First structural characterization of guanidine, $HN{=}C(NH_2)_2$

Michael Göbel and Thomas M. Klapötke*

Received (in Cambridge, UK) 4th April 2007, Accepted 10th May 2007
First published as an Advance Article on the web 29th May 2007
DOI: 10.1039/b705100j

Structural information about the free base guanidine in the solid state could be obtained for the first time by determining the crystal structures of the 1 : 1 as well as the 2 : 1 co-crystals consisting of neutral guanidine and 2-amino-4,6-dimethyl-1,3,5-triazine using single crystal X-ray diffraction.

Due to its high basicity, guanidine (aminoformamidine) was considered to be the strongest neutral organic base ($pK_a = 13.6$)[1] until proton sponges[2,3] were synthesized. The question of its molecular structure and the reason for its exceptional properties inspired several controversial theoretical works[4–13] since an experimentally determined structure for guanidine was not available.† To our knowledge, only a few neutral derivatives of guanidines containing sterically demanding organic substituents have been structurally characterized using single-crystal X-ray diffraction. Rare examples describe 1,1,3,3-tetrasubstituted[14,15] as well as 1,2,3-trisubstituted[16] guanidine derivatives acting as ligands in transition metal complexes. In contrast, here we report crystal structures containing the unsubstituted free base guanidine and 2-amino-4,6-dimethyl-1,3,5-triazine.

Single crystals consisting of guanidine and 2-amino-4,6-dimethyl-1,3,5-triazine were obtained when acetonitrile was allowed to slowly diffuse into a methanolic solution of guanidine.‡ The presence of 2-amino-4,6-dimethyl-1,3,5-triazine in the crystal structures of the 1 : 1 co-crystal (**1**) as well as the 2 : 1 co-crystal (**2**) corresponds to and confirms the formation of substituted 2-aminotriazines from aliphatic nitriles and guanidine in the presence of alcoholates.[17] A comparison of 2-amino-4,6-dimethyl-1,3,5-triazine in the crystal structures of **1** and **2** (Fig. 1 and 2) with the earlier reported crystal structure of the pure compound[18] reveals the same planar triazine ring and a similar packing with the formation of dimers due to hydrogen bonding between the two terminal amino groups and two ring nitrogen atoms (Fig. 3 and 4). The N–H···N distance reported for the pure substance (3.070(4) Å) is in good agreement with our findings (2.978 Å (**1**) and 3.006 Å (**2**)). The $C–NH_2$ and C–NH hydrogen atoms of the guanidine molecules in **1** and **2** were directly located in the crystallographic study using difference Fourier maps. The attachment to the imino nitrogen atoms of the guanidine is further confirmed from the observation that the C–NH bonds between the central guanidine carbon atoms and the attached nitrogen atoms [range 1.295(2) Å–1.304(2) Å] are significantly shorter than the remaining $C–NH_2$ bonds to these carbons [range 1.350(3) Å–1.366(2) Å]. A summary of selected bond lengths and angles is given in Table 1. The central carbon atom of the guanidine molecule in structures **1** and **2** forms

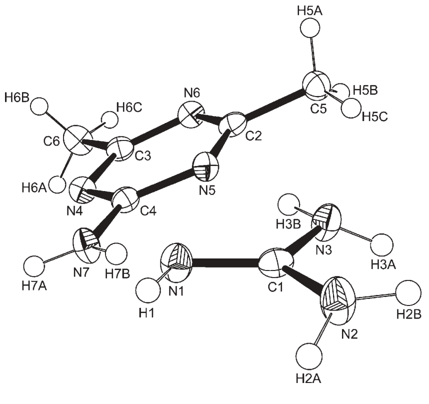

Fig. 1 Ortep representation of the structure of 2-amino-4,6-dimethyl-1,3,5-triazine·guanidine (**1**). The thermal ellipsoids are shown at the 50% probability level.

