

RK is grateful to the Academy of Finland.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1061). Services for accessing these data are described at the back of the journal.

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N,N'-Diphenylbenzamidinium nitrate

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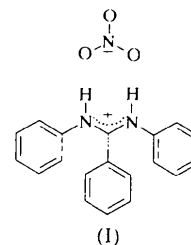
Abstract

The title compound, C₁₉H₁₇N₂⁺·NO₃⁻, consists of a diphenylbenzamidinium cation [Ph(H)NC(Ph)N(H)Ph]⁺ hydrogen-bonded to a planar nitrate anion through an N—H···O interaction; both ions lie on a twofold

axis. The hydrogen-bonded N···O distance is short at 2.7767(19) Å, and placing the N—H protons in calculated positions gives an N—H···O angle of 173°. There are no other significant intermolecular interactions between the ions.

Comment

Following our earlier work on gallium complexes involving amidine ligands (Barker *et al.*, 1996), we are now investigating the properties of solutions containing amidines in the presence of gallium and nitrate ions in view of the pharmaceutical effects provided by the synergism of the species within such mixtures (Fimiani *et al.*, 1990; Bradley *et al.*, 1992). In the course of this work, crystals of the title compound, (I), were isolated from solutions containing gallium nitrate and the amidinium anion. The crystal structure of this material has been determined since it affords an opportunity to study the structural features of an *N,N'*-disubstituted amidinium cationic system for which only limited data have been published previously (Krechl *et al.*, 1989; Caron & Donohue, 1969). The structural details of these systems are also relevant to the emerging field of imprintable polymers (Wulff *et al.*, 1997; Wulff & Schonfeld, 1998).



The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are listed in Table 1. The illustrated structural unit has a twofold rotational axis through atoms O2, N1, C5, C4 and C1, which implies that the nitrate anion is accurately planar. The overall configuration of the amidinium cation resembles that of the [PhNC(Ph)NPh]⁻ anion coordinated to a GaMe₂ fragment (Barker *et al.*, 1996). Thus, the phenyl ring on the central C atom is in a *cis* (*Z*) orientation with respect to the rings on the amine N atoms, and the two C—N bond lengths of the N—C—N amidine skeleton are now identical at 1.3266(18) Å, rather than different [1.351(7) and 1.295(6) Å] as observed in the free ligand *N,N'*-diphenylbenzamidinium (Alcock *et al.*, 1988). There is a slight twist in the C6—N2—C5—C4 fragment, with a torsion angle of 10.1(2)°; furthermore, the plane of the central phenyl ring is aligned at 65.8(1)° with respect to the plane of the terminal phenyl rings.

A notable feature of the structure is the significant hydrogen bonding between the N—H protons of the cation and the nitrate O atoms, which is consistent with both the broad N—H absorption at 3290 cm⁻¹ in the

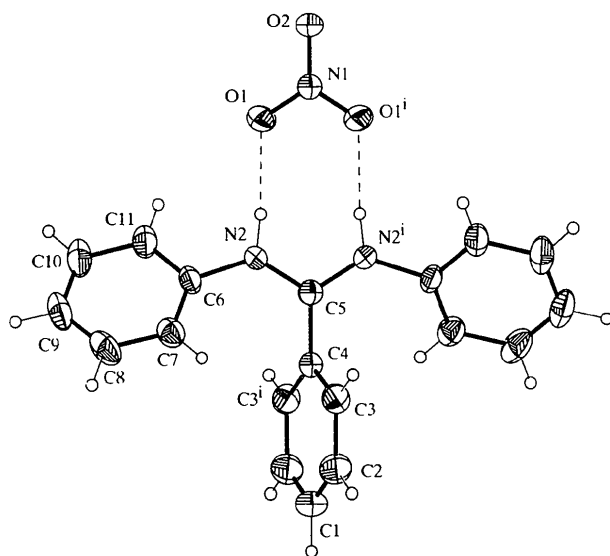


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

IR and the short N2··O1 separation of 2.7767 (19) Å, compared with the sum of van der Waals radii of 3.07 Å (Bondi, 1964). Placing the N—H protons in their calculated positions, for example, leads to an N2—H2··O1 angle of 173°. The plane of the N2—C5—N2($-x, y, \frac{1}{2} - z$) unit is twisted through 18.1 (1)° with respect to the plane of the nitrate ion. There are no significant interactions between the nitrate ion and other amidinium cations in the lattice; the next nearest distances between O2 and adjacent amidinium cations are at 3.35 and 3.38 Å for C1 and C9 atoms, respectively. The molecular units pack with their twofold axes aligned parallel to the *b* axis.

Experimental

The reaction of gallium nitrate (2.5 g, 9.9 mmol), *N,N'*-diphenylbenzamidinium (2.7 g, 10.0 mmol), lithium hydroxide (0.44 g, 10 mmol) and methanol (150 ml) under reflux for 2 h, followed by removal of solvent yielded a yellow solid. Recrystallization from methanol yielded the product as yellow crystals (yield 42%). Elemental analysis found: C 68.0, H 5.4, N 12.2%; calculated for C₁₉H₁₇N₃O₃: C 68.0, H 5.1, N 12.5%; IR (nujol) ν_{\max} : 3290, 1717, 1628, 1565, 1377, 833, 768, 758 and 737 cm⁻¹; ¹H NMR (250 MHz, CDCl₃): δ 7.42–6.99 p.p.m (Ar—H); ¹³C NMR: δ 157.3 (N—C—N), 141.7, 130.3, 129.3, 129.0, 128.2, 124.2 and 122.3 p.p.m (Ar).

