Structural Studies on Biguanide and Related Species. Correlation of Protonation Energy with Molecular Structure

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The crystal structures of biguanide (bg), dibiguanidinium carbonate, $[Hbg]_2[CO_3]$, dibiguanidinium sulphate, $[Hbg]_2[SO_4]\cdot 2H_2O$, biguanidinium sulphate, $[H_2bg][SO_4]\cdot H_2O$, and malondiamidinium sulphate, $[H_2maldm][SO_4]$, have been determined from diffractometer data: bg, monoclinic, $a = 9.522(2)$, $b = 5.061(1)$, $c = 9.998(2)$ Å, $\beta = 102.95(2)°$, space group $P2_1/n$, $Z = 4$, $R = 0.037$; $[Hbg]_2[CO_3]$, monoclinic, $a = 7.075(2)$, $b = 9.373(2)$, $c = 9.474(3)$ Å, $\beta = 109.52(2)°$, space group $P2_1$, $Z = 2$, $R = 0.030$; $[Hbg]_2[SO_4]\cdot 2H_2O$, triclinic, $a = 9.012(2)$, $b = 9.055(2)$, $c = 9.974(2)$ Å, $\alpha = 89.69(2)$, $\beta = 100.06(2)$, $\gamma = 114.78(2)°$, space group $P\bar{1}$, $Z = 2$, $R = 0.042$; $[H_2bg][SO_4]\cdot H_2O$, orthorhombic, $a = 7.208(1)$, $b = 11.805(3)$, $c = 20.507(6)$ Å, space group *Pbca*, $Z = 8$, $R = 0.046$; and $[H_2maldm][SO_4]$, triclinic, $a = 6.300(1)$, $b = 6.985(1)$, $c = 10.030(1)$ Å, $\alpha = 91.30(1)$, $\beta = 105.59(1)$, $\gamma = 106.00(1)°$, space group $P\bar{1}$, $Z = 2$, $R = 0.027$. The C–N bonds in all the molecules have varying degrees of multiple character. π Bonding through bridging nitrogen is important in all cases, but planarity in $[Hbg]^+$ and $[H_2bg]^{2+}$ is destroyed due to steric interactions. Neutral bg is approximately planar but asymmetric; $[H_2maldm]^{2+}$ is non-planar due to the absence of bridge π bonding. All the ionic structures have well defined hydrogen-bonding schemes. Neutral bg is intramolecularly hydrogen bonded. The energy of protonation of bg and $[Hbg]^+$ are discussed in structural terms and with regard to the proposed bonding scheme. Bonding parameters are compared with those found in transition-metal complexes of these compounds.

It was recently reported [1] that the energy of protonation of biguanide (bg) was unusually high ($\Delta H = -95$ kJ mol^{-1}, $\Delta S = -71$ J K^{-1} mol^{-1}), and that the addition of a second proton was also rather energetic ($\Delta H = -21$ kJ mol^{-1}, $\Delta S = -13$ J K^{-1} mol^{-1}). The high enthalpy of protonation was interpreted as due to the replacement of two localised double bonds by the formation of a cation whose π electrons were delocalised over

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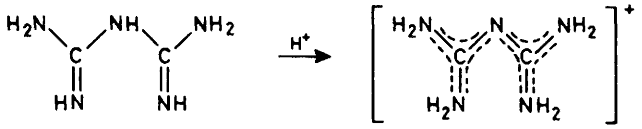
[1] L. Fabrizzi, M. Micheloni, P. Paoletti, and G. Schwarzenbach, *J. Amer. Chem. Soc.*, 1977, **99**, 5574.

the whole molecule. The negative entropy for the same process was attributed to the conversion of a flexible molecule into a rigid one. This interpretation is analogous to that proposed for guanidine.[1,2]



We have been interested for some time in the chemistry and structures of transition-metal complexes of biguanide and analogous diamidines. In order to discuss their structures in detail it became desirable to know the bonding parameters in the free ligands. In the hope of gaining some insight into the above protonation reactions, and to obtain data for unco-ordinated ligands, we report and discuss the structures of biguanide (bg), the monoprotonated cation ([Hbg]$^+$) as its sulphate and carbonate, the diprotonated cation ([H$_2$bg]$^{2+}$) as its sulphate, and the diprotonated malondiamidine cation ([H$_2$maldm]$^{2+}$) also as its sulphate. The latter was chosen because the possibility of π bonding through the bridge atom does not exist. The recent report of the structures of bg[3] and [Hbg]Cl[4] has prompted us to report our more complete study of these systems.

