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N-(2,4-Dimethoxybenzylideneamino)-guanidinium dihydrogenphosphate

Muharrem Dinçer,[a] Namık Özdemir,[a]* Emin Sarıpınar,[b] Lalehan Kulak[b] and Orhan Büyükgüngör[a]

[a]Department of Physics, Arts and Sciences Faculty, Ondokuz Mayıs University, 55139 Samsun, Turkey, and [b]Department of Chemistry, Arts and Sciences Faculty, Erciyes University, 38039 Kayseri, Turkey
Correspondence e-mail: namiko@omu.edu.tr

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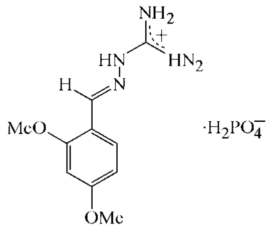
In the asymmetric unit of the title compound, $C_{10}H_{15}N_4O_2^+\cdot H_2PO_4^-$, there are two protonated aminoguanidinium cations and two dihydrogenphosphate anions. The positive charge on the protonated amidine group is delocalized over the three C—N bonds in a manner similar to that found in guanidinium salts. The aminoguanidinium cations are found to be the *E*-isomer structures. Intramolecular interactions of the N—H···N type are observed, leading to the formation of five-membered rings. Extensive networks of O—H···O, N—H···O and C—H···O hydrogen bonds stabilize the three-dimensional network. In the crystal structure, π–π interactions between the benzene rings, with a distance of 3.778 (2) Å between the ring centroids, also affect the packing of the molecules.

Comment

Aminoguanidine has been reported to be a potent inhibitor of nitric oxide synthase (Griffith & Gross, 1996). Guanylhydrazones (alkenylaminoguanidines, carboximideamide-hydrazones and diaminomethylene hydrazones) are condensation products of oxo compounds with aminoguanidines. This class of compounds has been known for some time (Thiele, 1892) and is of considerable interest due to the wide variety of different pharmacological activities found for many representatives (Richter *et al.*, 1993; Schleuder *et al.*, 1993). Furthermore, guanylhydrazones are valuable synthetic building blocks for ring-closure reactions, leading to several nitrogen-containing heterocycles (Sarıpınar *et al.*, 2005). Protomeric tautomerism is of much interest in experimental as well as theoretical chemistry, since it is an important reaction in biological processes. Guanylhydrazones can exist in two tautomeric forms (Zoltan *et al.*, 1999). They may undergo proton shifts (tautomerism) rapidly and easily, and the chemical reactivities of the two isomers may be quite different. Molecular assembly in a crystal is predominantly governed by intermolecular forces, conventionally described by strong and directional N—H···O, O—H···O and O—H···N hydrogen bonds (Desiraju, 2002). In molecules having an imbalance of hydrogen-bond donors and acceptors, the deficiency in either donors or acceptors is fulfilled by other types of weak and less-directional forces. Interactions involving the π cloud in aromatic compounds also belong to this category. We present here the complete geometric characterization of the title compound, (I), in the solid state, together with a comparison of the molecular structure with those of related compounds and an analysis of their intermolecular interactions in the crystal network.



(I)

The asymmetric unit of (I) consists of two protonated amidinium cations, denoted *A* (O1/O2/N1–N4/C1–C10) and *B* (O7/O8/N5–N8/C11–C20), and two dihydrogenphosphate anions, denoted *A*′ (P1/O3–O6) and *B*′ (P2/O9–O12). The two independent aminoguanidinium cations have very similar molecular dimensions (Fig. 1 and Table 1); this is also the case for the two dihydrogenphosphate anions, whose geometries are normal (Allen *et al.*, 1987). In the following discussion, parameters for molecules *B* are quoted in square brackets.

In the aminoguanidine moiety, the N—N bond length is 1.394 (3) Å [1.395 (3) Å], approximating to a pure single bond (1.41 Å; Burke-Laing & Laing, 1976). Similarly, the corresponding N═C bond length of 1.279 (4) Å [1.275 (4) Å] has pure double-bond character (1.27 Å). That the lone-pair electrons on atom N2 [N6] are delocalized through conjugation with the amidine group rather than the N1═C9

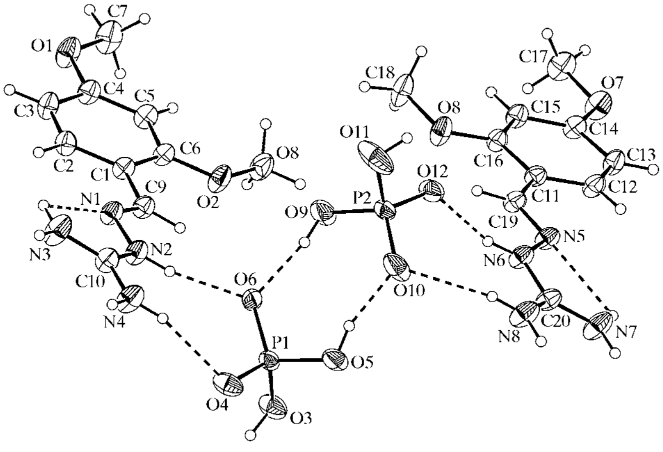


Figure 1
A view of the asymmetric unit of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate the N—H···O, N—H···N and O—H···O interactions.