Crystal data

C₁₉H₁₇N₂⁺·NO₃⁻
M_r = 335.36

Mo K α radiation
 λ = 0.71073 Å

Monoclinic

C2/*c*
a = 15.8043 (16) Å
b = 12.8885 (12) Å
c = 11.4501 (11) Å
 β = 132.195 (2)°
V = 1727.9 (3) Å³
Z = 4
D_x = 1.289 Mg m⁻³
D_m not measured

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 4341 measured reflections
 1594 independent reflections
 1118 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.119$
S = 1.002
 1594 reflections
 117 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0675P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

Cell parameters from 2217 reflections
 θ = 2.35–25.49°
 μ = 0.089 mm⁻¹
T = 180 (2) K
 Block
 0.32 × 0.10 × 0.10 mm
 Yellow

$R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 25.49^\circ$
 $h = -18 \rightarrow 19$
 $k = -15 \rightarrow 11$
 $l = -13 \rightarrow 13$
 Intensity decay: none

$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
 Extinction correction:
 SHELXL97 (Sheldrick, 1997)
 Extinction coefficient:
 0.0051 (11)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

N1—O2	1.227 (3)	N2—C6	1.433 (2)
N1—O1	1.2460 (15)	C4—C5	1.481 (3)
N2—C5	1.3266 (18)		
O2—N1—O1	120.00 (10)	N2'—C5—N2	116.7 (2)
O1—N1—O1'	120.0 (2)	N2'—C5—C4	121.63 (10)
C5—N2—C6	130.11 (15)		
C2—C3—C4—C5	179.63 (13)	C3'—C4—C5—N2	61.37 (11)
C6—N2—C5—C4	10.11 (19)	N2—C6—C7—C8	177.71 (17)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1	0.88	1.90	2.7767 (19)	173

Data collection: SMART (Siemens, 1994). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXTLPC (Sheldrick, 1994). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: SHELXTLPC. Software used to prepare material for publication: SHELXTLPC.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). We also acknowledge the EPSRC and Siemens Analytical Instruments Inc. for grants to purchase the diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1345). Services for accessing these data are described at the back of the journal.

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1,3-Dimethylisoguanine trihydrate

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Abstract

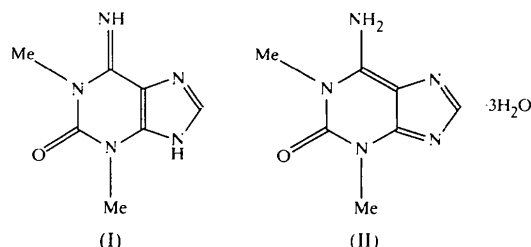
The title compound, isolated from the marine sponge *Amphimedon viridis*, crystallizes with three molecules of water, $C_7H_9N_5O \cdot 3H_2O$. The water molecules are involved in four hydrogen bonds with 1,3-dimethylisoguanine, having N...O distances 3.010 (3), 2.857 (3), 2.762 (3) and 2.810 (3) Å. The molecules are linked together through four water–water hydrogen bonds,

having O...O distances 2.812 (3), 2.739 (2), 2.784 (3) and 2.796 (3) Å.

Comment

Recently Chehade *et al.* (1997) and Mitchell *et al.* (1997) reported the isolation and the identification of a new biologically active purine, 1,3-dimethylisoguanine, (I), from the marine sponge *Amphimedon viridis*. In both communications, the structure was established by analysis of spectroscopic data, mainly NMR and mass spectrometry analysis. However, some discrepancies were observed in the 1H NMR and ^{13}C NMR data reported.

In order to confirm the structure proposed, we have achieved the recrystallization of the compound in methanol and performed the X-ray diffraction analysis. The results show that 1,3-dimethylisoguanine exists in a different tautomeric form, (II), than that previously reported (Chehade *et al.*, 1997; Mitchell *et al.*, 1997).



1,3-Dimethylisoguanine crystallizes with three molecules of water linked through four hydrogen bonds, N13...OW1 [3.010 (3) Å], N13...OW2 [2.857 (3) Å], N7...OW1 [2.762 (3) Å] and N9...OW3 [2.810 (3) Å] (Fig. 1).

The C8=N7 [1.325 (3) Å] and C4=N9 [1.336 (3) Å] bond lengths have a significant double-bond character which is consistent with the canonical form, (II). The C10—N1 [1.475 (3) Å] and C12—N3 [1.458 (3) Å] bond lengths have expected Csp^3 —N values (Allen *et al.*, 1987). The Csp^2 —N bond lengths have normal values except C6—N13 due to a π -electron delocalization. This can be inferred from a shortening of the C4—C5 [1.377 (3) Å] and C6—N13 [1.325 (3) Å] single bonds, and a lengthening of the C5=C6 [1.395 (3) Å] double bond.

The purine system is almost planar [maximum deviation 0.014 (1) Å for C2] and N13, O11, C10 and C12 lie -0.018 (3), 0.037 (2), -0.014 (3) and -0.023 (3) Å, respectively, out of the plane.

The imidazole ring is planar within experimental error and the pyrimidine ring is slightly puckered [maximum deviation 0.007 (1) Å for C2]. The dihedral angle between the planes through the two rings is 0.78 (2)°, similar to those observed in several other purine derivatives (Sletten & Jensen, 1969; Rosen & Hybl, 1971; Rasmussen & Sletten, 1973).