EXPERIMENTAL

Suitable crystals of neutral bg were obtained from the commercially (Aldrich) available product. Crystallisation of bg from aqueous ethanol overnight yielded crystals of the carbonate, [Hbg]$_2$[CO$_3$]. Slow evaporation of an aqueous solution of commercial (Aldrich) [Hbg]$_2$[SO$_4$]·2H$_2$O gave well formed crystals. Careful acidification of a similar solution with dilute sulphuric acid yielded the diprotonated sulphate, [H$_2$bg][SO$_4$]·H$_2$O, as small crystals. Reaction of [H$_2$maldm]Cl$_2$ (gift from Professor G. Schwarzenbach) with a stoicheiometric quantity of Ag$_2$[SO$_4$] in aqueous solution gave crystals of [H$_2$maldm][SO$_4$] on slow evaporation of the filtrate. All *X*-ray measurements were carried out at 20 °C with a Syntex *P*2$_1$ automatic four-circle diffractometer. Unit-cell parameters were determined on the diffractometer from 25 accurately centred reflections at $2\theta \sim 30°$. Intensities were measured with 2θ—θ scans using niobium-filtered molybdenum *X*-radiation (λ 0.710 69 Å). Backgrounds were estimated from an analysis of the scan profile.[5] No absorption corrections were applied. The relevant crystallographic data are presented in Table 1.

TABLE 1

Crystallographic data

	bg C$_2$H$_7$N$_5$	[Hbg]$_2$[CO$_3$] C$_5$H$_{16}$N$_{10}$O$_3$	[Hbg]$_2$[SO$_4$]·2H$_2$O C$_4$H$_{20}$N$_{10}$O$_6$S	[H$_2$bg][SO$_4$]·H$_2$O C$_2$H$_{11}$N$_5$O$_5$S	[H$_2$maldm][SO$_4$] C$_3$H$_{10}$N$_4$O$_4$S
M	101.11	264.25	336.33	217.20	198.20
Crystal size (mm)	0.30 × 0.20 × 0.15	0.25 × 0.20 × 0.15	0.25 × 0.15 × 0.08	0.25 × 0.20 × 0.08	0.24 × 0.18 × 0.06
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic
a/Å	9.522(2)	7.075(2)	9.012(2)	7.208(1)	6.300(1)
b/Å	5.061(1)	9.373(2)	9.055(2)	11.805(3)	6.985(1)
c/Å	9.998(2)	9.474(3)	9.974(2)	20.507(6)	10.030(1)
α/°			89.62(2)		91.30(1)
β/°	102.95(2)	109.52(2)	100.06(2)		105.59(1)
γ/°			114.78(2)		106.00(1)
U/Å^3	496.6(2)	592.1(3)	725.5(3)	1 744.9(7)	406.4(1)
Space group	$P2_1/n$ [a]	$P2_1$ [b]	$P\bar{1}$ [c]	$Pbca$ [a]	$P\bar{1}$ [c]
D_m/g cm^{-3}	1.44	1.47	1.54	1.65	1.62
D_c/g cm^{-3}	1.43	1.48	1.54	1.65	1.62
Z	4	2	2	8	2
F(000)	216	280	356	912	208
Reflections measured	1 083	1 118	2 569	1 547	1 075
No. of reflections unobserved, $I < 3\sigma(I)$	299	75	862	496	187
$[(\sin\theta)/\lambda]_{max.}$	0.65	0.60	0.60	0.60	0.54
μ(Mo-K_α)/cm^{-1}	1.2	1.3	2.7	3.8	3.8
R	0.037	0.030	0.042	0.046	0.027

[a] From systematic absences. [b] From systematic absences, reflection statistics, and successful refinement. [c] From successful refinement.