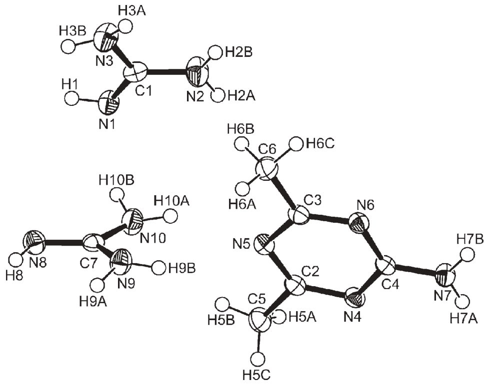

Fig. 2 Ortep representation of the structure of 2-amino-4,6-dimethyl-1,3,5-triazine·2 guanidine (**2**). The thermal ellipsoids are shown at the 50% probability level.

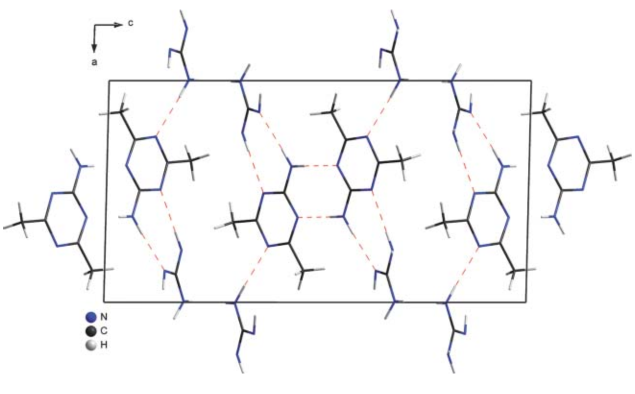

Fig. 3 Representation of the unit cell of **1** along the *b*-axis. Dashed lines indicate hydrogen bonding.

Department of Chemistry and Biochemistry, Ludwig-Maximilian University, Butenandtstr. 5-13 (Haus D), D-81377, Munich, Germany. E-mail: tmk@cup.uni-muenchen.de

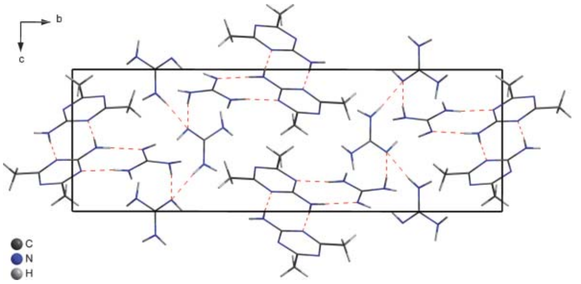

Fig. 4 Representation of the unit cell of **2** along the *a*-axis. Dashed lines indicate hydrogen bonding.

one plane with the three surrounding nitrogen atoms ($\Sigma_{NCN} = 360°$). In contrast, the two amino groups of guanidine show pyramidal geometries, confirming a theoretical study published by Frenking and Gobbi[13] where a non-planar geometry of the guanidine molecule with strongly pyramidal NH_2 groups was predicted at the MP2 level of theory using a 6-31G(d) basis set. In addition, our experimentally determined bond lengths agree well with the calculated ones of the theoretical study where values of 1.284 Å, 1.396 Å and 1.400 Å (MP2/6-31G(d)) were proposed. The deviations of the experimentally obtained values for the structure of guanidine in the solid state compared to the calculated equilibrium gas phase data are surprisingly small. Although the environments of the guanidine molecules in **1** and **2** are different and hydrogen bonding between guanidine itself as well as guanidine and 2-amino-4,6-dimethyl-1,3,5-triazine does occur (Table 2), a comparison of the three observed guanidine molecules shows that the interatomic distances and angles (Table 1) are in excellent agreement and are not noticeably influenced by packing effects of the crystal. The obtained geometrical data for the free base guanidine thus provide reliable experimental evidence for the nature of the molecular structure of guanidine for the first time.