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[N5=C19] double bond is also seen in the N2—C10 bond length of 1.335 (4) Å [1.329 (4) Å], which is intermediate between a single and a double bond, and similar to the two C—N bonds in the amidine moieties. Similar C—N bond distances have been found in a number of inorganic salts containing the guanidinium cation (see, for example, Katrusiak & Szafrański, 1994; Kettmann & Světlík, 2002).

In the cation, the dimethoxyphenyl and aminoguanidine fragments are planar, with maximum deviations of −0.033 (3) and 0.027 (3) Å [0.058 (3) and 0.067 (2) Å], respectively. The planes of these two moieties make a dihedral angle of 14.10 (15)° [13.46 (15)°], showing that the 2,4-dimethoxybenzylideneaminoguanidine molecules are almost flat. The 2,4-dimethoxybenzylideneaminoguanidine molecule can exist in two different configurations, as an *E* or a *Z* isomer, with respect to the C=N double bond. The N—N=C—C torsion angle is −178.6 (3)° [176.5 (3)°], and this reveals that the molecules have the *E*-isomer structure in (I).

Within the benzene ring in the aminoguanidine *A* molecule, there are significant differences between bond lengths: C1—C6 [1.400 (4) Å] is slightly longer than C2—C3 and C4—C5 [1.373 (4) and 1.374 (4) Å, respectively]. The remaining bond lengths in the ring are close to the C1—C6 bond length. In addition, the C6—C1—C2 bond angle is 118.4 (3)°, while the rest of the internal angles are almost equal to the normal value of 120° for the intra-ring bond angles of benzene rings. Similiar differences were also seen in the aminoguanidine *B* molecule: C11—C16 [1.398 (4) Å] is slightly longer than C12—C13 and C14—C15 [1.378 (4) and 1.372 (4) Å, respectively]. Moreover, the C16—C11—C12 bond angle is 118.0 (3)°, while the remaining bond angles are close to 120°. It is interesting to note that within the dimethoxyphenyl fragment the exocyclic C—C—O angles show an unusual pattern compared with those observed for methoxyaryl compounds (Seip & Seip, 1973; Ferguson *et al.*, 1996; Patterson *et al.*, 1998), in which the C—C—O angles *cisoid* to the substituents are much larger than 120°, while those *transoid* are very much smaller. At the same time, the C—O—C angles are well in excess of tetrahedral values, consistent with the occurrence of repulsive interactions between the methyl groups and the neighbouring aryl C—H unit.

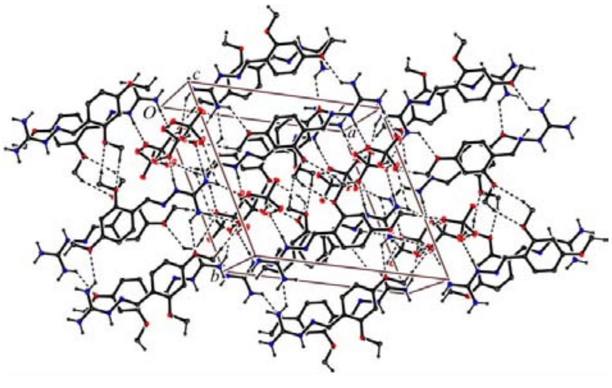

Figure 2
The molecular packing of (I), showing the intermolecular interactions (dashed lines). For clarity, only H atoms involved in the hydrogen bonding have been included.

In the aminoguanidinium cation, an intramolecular N3—H3*B*···N1 [N7—H7*E*···N5] hydrogen bond leads to the formation of a five-membered ring (Fig. 1). The crystal structure of (I) is stabilized by a network of N—H···O and O—H···O hydrogen bonds, in which amidine and methoxy groups, as well as $H_2PO_4^-$ anions, are involved (Table 2 and Fig. 2). Additionally, there are also C—H···O contacts. The O—H···O interactions formed between the $H_2PO_4^-$ anions are quite strong. Among the N—H···O interactions, the strongest is formed by amidine atom N2 [N6]. However, there are also one C—H···O and one N—H···O interaction, in which enol O atoms are involved as acceptors. The anion O atoms are involved as acceptors in different hydrogen-bond interactions, five for *A*′ and four for *B*′, and hence a three-centred contact is formed. Thus, the hydrogen-bond network linking adjacent cations and anions in the crystal structure of (I) is three-dimensional. In addition to these intra- and intermolecular interactions, intermolecular π–π stacking interactions between the benzene ring and its partner at $(2-x, 1-y, 1-z)$ are also observed along the *a* axis, with a distance of 3.778 (2) Å between the ring centroids. Full details of the hydrogen-bonding geometry are given in Table 2.