Structure Solution.—Scattering factors for the neutral atoms were taken from Cromer and Mann[6] (C, N, O, and S), and Stewart *et al.*[7] (H). All the computer programs used for data reduction, structure solution, and refinement were taken from the '*X*-RAY '72' program system[8] with the exception of MULTAN.[9] The Figures were prepared with the aid of the program ORTEP.[10]

The solution of the structures may be divided into two groups. For bg, [Hbg]$_2$[CO$_3$], and [Hbg]$_2$[SO$_4$]·2H$_2$O phases were generated with the program MULTAN and all the non-hydrogen atoms revealed by subsequent three-dimensional *E* maps. After refinement of the resulting

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[8] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, '*X*-RAY '72' program system, Technical Report TR-192, Computing Science Center, University of Maryland, June 1972 (as modified by D. Schwarzenbach).

[9] P. Main, G. Germain, and M. M. Woolfson, 1977, Program for the automatic solution of crystal structures.

[10] C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1971.

TABLE 2

Atomic co-ordinates

Atom	*x*	*y*	*z*
(*a*) Neutral bg			
N(1)	0.810 6(2)	−0.056 1(3)	−0.132 3(1)
N(2)	0.621 9(2)	0.149 2(4)	−0.066 6(2)
N(3)	0.863 9(1)	0.261 5(3)	0.033 7(1)
N(4)	0.696 9(2)	0.495 2(3)	0.134 5(2)
N(5)	0.942 8(2)	0.613 2(3)	0.173 7(1)
C(1)	0.763 1(2)	0.122 1(3)	−0.050 6(1)
C(2)	0.824 6(2)	0.460 6(3)	0.112 5(1)
H(1)	0.748(2)	−0.176(4)	−0.172(2)
H(2)	0.907(2)	−0.107(3)	−0.107(2)
H(3)	0.592(2)	0.285(4)	−0.012(2)
H(4)	0.564(2)	0.067(4)	−0.139(2)
H(5)	1.009(2)	0.637(3)	0.117(2)
H(6)	0.919(2)	0.766(4)	0.214(2)
H(7)	0.696(2)	0.630(4)	0.188(2)
(*b*) $[Hbg]_2[CO_3]$			
N(1)	0.489 9(5)	0.0	0.193 5(3)
N(2)	0.745 2(4)	0.112 7(4)	0.372 7(3)
N(3)	0.498 4(4)	0.243 6(3)	0.184 9(2)
N(4)	0.497 2(5)	0.485 6(3)	0.169 4(3)
N(5)	0.572 5(5)	0.388 2(4)	0.401 3(3)
N(6)	0.993 8(5)	0.948 2(3)	−0.221 5(3)
N(7)	0.973 0(4)	0.720 9(3)	−0.149 4(3)
N(8)	1.059 6(4)	0.909 5(3)	0.028 9(2)
N(9)	1.084 6(5)	0.885 6(3)	0.274 8(3)
