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Guaninium dichloride

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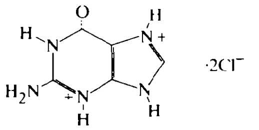
Abstract

The title compound, 2-amino-1,6-dihydro-6-oxo-9*H*-purine-3,7-diium dichloride, consists of guaninium $C_5H_7N_5O^{2+}$ cations and Cl^- anions; all atoms, including H, lie in a mirror plane. The rings are protonated at N3 and N7. There is one hydrogen bond between two guaninium ions [N9—H···O1 2.797 (3) Å] and six others interconnecting the guaninium and chlorine ions in the plane [N—H···Cl 3.050 (3)–3.207 (2) Å].

Comment

In the study of radiation effects on DNA, crystals of the DNA components are used (Sanković *et al.*, 1988, 1996; Herak *et al.*, 1994, 1997). A new salt was found during the crystallization of guanine salts, and it was of interest to solve the structure of this new salt for further EPR studies of irradiated crystals. Two structures of guanine hydrochloride salts were previously known: guanine hydrochloride monohydrate (Broomhead, 1951; Maixner & Zachová, 1991) and dihydrate (Iball & Wilson, 1963). We report here the structure of guaninium dichloride, (I) (guanine dihydrochloride).



(I)

All atoms (including H) of the guaninium cation $C_5H_7N_5O^{2+}$, and also the two Cl^- anions, lie in the crystallographic mirror plane. In the structure of guanine hydrochloride monohydrate, the dihedral angle between the imidazole and pyridine rings is 1.70 (15)°, so there is no significant deviation from planarity (Maixner & Zachová, 1991). The greatest differences between the hydrochloride and the present dihydrochloride structure are in the bond lengths and angles involving N3, which is protonated in (I). The C2—N3 and N3—C4 distances of 1.361 (3) and 1.362 (4) Å, and the C2—N3—C4 angle of 117.5 (2)°, are larger than in the hydrochloride monohydrate structure [1.336 (2) and 1.345 (2) Å, and 112.2 (1)°, respectively]. The N1—C2—N3 and N3—C4—C5 angles decrease correspondingly by 3.9 and 4.6°, respectively. The shortest C—N bonds are C2—N10 [1.318 (4) Å] and N7—C8 [1.326 (3) Å], which have a high degree of double-bond character. However, delocalization of electron density is also present, as can be seen from the interatomic distances.

Shortening of the C2—N10 bond is influenced by two N10—H···Cl hydrogen bonds involving both H

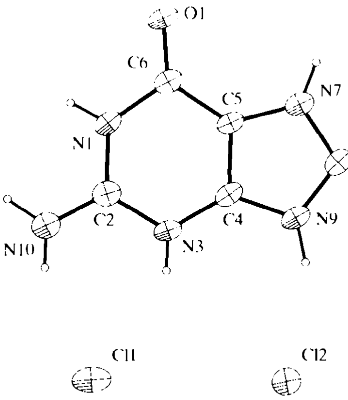


Fig. 1. View of the title structure with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as circles of an arbitrary radius.

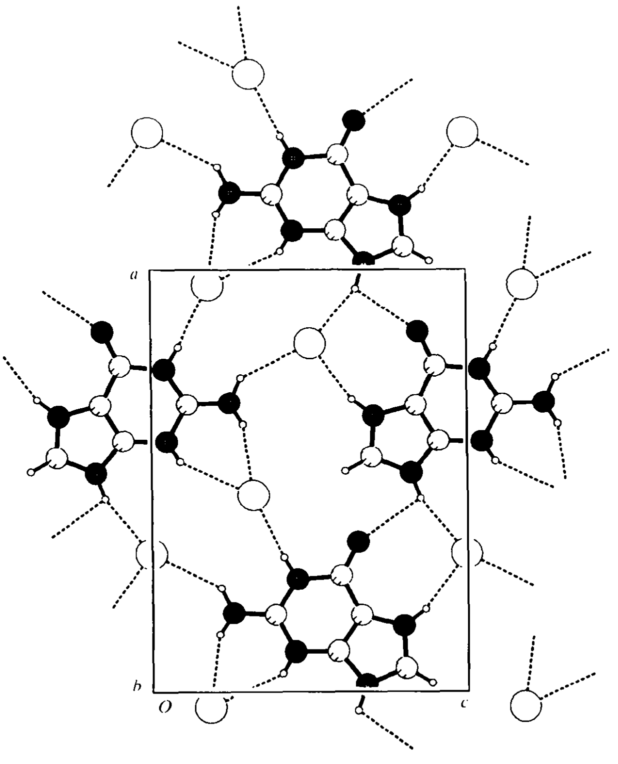


Fig. 2. Packing of the guaninium and chlorine ions in the plane at *y* = 0.25. Hydrogen bonds are indicated by dashed lines.

atoms on N10, whereas in the hydrochloride structure only one H is involved in hydrogen bonding. Indeed, an interesting hydrogen-bonding network, shown in Fig. 2, is formed in the plane. Apart from the hydrogen bonds mentioned above, there are three N—H···Cl hydrogen bonds involving N1, N3 and N7. The H atom at N9 forms a three-centre hydrogen bond with O1 from a symmetry-related guaninium ion and with Cl2.

