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## 1-Phenethylguanidinium Chloride

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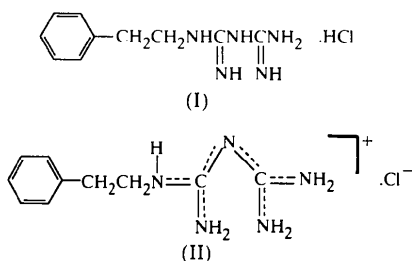
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### Abstract

The asymmetric unit of the title compound,  $C_{10}H_{16}N_5^+ \cdot Cl^-$ , contains two molecules with quite different conformations of the biguanide moiety. The crystal structure determined by Herrnstadt *et al.* [*J. Chem. Soc. Perkin Trans. 2* (1979), pp. 735–740] is properly refined, the H-atom positions on the biguanide moiety are evident and the hydrogen-bonding scheme is clarified. Protonation of the biguanide moiety produces a rearrangement of protons in this part of the molecule. The two independent protonated molecules in the crystal form a hydrogen-bonded dimer through two intermolecular N—H...N hydrogen bonds. In addition, the molecules are held together by van der Waals forces and several N—H...Cl intermolecular interactions.

### Comment

The title compound, (I), was investigated as part of structural studies on hypoglycemic agents (Shapiro *et al.*, 1959). There are two independent molecules in the asymmetric unit, denoted by primed and unprimed atom labels. Both molecules are closely similar in terms of bond lengths and angles, but quite different in terms of torsion angles. The main torsion-angle differences occur in the side chains at the C1 and C1' atoms, giving rise to these two different structures.



Protonation of the biguanide moiety at N11 or N14 yielded the locations of two H atoms on both N11 and N14. These positions were not clear in the previous

determination (Herrnstadt *et al.*, 1979). This could be interpreted in terms of a new preferred tautomeric form of the biguanide moiety found in the solid state, (II). The biguanide fragment is not altogether planar [maximum deviations from the plane are 0.592 (3), 0.539 (3) and  $-0.500$  (3) Å for atoms N11, N15 and N9, respectively, and  $-0.599$  (3), 0.542 (3) and 0.408 (2) Å for atoms N11', N14' and N9', respectively] and forms a dihedral angle of 54.8 (1)° [72.5 (1)° for the primed molecule] with the phenyl group.

There are two short intramolecular N—H...N contacts [N15...N9 3.012 (4), H15B...N9 2.62 (3) Å and N15—H15B...N9 112 (3)°; N14'...N11' 2.947 (4), H14D...N11' 2.53 (3) Å and N14'—H14D...N11' 115 (3)°]. The molecular packing is shown in Fig. 2. There are two intermolecular N—H...N contacts forming a dimer [N14...N12<sup>ii</sup> 2.991 (3), H14B...N12<sup>ii</sup> 2.08 (3) Å and N14—H14B...N12<sup>ii</sup> 175 (2)°; N15'...N12<sup>ii</sup> 3.002 (3), H15C...N12<sup>ii</sup> 2.15 (2) Å and N15'—H15C...N12<sup>ii</sup> 171 (3)°; symmetry codes: (i)  $-x + \frac{3}{2}$ ,  $y - \frac{1}{2}$ ,  $-z + \frac{1}{2}$ ; (ii)  $-x + \frac{3}{2}$ ,  $y + \frac{1}{2}$ ,  $-z + \frac{1}{2}$ ]. The previous interactions suggest two weak N—H...N hydrogen bonds may be present. It should be mentioned that the hydrogen-bonded dimer through two N—H...N hydrogen bonds was described in the previous determination (Herrnstadt *et al.*, 1979), but the positions of the H atoms involved in this hydrogen-bond pattern did not show up in the difference electron-density map. Consequently, a different tautomeric form of the biguanide moiety was proposed. In addition, the molecules in the crystal are held together by van der Waals forces and six intermolecular N—H...Cl interactions (Desiraju, 1991) [N11...Cl1<sup>iii</sup>, N14...Cl1<sup>iv</sup>, N15...Cl2<sup>iv</sup>, N11'...Cl2<sup>v</sup>, N14'...Cl2<sup>vi</sup> and N15'...Cl2<sup>vi</sup> of 3.286 (3), 3.272 (3), 3.280 (2), 3.284 (3), 3.386 (3) and 3.263 (2) Å, respectively; symmetry codes: (iii)  $-x + 1$ ,  $-y + 2$ ,  $-z$ ; (iv)  $-x + 1$ ,  $-y + 1$ ,  $-z$ ; (v)  $-x + \frac{1}{2}$ ,  $y + \frac{1}{2}$ ,  $-z + \frac{1}{2}$ ; (vi)  $x$ ,  $y + 1$ ,  $z$ ].