N(10)	0.837 1(4)	0.760 7(3)	0.105 1(3)
C(1)	0.578 4(5)	0.122 3(3)	0.254 0(3)
C(2)	0.527 6(4)	0.369 8(4)	0.254 6(3)
C(3)	1.004 6(4)	0.857 2(4)	−0.112 5(3)
C(4)	0.992 7(5)	0.851 2(3)	0.132 0(3)
C(5)	0.763 6(4)	0.735 9(4)	0.459 2(3)
O(1)	0.641 3(3)	0.737 9(2)	0.323 4(2)
O(2)	0.914 8(3)	0.821 9(2)	0.497 6(2)
O(3)	0.735 4(3)	0.648 5(2)	0.553 5(2)
H(1)	0.547(5)	−0.083(4)	0.241(3)
H(2)	0.357(5)	0.008(3)	0.131(3)
H(3)	0.795(5)	0.027(4)	0.411(4)
H(4)	0.832(5)	0.181(3)	0.401(3)
H(5)	0.526(5)	0.566(4)	0.213(3)
H(6)	0.490(5)	0.480(4)	0.075(3)
H(7)	0.594(5)	0.475(4)	0.437(4)
H(8)	0.559(6)	0.330(4)	0.449(4)
H(9)	0.974(5)	0.916(4)	−0.318(4)
H(10)	1.009(6)	1.036(4)	−0.197(4)
H(11)	0.903(5)	0.700(4)	−0.259(4)
H(12)	0.970(5)	0.652(4)	−0.075(4)
H(13)	1.183(5)	0.948(4)	0.299(4)
H(14)	1.027(5)	0.867(4)	0.353(4)
H(15)	0.781(4)	0.757(3)	0.177(3)
H(16)	0.758(5)	0.756(4)	0.013(3)
(*c*) $[Hbg]_2[SO_4]\cdot 2H_2O$			
N(1)	0.319 0(3)	0.489 6(3)	0.121 7(3)
N(2)	0.548 4(4)	0.532 2(3)	0.281 2(3)
N(3)	0.552 2(3)	0.723 2(3)	0.116 7(2)
N(4)	0.804 2(4)	0.924 9(3)	0.097 2(3)
N(5)	0.747 5(4)	0.881 1(3)	0.311 4(3)
N(6)	0.063 1(3)	0.309 2(3)	0.885 8(3)
N(7)	0.032 3(4)	0.356 5(3)	0.685 4(3)
N(8)	0.132 5(3)	0.564 2(3)	0.865 2(2)
N(9)	0.377 7(3)	0.780 8(3)	0.848 2(3)
N(10)	0.159 8(4)	0.707 5(3)	0.667 0(3)
C(1)	0.476 6(4)	0.585 6(3)	0.176 1(3)
C(2)	0.702 0(4)	0.840 1(3)	0.177 7(3)
C(3)	0.033 2(4)	0.413 6(3)	0.808 5(3)
C(4)	0.223 1(4)	0.683 0(3)	0.790 8(3)
H(1)	0.271(4)	0.518(4)	0.046(3)
H(2)	0.266(4)	0.389(4)	0.150(3)
H(3)	0.643(4)	0.583(4)	0.310(3)
H(4)	0.492(4)	0.428(4)	0.315(3)
H(5)	0.899(4)	0.999(4)	0.136(3)
H(6)	0.777(4)	0.883(4)	0.002(3)
H(7)	0.685(5)	0.830(4)	0.376(4)
H(8)	0.858(4)	0.948(4)	0.353(3)
(*c*) $[Hbg]_2[SO_4]\cdot 2H_2O$ (*continued*)			
H(9)	−0.072(4)	0.349(3)	0.963(3)
H(10)	−0.133(4)	0.217(4)	0.848(3)
H(11)	0.092(3)	0.424(3)	0.626(3)
H(12)	−0.022(4)	0.251(4)	0.660(3)
H(13)	0.418(5)	0.753(4)	0.938(4)
H(14)	0.446(4)	0.859(4)	0.796(3)
H(15)	0.218(5)	0.779(4)	0.613(3)
H(16)	0.048(5)	0.657(4)	0.631(3)
H(17)	0.757(4)	0.468(4)	0.554(3)
H(18)	0.747(6)	0.632(5)	0.577(4)
