

Redetermination of phenylbiguanide hydrochloride

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The crystal structure of the title compound, *N*-phenylimidocarbonimidic diamide hydrochloride (phenylbiguanide hydrochloride), $C_8H_{12}N_5^+ \cdot Cl^-$, $(BIGH)^+ \cdot Cl^-$, has been redetermined with higher precision and with the location and free refinement of all H atoms.

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Key indicators

Single-crystal X-ray study

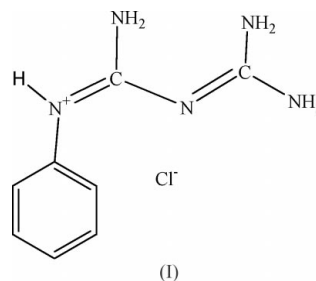
 $T = 298\text{ K}$ Mean $\sigma(C-C) = 0.004\text{ \AA}$ R factor = 0.063 wR factor = 0.192

Data-to-parameter ratio = 16.4

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

Comment

The rational design of supramolecular structures can be realised through crystal engineering based on relatively weak intermolecular forces (Desiraju, 1995). Among these forces, hydrogen bonding is by far the most common (HDA, hydrogen donor–acceptor complexation). Multiple-hydrogen-bonding systems offer more possibilities for forming stronger networks than common double-hydrogen-bonding systems. Hence biguanide derivatives, characterized by multiple-hydrogen-bond donor sites, are good candidates to be associated in the crystal structure with carefully selected molecules having multiple hydrogen bond acceptor sites.



With this aim, phenylbiguanide hydrochloride, (I), poorly analysed some twenty years ago (Amigó *et al.*, 1985) with a high R value (0.115) and without location of the H atoms, has been more precisely redetermined.

The asymmetric unit of $(BIGH)^+ \cdot Cl^-$ consists of a mono-protonated phenylbiguanidinium cation and a chloride anion; protonation occurs at the N atom (N1) attached to the phenyl ring (Fig. 1). The biguanidinium group is not planar; the planes defined by atoms N1, N2 and N3 and by atoms N2, N4 and N5 are inclined to each other by an angle of $51.9(3)^\circ$. Nevertheless, the equivalence of the C–N bond lengths (Table 1) suggests some degree of delocalization of π -electron density through this fragment. The biguanidinium group is rotated with respect to the phenyl ring by the rotation angle $\tau = 52.4(5)^\circ$ (the angle τ is defined as; $\tau = |\omega_1 + \omega_2 \pm \pi|/2$, the torsion angles ω_1 and ω_2 being respectively C6–C1–N1–C7 and C2–C1–N1–C7), in agreement with the corresponding angle in phenylbiguanide [$59.0(6)^\circ$; Dalpiaz *et al.*, 1996].

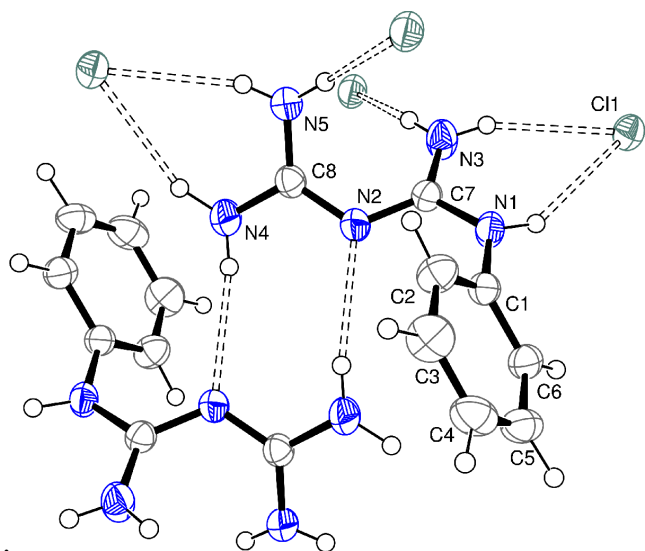


Figure 1
A drawing of the title compound, showing the atom labelling and the hydrogen-bonding scheme (dashed lines). Displacements ellipsoids are drawn at the 50% probability level.

The hydrogen-bonding scheme involves all H atoms of the (BIGH)⁺ cation (Table 2). It consists almost entirely of N—H···Cl[−] interactions and accounts for the rather high melting point of the compound (517–520 K). An N—H···N intermolecular hydrogen bond connects two centrosymmetrically related molecules, just forming a well known *R*₂²(8) (Etter *et al.*, 1990) supramolecular synthon (Fig. 1).