There are no direct stacking interactions between the guaninium ions. The N—H···Cl hydrogen bonds help delocalize the charges, allowing packing without short contacts between the N and Cl ions of two neighbouring planes. Atom Cl1 lies between two C8 atoms, while Cl2 lies approximately between the centroids of the pyridine rings.

Experimental

A saturated solution of guanine (Aldrich) in 20% HCl was prepared at 323 K. The solution was left in a beaker covered with a watch glass in a desiccator at 318 K. Crystals of good quality were obtained after 1 month. When exposed to atmospheric moisture the crystals decompose within a day.

Crystal data

$C_5H_7N_5O^{2+}\cdot 2Cl^-$
$M_r = 224.06$
Orthorhombic
Pnma
$a = 13.590 (2)$ Å
$b = 6.5810 (11)$ Å
$c = 9.9321 (14)$ Å
$V = 888.3 (2)$ Å^3
$Z = 4$
$D_x = 1.675$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 8–18°$
$\mu = 0.697$ mm^{-1}
$T = 293 (2)$ K
Prism
0.60 × 0.60 × 0.54 mm
Colourless

Data collection

Philips PW1100 diffractometer, updated by Stoe & Cie
$\omega/2\theta$ scans
Absorption correction: none
4221 measured reflections
1407 independent reflections
853 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.038$
$\theta_{\rm max} = 30.06°$
$h = -19 \rightarrow 19$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 6.1%

Refinement

Refinement on F^2
$R(F) = 0.039$
$wR(F^2) = 0.108$
$S = 1.016$
1222 reflections
100 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 0.2891P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.238$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.227$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl1	−0.03600 (5)	1/4	0.18051 (9)	0.0517 (2)
Cl2	−0.17508 (5)	1/4	0.50317 (7)	0.0386 (2)
O1	0.35262 (13)	1/4	0.6529 (2)	0.0599 (7)
N1	0.2639 (2)	1/4	0.4586 (2)	0.0348 (6)
C2	0.1797 (2)	1/4	0.3870 (3)	0.0331 (6)
N3	0.0916 (2)	1/4	0.4521 (2)	0.0330 (5)
C4	0.0932 (2)	1/4	0.5892 (3)	0.0293 (6)
C5	0.1782 (2)	1/4	0.6619 (3)	0.0315 (6)
C6	0.2725 (2)	1/4	0.5988 (3)	0.0364 (7)
N7	0.15223 (15)	1/4	0.7957 (2)	0.0358 (6)
C8	0.0548 (2)	1/4	0.8029 (3)	0.0366 (7)
N9	0.01717 (15)	1/4	0.6779 (2)	0.0344 (5)
N10	0.1835 (2)	1/4	0.2545 (3)	0.0469 (7)

Table 2. *Selected geometric parameters (Å, °)*

O1—C6	1.214 (3)	C4—N9	1.358 (3)
N1—C2	1.347 (3)	C4—C5	1.362 (3)
N1—C6	1.397 (4)	C5—N7	1.375 (3)
C2—N10	1.318 (4)	C5—C6	1.427 (3)
C2—N3	1.361 (3)	N7—C8	1.326 (3)
N3—C4	1.362 (4)	C8—N9	1.343 (4)
C2—N1—C6	126.7 (2)	C4—C5—C6	122.0 (2)
N10—C2—N1	119.7 (3)	N7—C5—C6	130.9 (2)
N10—C2—N3	120.6 (3)	O1—C6—N1	121.1 (2)
N1—C2—N3	119.8 (2)	O1—C6—C5	127.7 (3)
C2—N3—C4	117.5 (2)	N1—C6—C5	111.2 (2)
N9—C4—C5	107.6 (2)	C8—N7—C5	108.0 (2)
N9—C4—N3	129.5 (2)	N7—C8—N9	109.3 (2)
C5—C4—N3	122.9 (2)	C8—N9—C4	108.0 (2)
C4—C5—N7	107.1 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1$^{\rm i}$	0.82 (4)	2.24 (4)	3.050 (3)	174 (4)
N3—H3···Cl1	0.77 (3)	2.53 (3)	3.207 (2)	148 (3)
N7—H7···Cl2$^{\rm ii}$	0.87 (3)	2.23 (3)	3.082 (2)	164 (3)
N9—H9···O1$^{\rm iii}$	0.88 (4)	2.41 (3)	2.797 (3)	107 (2)
N9—H9···Cl2	0.88 (4)	2.30 (4)	3.137 (2)	159 (3)
N10—H101···Cl2$^{\rm i}$	0.90 (3)	2.45 (3)	3.201 (3)	141 (2)
N10—H102···Cl1	0.81 (4)	2.32 (4)	3.072 (3)	155 (3)