H(19)	0.421(5)	0.774(5)	0.407(4)
H(20)	0.357(5)	0.873(5)	0.391(4)
O(1)	0.893 4(2)	1.011 5(2)	0.619 0(2)
O(2)	0.671 1(3)	0.993 6(2)	0.729 5(2)
O(3)	0.835 4(3)	0.848 9(2)	0.811 6(2)
O(4)	0.646 2(2)	0.760 1(2)	0.595 5(2)
O(5)	0.808 3(3)	0.555 5(3)	0.551 0(2)
O(6)	0.366 4(4)	0.784 2(4)	0.453 2(3)
S(1)	0.763 0(1)	0.904 55(9)	0.689 28(8)
(*d*) $[H_2bg][SO_4]\cdot H_2O$			
N(1)	0.257 9(6)	0.025 2(4)	0.478 6(2)
N(2)	0.055 9(6)	0.173 5(3)	0.461 9(2)
N(3)	0.082 3(5)	0.029 0(3)	0.385 8(1)
N(4)	0.091 3(5)	0.189 3(3)	0.319 1(2)
N(5)	−0.030 9(6)	0.022 3(3)	0.281 8(2)
C(1)	0.135 4(6)	0.079 8(3)	0.443 6(2)
C(2)	0.047 4(6)	0.083 2(3)	0.327 8(2)
H(1)	0.306(6)	−0.025(3)	0.464(2)
H(2)	0.297(7)	0.057(4)	0.519(2)
H(3)	−0.059(6)	0.191(3)	0.443(2)
H(4)	0.096(6)	0.195(4)	0.492(2)
H(5)	0.094(5)	−0.045(3)	0.386(2)
H(6)	0.178(6)	0.222(4)	0.344(2)
H(7)	0.081(6)	0.219(3)	0.281(2)
H(8)	−0.034(6)	0.057(3)	0.243(2)
H(9)	−0.077(6)	−0.044(4)	0.291(2)
H(10)	0.366(7)	0.371(4)	0.123(2)
H(11)	0.426(9)	0.489(5)	0.116(3)
O(1)	0.161 8(4)	0.300 1(2)	0.186 1(1)
O(2)	−0.105 3(3)	0.299 1(2)	0.114 5(1)
O(3)	0.006 2(4)	0.124 4(2)	0.160 2(1)
O(4)	0.186 5(4)	0.220 9(2)	0.077 8(1)
O(5)	0.432 5(5)	0.424 3(3)	0.099 9(2)
S(1)	0.063 6(1)	0.236 00(8)	0.134 82(4)
(*e*) $[H_2maldm][SO_4]$			
N(1)	0.354 5(5)	0.709 1(4)	0.117 4(3)
N(2)	0.584 3(5)	0.803 0(4)	−0.023 6(2)
N(3)	0.729 9(5)	0.850 9(4)	0.407 5(3)
N(4)	0.745 8(4)	0.527 7(4)	0.403 4(3)
C(1)	0.552 4(5)	0.738 2(4)	0.092 9(3)
C(2)	0.751 0(5)	0.695 2(5)	0.195 8(3)
C(3)	0.740 8(4)	0.691 0(4)	0.343 3(3)
H(1)	0.319(5)	0.651(4)	0.183(3)
H(2)	0.232(5)	0.729(4)	0.050(3)
H(3)	0.467(5)	0.815(4)	−0.092(3)
H(4)	0.710(6)	0.812(4)	−0.038(3)
H(5)	0.760(4)	0.570(4)	0.166(2)
H(6)	0.878(5)	0.789(4)	0.194(3)
H(7)	0.733(5)	0.858(4)	0.499(3)
H(8)	0.749(5)	0.958(4)	0.366(3)
H(9)	0.749(5)	0.415(5)	0.354(3)
H(10)	0.755(5)	0.524(4)	0.488(3)
O(1)	0.023 7(3)	0.249 2(3)	0.085 1(2)
O(2)	0.169 8(3)	0.461 5(3)	0.302 6(2)
O(3)	0.173 3(3)	0.117 6(3)	0.298 3(2)
O(4)	−0.187 1(3)	0.197 7(3)	0.255 8(2)
S(1)	0.048 0(1)	0.255 6(1)	0.235 58(7)