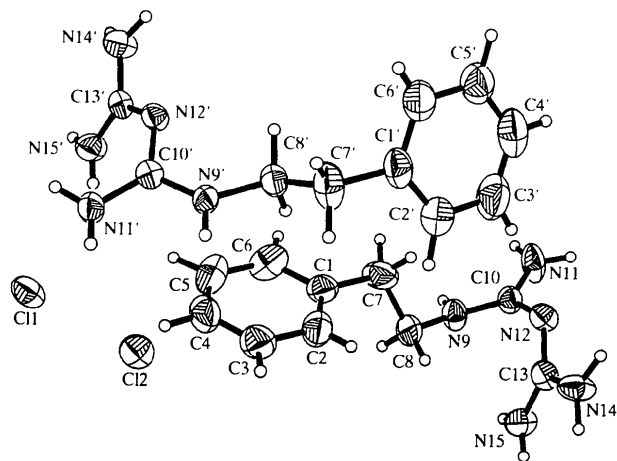


Fig. 1. The molecular structure of the title compound with the atom labelling and 50% probability displacement ellipsoids.

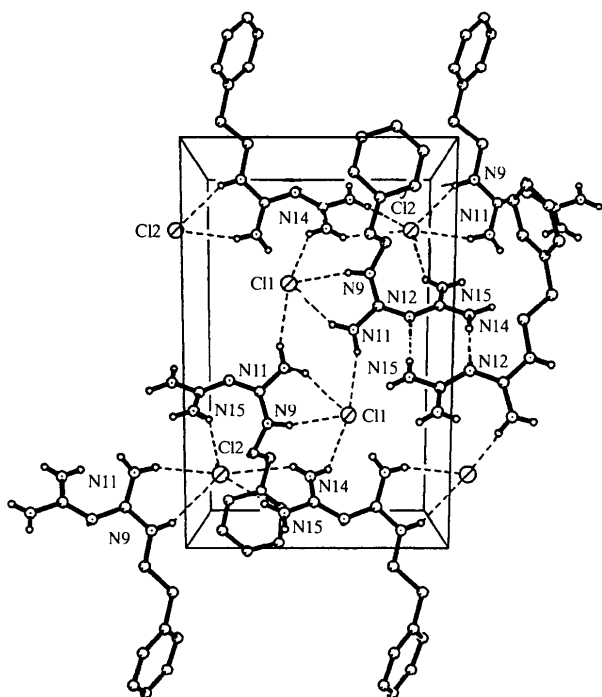


Fig. 2. A perspective drawing of the packing arrangement along the *c* axis. Dashed lines indicate N—H...N and N—H...Cl interactions. Only the H atoms that participate in the interactions are shown.

## Experimental

The title compound was purchased from the Sigma Chemical Company and recrystallized from 2-propanol at room temperature.

### Crystal data

C<sub>10</sub>H<sub>16</sub>N<sub>5</sub><sup>+</sup>.Cl<sup>-</sup>

*M<sub>r</sub>* = 241.73

Monoclinic

*P*2<sub>1</sub>/*n*

*a* = 14.916 (3) Å

*b* = 9.372 (2) Å

*c* = 19.076 (4) Å

β = 107.64 (1)°

*V* = 2541.3 (9) Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 1.264 Mg m<sup>-3</sup>

*D<sub>m</sub>* = 1.260 Mg m<sup>-3</sup>

*D<sub>m</sub>* measured by flotation in bromoform/benzene

### Data collection

Siemens *R3m/V* diffractometer

θ/2θ scans

Absorption correction: none

7413 measured reflections

7399 independent reflections

3267 reflections with

*I* > 2σ(*I*)