Financial support of this work by the University of Munich (LMU) and the Fonds der Chemischen Industrie is gratefully acknowledged. We are grateful to the Cusanuswerk for a fellowship to M. Göbel.

Notes and references

† There are two CSD entries where neutral guanidine molecules are reported (CSD refcodes ACBRHG and BANDAV). However, the corresponding guanidine molecules are guanidinium cations (see ref. 19).

‡ *Preparation of guanidine*: guanidine was prepared by adding a THF solution of guanidinium chloride (16.7 mmol, 24 ml) to a THF solution of sodium methanolate (16.8 mmol, 24 ml) using standard Schlenk techniques. Acetonitrile was allowed to slowly diffuse into the solution until crystals suitable for X-ray diffraction formed at 4 °C (**1**) or 25 °C (**2**).

Crystal data for **1**: $C_6H_{13}N_7$, $M = 183.23$, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.9182(3)$ Å, $b = 4.8503(2)$ Å, $c = 18.8708(7)$ Å, $\beta = 91.382(3)°$, $V = 907.54(6)$ Å^3, $T = 100$ K, $Z = 4$, $\mu = 0.094$ mm^{-1}, $D_c = 1.341$ g cm^{-3}, $F(000) = 392$, $\lambda = 0.71073$ Å, 4341 reflections collected ($R_{int} = 0.0193$), 1755 independent reflections, $R1$ [all data] = 0.0499, $wR2$ [all data] = 0.0837, $R1$ [$I > 2\sigma(I)$] = 0.0327, $wR2$ [$I > 2\sigma(I)$] = 0.0770, GOF = 0.969, completeness = 99.0%. The structure was solved and refined using SHELXS-97[20a] and SHELXL-97.[20b] CCDC 642807.

Crystal data for **2**: $C_7H_{18}N_{10}$, $M = 242.31$, monoclinic, space group $P2_1/c$ (No. 14), $a = 6.5743(2)$ Å, $b = 23.7968(7)$ Å, $c = 7.8931(2)$ Å, $\beta = 96.373(2)°$, $V = 1227.22(6)$ Å^3, $T = 100$ K, $Z = 4$, $\mu = 0.094$ mm^{-1}, $D_c = 1.311$ g cm^{-3}, $F(000) = 520$, $\lambda = 0.71073$ Å, 12 408 reflections collected ($R_{int} = 0.0385$), 2148 independent reflections, $R1$ [all data] = 0.0689, $wR2$ [all data] = 0.1144, $R1$ [$I > 2\sigma(I)$] = 0.0411, $wR2$

Table 1 Selected bond lengths and angles of the guanidine molecules

Structure	1		2			
Guanidine	#1		#2		#3	
d/Å	C1–N1	1.295(2)	C1–N1	1.304(2)	C7–N8	1.300(3)
	C1–N2	1.366(2)	C1–N2	1.350(3)	C7–N10	1.361(3)
	C1–N3	1.355(2)	C1–N3	1.359(3)	C7–N9	1.359(3)
Angle/°	N1–C1–N2	124(0)	N1–C1–N3	125(0)	N8–C7–N9	125(0)
	N1–C1–N3	120(0)	N1–C1–N2	120(0)	N8–C7–N10	120(0)
	N2–C1–N3	116(0)	N2–C1–N3	115(0)	N10–C7–N9	115(0)
	C1–N1–H1	110(1)	C1–N1–H1	109(1)	C7–N8–H8	110(1)
[a]/°	N2	356(4)	N2	359(5)	N10	348(5)
	N3	351(3)	N3	350(6)	N9	353(5)

[a] Degree of planarity given as the angle sum around the nitrogen atom of the corresponding amino group $\Sigma_{CNH,CNH,HNH}$.