structures by full-matrix or block-diagonal least squares with anisotropic temperature factors, difference-Fourier maps revealed all the hydrogen atoms. The final structures were refined as before with isotropic temperature factors for the hydrogen atoms. The function minimised was $\Sigma(1/\sigma^2)$-

$(|F_o| - |F_c|)^2$, where the estimated standard deviations of the structure factors were determined from counting statistics and the variation in the intensities of three periodically measured check reflections. The structures of $[H_2bg][SO_4]\cdot H_2O$ and $[H_2maldm][SO_4]$ were easily solved using three-dimensional Patterson maps and successive Fourier syntheses. In the former case the sulphur atom was found to have co-ordinates of *ca.* $x, \frac{1}{4}, \frac{1}{2}$ which required the solution of a four-fold ambiguity. Localisation of hydrogen atoms and final refinement was carried out as above.

Final atomic co-ordinates are reported in Table 2, and calculated bond lengths and angles in Tables 3—7. Tables of structure factors and temperature factors are available as Supplementary Publication No. SUP 22263 (41 pp.).*

TABLE 3

Bond lengths (Å) and angles (°) in bg with standard deviations in parentheses

C(1)–N(1)	1.361(2)	N(1)–H(2)	0.93(2)
C(1)–N(2)	1.325(2)	N(2)–H(3)	0.96(2)
C(1)–N(3)	1.329(2)	N(2)–H(4)	0.91(2)
C(2)–N(3)	1.382(2)	N(4)–H(7)	0.87(2)
C(2)–N(4)	1.295(2)	N(5)–H(5)	0.94(2)
C(2)–N(5)	1.389(2)	N(5)–H(6)	0.92(2)
N(1)–H(1)	0.88(2)		
N(1)–C(1)–N(2)	117.5(1)	C(1)–N(2)–H(3)	115(1)
N(1)–C(1)–N(3)	116.2(1)	C(1)–N(2)–H(4)	118(1)
N(2)–C(1)–N(3)	126.2(1)	H(3)–N(2)–H(4)	125(2)
N(3)–C(2)–N(4)	125.5(1)	C(1)–N(3)–C(2)	119.9(1)
N(3)–C(2)–N(5)	111.1(1)	C(2)–N(4)–H(7)	110(1)
N(4)–C(2)–N(5)	123.3(1)	C(2)–N(5)–H(5)	113(1)
C(1)–N(1)–H(1)	116(1)	C(2)–N(5)–H(6)	114(1)
C(1)–N(1)–H(2)	117(1)	H(5)–N(5)–H(6)	114(2)
H(1)–N(1)–H(2)	117(2)		

Hydrogen bonds

N(4) · · · H(3) *	1.90(2)	N(4)–H(3)–N(2)	132(2)
N(3) · · · H(5)	2.20(2)	N(3)–H(5)–N(5)	171(1)
N(3) · · · H(2)	2.29(2)	N(3)–H(2)–N(1)	175(2)
N(4) · · · H(6)	2.37(2)	N(4)–H(6)–N(5)	152(2)
N(5) · · · H(4)	2.17(2)	N(5)–H(4)–N(2)	173(2)

* Intramolecular.

RESULTS AND DISCUSSION

Perspective drawings of all the four molecules are presented in Figures 1—4. As previously reported,[3] the structure of bg (Figure 1) is not symmetric as had been proposed.[1] The molecule is roughly planar due in part to the presence of an intramolecular hydrogen bond. The twist between the two planar halves of the molecule is 12.5°. From the shortness of the C–N bonds (1.295—1.389 Å) and from the almost planar structure it must be assumed that there is a delocalisation of π-electron density throughout the molecule. The inequivalence of the bonds may be qualitatively explained by the difference in the basicity of the various nitrogen atoms. From the angles around these atoms it can be seen that the least basic ones [N(1) and N(5)] have some sp^3 character. Although the hydrogen bond holds the molecule in a planar conformation, it also pushes apart the two arms of the molecule in attempting to attain linearity.