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

Data were collected from a crystal sealed in a capillary. The structure was solved by direct methods in space group $Pna2_1$. The *MISSYM* (Le Page, 1987, 1988) program in *PLATON*97 (Spek, 1990) indicated higher symmetry, so further refinement was performed in space group *Pnma*. The H atoms were found in the difference Fourier map and were refined isotropically. An absorption correction on the basis of ψ scans was attempted, but led to no improvement of the final model.

Data collection: *STADI*4 (Stoe & Cie, 1995*a*). Cell refinement: *STADI*4. Data reduction: *X-RED* (Stoe & Cie, 1995*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *PLATON*97 and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97 and *PLATON*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1324). Services for accessing these data are described at the back of the journal.

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X-ray investigations of sulfur-containing fungicides. I. 4′-{[Benzoyl(4-tolylhydrazono)methyl]sulfonyl}acetanilide

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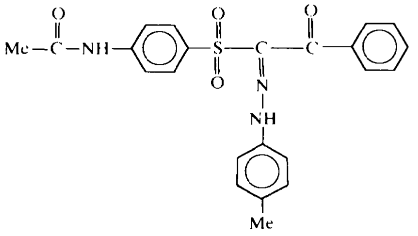
Abstract

The conformation of the title compound, $C_{23}H_{21}N_3O_4S$, is stabilized by a strong intramolecular hydrogen bond assisted by resonance connecting the hydrazone moiety and the sulfonyl group. The most important electronic interaction is electrostatic attraction of the oppositely charged carbonyl and sulfonyl groups which counteracts the strongly electron-withdrawing character of the latter group.

Comment

Sulfones, similarly to sulfonamides, show strong *in vitro* and *in vivo* antibacterial activity and for almost 60 years have been used successfully in medicine (Mandell & Sande, 1985). Certain sulfones also exhibit fungicidal activity. Preliminary tests have proved that substituted (2-oxo-2-phenylethyl) phenyl sulfones show fungicidal activity comparable to, or better than, commercial fungicides (Zakrzewski, 1996). The present work is part of a larger project in which we aim to identify molecular features which are responsible for the antimycotic action and to construct the best fungicide. The most effective way to fight fungi is to attack spores before they manage to germinate (Hassall, 1982). This requires long and continuous action of a fungicide. The goal of this project is to construct compounds which undergo slow photodynamic degradation in the presence of daylight and reduce themselves to compounds similar to (2-oxo-2-phenylethyl) phenyl sulfones. Although there are almost 100 β-keto sulfones in the Cambridge Structural Database (Allen *et al.*, 1979), to the best of my knowledge there has been no X-ray structure determination so far of the α-hydrazone-β-keto sulfones described in the scientific literature.



(I)

A view of the title compound (I) with atom numbering is shown in Fig. 1. The S=O2 sulfonyl double bond, the carbonyl group and the *p*-methylphenylhydrazone moiety are roughly coplanar. The molecular conformation of these three fragments is similar to that observed in β-diketo-arylhydrazones (Bertolasi, Gilli *et al.*, 1994) and can be defined as *EZE*. The three-letter symbol was initially introduced to describe the conformation of 2,2-diacylethenamines (Gómez-Sánchez *et al.*, 1987) and was further applied to β-diketo-arylhydrazones. In the title compound, the above three letters indicate, relative to the C1=N1 bond, the positions of the carbonyl C2=O3 and the sulfonyl S=O2 double bonds as well as the N2—C17 bond bearing the aryl substituent.

The central part of the molecule is stabilized by a strong intramolecular hydrogen bond, assisted by resonance (RAHB), connecting the hydrazone moiety and the sulfonyl group. With two π bonds and an n_p nitrogen lone pair this practically planar (mean deviation from the O2,S,C1,N1,N2,H2 plane is 0.03 Å) cyclic system follows Hückel's rule of aromaticity (March, 1992). Although several publications exist on