*R*<sub>int</sub> = 0.053

θ<sub>max</sub> = 31.16°

*h* = -20 → 20

*k* = 0 → 13

*l* = 0 → 26

3 standard reflections

every 97 reflections

intensity decay: 2.0%

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.071

*wR*(*F*<sup>2</sup>) = 0.051

*S* = 1.053

7399 reflections

385 parameters

H atoms: see below

*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0001*P*)<sup>2</sup>]

where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.007

Δρ<sub>max</sub> = 0.252 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.253 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for*

*Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

C1—C6	1.382 (4)	C1'—C6'	1.370 (4)
C1—C2	1.387 (4)	C1'—C2'	1.382 (4)
C1—C7	1.493 (4)	C1'—C7'	1.512 (4)
C2—C3	1.373 (4)	C2'—C3'	1.375 (5)
C3—C4	1.362 (5)	C3'—C4'	1.362 (5)
C4—C5	1.353 (5)	C4'—C5'	1.363 (5)
C5—C6	1.376 (5)	C5'—C6'	1.380 (4)
C7—C8	1.498 (4)	C7'—C8'	1.499 (4)
C8—N9	1.467 (4)	C8'—N9'	1.462 (3)
N9—C10	1.334 (3)	N9'—C10'	1.327 (3)
C10—N11	1.322 (3)	C10'—N11'	1.330 (3)
C10—N12	1.341 (3)	C10'—N12'	1.336 (3)
N12—C13	1.330 (3)	N12'—C13'	1.326 (3)
C13—N15	1.326 (3)	C13'—N15'	1.329 (3)
C13—N14	1.328 (3)	C13'—N14'	1.332 (3)
C6—C1—C2	116.4 (3)	C6'—C1'—C2'	118.5 (3)
C6—C1—C7	119.8 (3)	C6'—C1'—C7'	120.0 (3)
C2—C1—C7	123.9 (3)	C2'—C1'—C7'	121.5 (3)
C3—C2—C1	121.6 (3)	C3'—C2'—C1'	119.4 (3)
C4—C3—C2	120.4 (3)	C4'—C3'—C2'	121.4 (4)
C5—C4—C3	119.4 (3)	C5'—C4'—C3'	120.0 (3)
C4—C5—C6	120.6 (3)	C4'—C5'—C6'	118.9 (4)
C5—C6—C1	121.6 (3)	C1'—C6'—C5'	121.9 (3)
C1—C7—C8	113.3 (2)	C8'—C7'—C1'	110.9 (3)
N9—C8—C7	112.3 (3)	N9'—C8'—C7'	112.8 (2)
C10—N9—C8	125.1 (2)	C10'—N9'—C8'	123.4 (2)
N11—C10—N9	116.4 (3)	N9'—C10'—N11'	117.5 (2)
N11—C10—N12	117.4 (2)	N9'—C10'—N12'	118.6 (2)
N9—C10—N12	126.1 (2)	N11'—C10'—N12'	123.8 (2)
C13—N12—C10	123.1 (2)	C13'—N12'—C10'	123.8 (2)
N15—C13—N12	125.8 (2)	N12'—C13'—N15'	117.2 (2)
N15—C13—N14	117.4 (3)	N12'—C13'—N14'	125.6 (2)
N12—C13—N14	116.7 (2)	N15'—C13'—N14'	117.1 (2)
C1—C7—C8—N9	168.0 (3)		
C7—C8—N9—C10	81.0 (4)		
C8—N9—C10—N11	-147.9 (3)		
C8—N9—C10—N12	28.7 (5)		
N11—C10—N12—C13	-140.8 (3)		
N9—C10—N12—C13	42.7 (4)		
C10—N12—C13—N15	12.6 (4)		
C10—N12—C13—N14	-171.3 (3)		
C1'—C7'—C8'—N9'	178.4 (3)		
C7'—C8'—N9'—C10'	151.5 (3)		
C8'—N9'—C10'—N11'	161.5 (3)		
C8'—N9'—C10'—N12'	-21.3 (4)		
N9'—C10'—N12'—C13'	147.1 (3)		
N11'—C10'—N12'—C13'	-36.0 (4)		
C10'—N12'—C13'—N15'	165.3 (3)		
C10'—N12'—C13'—N14'	-17.5 (4)		

All H atoms were located from a difference Fourier map and were refined with a constant isotropic displacement parameter *U* of 0.06 Å<sup>2</sup> and included in the structure-factor calculations.