Experimental

The title compound (purchased from Sigma Aldrich at 98% purity) was recrystallized from water by slow evaporation of the solvent.

Crystal data

C ₈ H ₁₂ N ₅ ⁺ ·Cl [−]	<i>D</i> _x = 1.374 Mg m ^{−3}
<i>M</i> _r = 213.68	Mo Kα radiation
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cell parameters from 30 reflections
<i>a</i> = 9.3421 (14) Å	<i>θ</i> = 10.0–21.0°
<i>b</i> = 6.6804 (11) Å	<i>μ</i> = 0.34 mm ^{−1}
<i>c</i> = 17.297 (6) Å	<i>T</i> = 298 (2) K
<i>β</i> = 106.82 (2)°	Tablet, colourless
<i>V</i> = 1033.3 (4) Å ³	0.30 × 0.30 × 0.10 mm
<i>Z</i> = 4	

Data collection

Huber CS four-circle diffractometer	<i>θ</i> _{max} = 35.0°
<i>ω</i> scans	<i>h</i> = 0 → 14
Absorption correction: none	<i>k</i> = 0 → 10
5323 measured reflections	<i>l</i> = −26 → 25
2672 independent reflections	3 standard reflections
2659 reflections with <i>I</i> > 2σ(<i>I</i>)	every 97 reflections
<i>R</i> _{int} = 0.043	intensity decay: <3%

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.122P)^2 + 0.6386P]$
$R[F^2 > 2\sigma(F^2)] = 0.063$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.192$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.14	$\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{Å}^{-3}$
2672 reflections	$\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{Å}^{-3}$
163 parameters	
Only coordinates of H atoms refined	

Table 1

Selected geometric parameters (Å, °).

N1—C7	1.357 (3)	C1—C6	1.387 (3)
N1—C1	1.422 (3)	C1—C2	1.391 (4)
N2—C7	1.335 (3)	C2—C3	1.394 (4)
N2—C8	1.336 (3)	C3—C4	1.385 (5)
N3—C7	1.337 (3)	C4—C5	1.385 (5)
N4—C8	1.332 (3)	C5—C6	1.392 (4)
N5—C8	1.333 (3)		
C7—N1—C1	123.6 (2)	C4—C5—C6	119.9 (3)
C7—N2—C8	122.1 (2)	C1—C6—C5	119.8 (3)
C6—C1—C2	120.3 (2)	N2—C7—N3	124.9 (2)
C6—C1—N1	119.0 (2)	N2—C7—N1	118.2 (2)
C2—C1—N1	120.7 (2)	N3—C7—N1	116.8 (2)
C1—C2—C3	119.7 (3)	N4—C8—N5	118.1 (2)
C4—C3—C2	119.9 (3)	N4—C8—N2	117.6 (2)
C5—C4—C3	120.4 (3)	N5—C8—N2	124.2 (2)
C7—N1—C1—C6	128.2 (3)	C8—N2—C7—N1	153.0 (2)
C7—N1—C1—C2	−52.9 (4)	C1—N1—C7—N2	−10.9 (4)
N1—C1—C2—C3	179.4 (3)	C1—N1—C7—N3	172.5 (2)
N1—C1—C6—C5	180.0 (2)	C7—N2—C8—N4	151.8 (3)
C8—N2—C7—N3	−30.8 (4)	C7—N2—C8—N5	−31.7 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H11···Cl1	0.91 (3)	2.57 (3)	3.373 (2)	148 (3)
N3—H31···Cl1	0.84 (4)	2.49 (4)	3.273 (3)	156 (3)
N3—H32···Cl1 ⁱ	0.86 (4)	2.54 (4)	3.353 (3)	157 (3)
N4—H41···Cl1 ⁱⁱ	0.93 (4)	2.51 (4)	3.387 (3)	157 (3)
N4—H42···N2 ⁱⁱⁱ	0.85 (4)	2.41 (4)	3.243 (4)	164 (3)
N5—H51···Cl1 ⁱⁱ	0.81 (4)	2.55 (4)	3.324 (3)	160 (3)
N5—H52···Cl1 ^{iv}	0.87 (4)	2.62 (4)	3.432 (3)	155 (3)

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

All the H atoms were located in a difference synthesis and their coordinates were refined; *U*_{iso}(H) was constrained to be equal to *U*_{eq} of the parent atom.

Data collection: *XCS* (Colapietro *et al.*, 1992); cell refinement: *XCS*; data reduction: *XCS*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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