Experimental

2,4-Dimethoxybenzaldehyde (1.66 g) and aminoguanidinebicarbonate (1.36 g) were refluxed in a boiling water solution (20 ml) of 1 *N* H_3PO_4 for 1 h and, after cooling, the precipitate was collected, yielding 2.24 g (70%) of (I). The crude product was recrystallized from methanol and allowed to dry over P_2O_5 (m.p. 529 K). Analysis calculated for $C_{10}H_{17}N_4O_6P$: C 37.50, H 5.31, N 17.50%; found: C 37.33, H 5.21, N 17.39%.

Crystal data

$C_{10}H_{15}N_4O_2^+\cdot H_2PO_4^-$
$M_r = 320.25$
Triclinic, $P\overline{1}$
$a = 8.4822$ (5) Å
$b = 13.6287$ (9) Å
$c = 14.3131$ (9) Å
$\alpha = 63.081$ (5)°
$\beta = 81.702$ (5)°
$\gamma = 85.936$ (5)°
$V = 1459.86$ (16) Å^3
$Z = 4$
$D_x = 1.457$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17194 reflections
$\theta = 2.4$–27.9°
$\mu = 0.22$ mm^{-1}
$T = 296$ K
Rod, colourless
0.75 × 0.38 × 0.19 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.888$, $T_{\max} = 0.969$
18714 measured reflections
5746 independent reflections
4086 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.096$
$\theta_{\max} = 26.0$°
$h = -10 \rightarrow 10$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.153$
$S = 1.03$
5746 reflections
387 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.6872P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.58$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C4	1.372 (3)	N7—C20	1.309 (4)
O1—C7	1.433 (4)	N8—C20	1.328 (4)
O2—C6	1.354 (4)	C11—C12	1.391 (4)
O2—C8	1.419 (4)	C11—C19	1.459 (4)
N3—C10	1.310 (4)	C13—C14	1.386 (4)
N4—C10	1.324 (4)	C15—C16	1.390 (4)
C1—C2	1.393 (4)	P1—O6	1.4992 (19)
C1—C9	1.465 (4)	P1—O4	1.501 (2)
C3—C4	1.385 (4)	P1—O3	1.555 (2)
C5—C6	1.397 (4)	P1—O5	1.560 (2)
O7—C14	1.368 (3)	P2—O10	1.480 (2)
O7—C17	1.426 (4)	P2—O12	1.491 (2)
O8—C16	1.357 (4)	P2—O9	1.547 (3)
O8—C18	1.433 (4)	P2—O11	1.562 (3)
C4—O1—C7	116.9 (3)	C14—O7—C17	117.8 (3)
C6—O2—C8	118.3 (2)	C16—O8—C18	117.8 (2)
C9—N1—N2	113.5 (2)	C19—N5—N6	113.6 (3)
C10—N2—N1	117.8 (3)	C20—N6—N5	118.7 (3)
O1—C4—C5	123.5 (3)	O7—C14—C15	123.9 (3)
O1—C4—C3	115.2 (3)	O7—C14—C13	115.0 (3)
O2—C6—C5	123.1 (3)	O8—C16—C15	123.0 (3)
O2—C6—C1	116.6 (2)	O8—C16—C11	116.3 (2)
N1—C9—C1	121.0 (3)	N5—C19—C11	121.2 (3)
N3—C10—N4	121.1 (3)	N7—C20—N8	121.5 (3)
N3—C10—N2	120.9 (3)	N7—C20—N6	121.1 (3)
N4—C10—N2	117.9 (3)	N8—C20—N6	117.4 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O6	0.86	1.94	2.780 (3)	167
N3—H3*A*···O10^{i}	0.86	2.48	3.260 (5)	152
N3—H3*B*···O1^{ii}	0.86	2.59	3.175 (4)	127
N3—H3*B*···N1	0.86	2.33	2.662 (4)	103
N4—H4*A*···O11^{i}	0.86	2.13	2.959 (4)	161
N4—H4*B*···O4	0.86	2.13	2.969 (4)	166
N6—H6···O12	0.86	1.90	2.736 (3)	162
N7—H7*D*···O4^{iii}	0.86	2.34	3.177 (4)	165
N7—H7*E*···N5	0.86	2.35	2.678 (4)	103
N7—H7*E*···O7^{iv}	0.86	2.48	3.060 (4)	125
N8—H8*D*···O5^{iii}	0.86	2.21	2.976 (3)	148
N8—H8*E*···O10	0.86	2.33	3.173 (5)	169
O3—H3O···O12^{v}	0.82	1.74	2.546 (3)	168
O5—H5O···O10	0.82	1.68	2.475 (3)	163
O9—H9O···O6	0.82	1.74	2.543 (3)	166
O11—H11O···O4^{vi}	0.82	1.73	2.519 (3)	161
C7—H7*A*···O10^{vii}	0.96	2.42	3.373 (4)	171

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

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.82, 0.86, 0.93 and 0.96 Å for OH, NH/NH$_2$, CH and aromatic, and CH$_3$ H atoms, respectively. The displacement parameters of the H atoms were constrained as $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent), or $1.5U_{\rm eq}$(C) for methyl H atoms.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1076). Services for accessing these data are described at the back of the journal.

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