Table 2 Hydrogen bonding in structures **1** and **2**

Structure	D–H···A[a]	d (D–H)/Å	d (H···A)/Å	d (D···A)/Å	Angle DHA/°
1	N3–H3B···N5	0.908(15)	2.202(16)	3.1100(16)	178.7(13)
	N2–H2A···$N6^{I}$	0.927(18)	2.177(19)	3.1021(17)	175.7(15)
	N7–H7A···$N4^{II}$	0.856(15)	2.122(16)	2.9777(17)	177.6(12)
	N7–H7B···N1	0.915(15)	2.018(16)	2.9273(16)	172.50(13)
2	N2–H2A···$N4^{III}$	0.89(3)	2.17(3)	3.052(3)	170(2)
	N3–H3A···$N8^{IV}$	0.88(3)	2.17(3)	3.041(3)	171(2)
	N9–H9A···$N8^{V}$	0.93(2)	2.11(3)	3.030(3)	170.2(18)
	N7–H7A···$N1^{III}$	0.88(2)	2.05(2)	2.934(3)	178(2)
	N7–H7B···$N6^{VI}$	0.93(2)	2.08(2)	3.006(2)	176.7(19)

[a] Symmetry codes: (I) $x + 1, y, z$; (II) $-x + 1, -y, -z$; (III) $-x + 2, -y, -z$; (IV) $x + 1, y, z$; (V) $x, -y + 1/2, z + 1/2$; (VI) $-x + 3, -y, -z + 1$.

[$I > 2\sigma(I)$] = 0.0987, GOF = 1.017, completeness = 99.1%. The structure was solved and refined using SHELXS-97[20a] and SHELXL-97.[20b] CCDC 642808. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b705100j

1 S. J. Angyal and W. K. Warburton, *J. Chem. Soc.*, 1951, 2492.

2 R. W. Alder, M. R. Bryce, N. C. Goode, N. Miller and J. Owen, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2840.

3 H. A. Staab and T. Saupe, *Angew. Chem.*, 1988, **100**, 895, (*Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 865).

4 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 3rd edn, 1960, p. 286.

5 P. Gund, *J. Chem. Educ.*, 1972, **49**, 100.

6 P. Kollman, J. McKelvey and P. Gund, *J. Am. Chem. Soc.*, 1975, **97**, 1640.

7 J. F. Capitani and L. Pedersen, *Chem. Phys. Lett.*, 1978, **54**, 547.

8 A. M. Sapse and L. J. Massa, *J. Org. Chem.*, 1980, **45**, 719.

9 T. Ohwada, A. Itai, T. Ohta and K. Shudo, *J. Am. Chem. Soc.*, 1987, **109**, 7036.

10 N. Sreerama and S. Vishveshwara, *J. Mol. Struct.*, 1989, **194**, 61.

11 M. L. Williams and J. E. Gready, *J. Comput. Chem.*, 1989, **10**, 35.

12 K. B. Wiberg, *J. Am. Chem. Soc.*, 1990, **112**, 4177.

13 A. Gobbi and G. Frenking, *J. Am. Chem. Soc.*, 1993, **115**, 2362.

14 N. de Vries, C. E. Costello, A. G. Jones and A. Davidson, *Inorg. Chem.*, 1990, **29**, 1348.

15 W. P. Fehlhammer, R. Metzner and W. Sperber, *Chem. Ber.*, 1994, **127**, 829.

16 P. J. Bailey, K. J. Grant, S. Pace, S. Parsons and L. J. Stewart, *J. Chem. Soc., Dalton Trans.*, 1997, 4263.

17 H. J. Kabbe, K. Eiter and F. Möller, *Justus Liebigs Ann. Chem.*, 1967, **704**, 140.

18 M. Becker and M. Jansen, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1999, **55**, IUC9900094.

19 L. M. Dikareva, *Zh. Neorg. Khim.*, 1980, **25**, 3146; Yu N. Mikhailov, *Russ. J. Inorg. Chem. (Transl. of Zh. Neorg. Khim.)*, 1981, **26**, 718.

20 (*a*) G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.