1750.1(11)\text{ \AA}^3$   
 $Z = 4$

$D_x = 1.330\text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 22 reflections  
 $\theta = 17.9\text{--}19.9^\circ$   
 $\mu = 0.10\text{ mm}^{-1}$   
 $T = 293(2)\text{ K}$   
 Prismatic, colorless  
 $0.21 \times 0.19 \times 0.19\text{ mm}$

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$ – $2\theta$  scans  
 8538 measured reflections  
 4209 independent reflections  
 2691 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$   
 $\theta_{\text{max}} = 28.0^\circ$

$h = -20 \rightarrow 16$   
 $k = -14 \rightarrow 14$   
 $l = 0 \rightarrow 17$   
 3 standard reflections every 500 reflections  
 frequency: 120 min  
 intensity decay: 0.8%



**Figure 2**  
Packing of the molecules, viewed down the  $b$  axis. The hydrogen bonds are indicated by dotted lines.

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.126$   
 $S = 1.02$   
 4209 reflections  
 232 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 0.1716P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.013$   
 $\Delta\rho_{\text{max}} = 0.17\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.21\text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: none

**Table 1**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{OW--HW1}\cdots\text{O3}$	0.87 (2)	1.94 (3)	2.7899 (19)	165 (2)
$\text{OW--HW2}\cdots\text{O1}^i$	0.86 (3)	2.03 (3)	2.868 (2)	166 (2)
$\text{N21--H21A}\cdots\text{OW}^{ii}$	0.86	2.01	2.866 (2)	170
$\text{N21--H21B}\cdots\text{OW}^{iii}$	0.86	2.51	3.067 (2)	123
$\text{N22--H22A}\cdots\text{O2}^{ii}$	0.86	2.12	2.8830 (19)	147
$\text{N22--H22B}\cdots\text{O2}$	0.86	1.91	2.769 (2)	175
$\text{N23--H23}\cdots\text{O1}$	0.86	1.91	2.750 (2)	164
$\text{N11--H11A}\cdots\text{O2}^{iv}$	0.86	2.05	2.889 (2)	164
$\text{N11--H11B}\cdots\text{O3}$	0.86	1.98	2.831 (2)	170
$\text{N12--H12A}\cdots\text{O3}^{iv}$	0.86	2.03	2.878 (2)	167
$\text{N13--H13}\cdots\text{O1}$	0.86	1.94	2.7721 (17)	163

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); data reduction: *DATARED* (Vasilev, unpublished); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976).

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