Data collection: Siemens *R3m/V* diffractometer software. Cell refinement: *XSCANS* (Siemens, 1991). Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-*

Plus (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1267). Services for accessing these data are described at the back of the journal.

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## Cyclopropylcarboxamidinium Chloride

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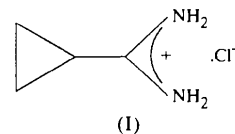
## Abstract

Cyclopropylcarboxamidinium hydrochloride,  $C_4H_9N_2^+.Cl^-$ , the first structural example of an alicyclic central C-atom substituted amidine, contains almost equal C—N bond lengths of 1.316 (4) and 1.304 (4) Å, indicating that it is an amidinium salt.

## Comment

The widespread interest in amidines as a result of their importance in the pharmaceutical, biological and coordination chemistry fields is reflected in the number

of structural papers which have appeared (Dehnicke, 1990; Edelmann, 1994; Barker & Kilner, 1994; Alcock *et al.*, 1994; Barker *et al.*, 1997). The present study of cyclopropylcarboxamidinium hydrochloride, (I), was carried out to furnish data with regard to the effect of an alicyclic group on the amidine fragment.



The C—N bond lengths [1.316 (4) and 1.304 (4) Å] are neither single nor double bond in character. They are similar to those found in the straight-chain isopropylamidinium hydrochloride analogue, (II) [with mean bond lengths 1.317 (5) and 1.300 (6) Å; Barker & Powell, 1996], acetamidinium chloride, (III) [1.305 (2) and 1.310 (3) Å; Cannon *et al.*, 1976], and bis-(acetamidinium) carbonate monohydrate, (IV) [1.308 (5) and 1.315 (5) Å; Norrestam, 1984], but differ somewhat from those found for benzamidinium hydrochloride monohydrate, (V) [1.293 (7) and 1.328 (7) Å; Thailambal *et al.*, 1986]. These C—N bond lengths are indicative of an amidinium salt configuration. Comparison of their C—N bond lengths shows the aryl substituent to be more restrictive toward delocalization than the alicyclic group. The N—C—N angle [120.5 (3)°] is similar to that of compounds (II) [120.4 (4)°] and (III) [120.5 (2)°], and there is a slight (but statistically insignificant) deviation from those found for (IV) [121.6 (3)°] and (V) [121.6 (4)°]. This indicates that the amidinium-

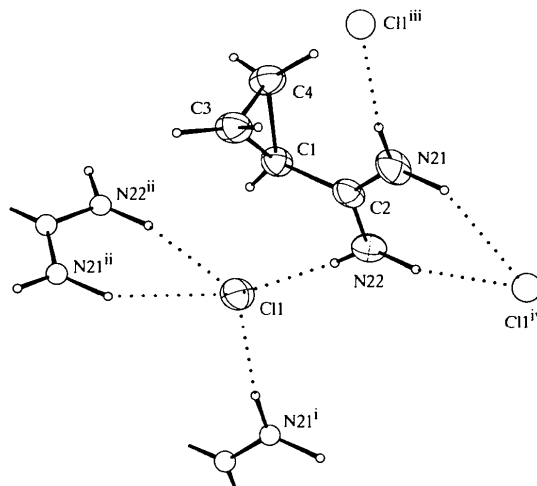


Fig. 1. The molecular structure of cyclopropylamidinium chloride showing the hydrogen bonding of both counterions. The asymmetric unit is drawn with 50% probability displacement ellipsoids and symmetry-related atoms with spheres. The symmetry codes are: (i)  $x - \frac{1}{2}, \frac{1}{2} + y, z$ ; (ii)  $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$ ; (iii)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (iv)  $x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$ .