The cation $[Hbg]^+$ (Figure 2) determined as the carbonate and sulphate has qualitatively the same structure as previously reported for the chloride,[4] and is also quite similar to the structure of the dication $[H_2bg]^{2+}$ (Figure 3). For this reason these two ionic structures will be discussed together. The ions are composed of two almost perfectly planar halves with one atom in common. The two planar parts are twisted with respect to one another by 47.6° in the monoprotonated ion, and by 48.4° in the dication (but see below). The C–N bond lengths are all short and almost equivalent. From this and the planarity of the halves it is evident that there is a strong π contribution to all the bonds. The lack of complete planarity of the ions is due to steric interaction between the hydrogen atoms. This interaction induces a strain in the molecules which is manifested in $[Hbg]^+$ by a distortion of the angles at the sp^2 carbon atoms, and in $[H_2bg]^{2+}$ by the opening of the

TABLE 4

Bond lengths (Å) and angles (°) for $[Hbg]_2[CO_3]$ with standard deviations in parentheses

(*a*) Molecule 1

C(1)–N(1)	1.340(3)	N(1)–H(2)	0.93(3)
C(1)–N(2)	1.333(4)	N(2)–H(3)	0.90(4)
C(1)–N(3)	1.340(4)	N(2)–H(4)	0.86(3)
C(2)–N(3)	1.337(4)	N(4)–H(5)	0.85(3)
C(2)–N(4)	1.327(4)	N(4)–H(6)	0.88(3)
C(2)–N(5)	1.329(4)	N(5)–H(7)	0.88(4)
N(1)–H(1)	0.92(3)	N(5)–H(8)	0.73(4)
N(1)–C(1)–N(2)	117.3(3)	C(1)–N(2)–H(4)	123(2)
N(1)–C(1)–N(3)	117.1(2)	H(3)–N(2)–H(4)	113(3)
N(2)–C(1)–N(3)	125.5(3)	C(1)–N(3)–C(2)	122.6(2)
N(3)–C(2)–N(4)	117.1(3)	C(2)–N(4)–H(5)	118(2)
N(3)–C(2)–N(5)	125.1(3)	C(2)–N(4)–H(6)	121(2)
N(4)–C(2)–N(5)	117.6(3)	H(5)–N(4)–H(6)	118(3)
C(1)–N(1)–H(1)	117(2)	C(2)–N(5)–H(7)	118(2)
C(1)–N(1)–H(2)	116(2)	C(2)–N(5)–H(8)	121(3)
H(1)–N(1)–H(2)	124(3)	H(7)–N(5)–H(8)	120(4)
C(1)–N(2)–H(3)	121(2)		

(*b*) Molecule 2

C(3)–N(6)	1.321(5)	N(6)–H(10)	0.85(4)
C(3)–N(7)	1.323(5)	N(7)–H(11)	1.01(3)
C(3)–N(8)	1.356(4)	N(7)–H(12)	0.96(4)
C(4)–N(8)	1.336(4)	N(9)–H(13)	0.87(4)
C(4)–N(9)	1.331(4)	N(9)–H(14)	0.97(4)
C(4)–N(10)	1.344(4)	N(10)–H(15)	0.90(3)
N(6)–H(9)	0.93(3)	N(10)–H(16)	0.87(2)
N(6)–C(3)–N(7)	117.2(3)	C(3)–N(7)–H(12)	120(2)
N(6)–C(3)–N(8)	117.5(3)	H(11)–N(7)–H(12)	120(3)
N(7)–C(3)–N(8)	125.2(3)	C(3)–N(8)–C(4)	121.3(3)
N(8)–C(4)–N(9)	118.2(3)	C(4)–N(9)–H(13)	120(2)
N(8)–C(4)–N(10)	125.9(2)	C(4)–N(9)–H(14)	123(2)
N(9)–C(4)–N(10)	115.9(3)	H(13)–N(9)–H(14)	115(3)
C(3)–N(6)–H(9)	121(2)	C(4)–N(10)–H(15)	115(2)
C(3)–N(6)–H(10)	116(3)	C(4)–N(10)–H(16)	116(2)
H(9)–N(6)–H(10)	123(3)	H(15)–N(10)–H(16)	117(2)
C(3)–N(7)–H(11)	116(2)		

(*c*) Hydrogen bonds

O(1) · · · H(1)	1.88(3)	O(1)–H(1)–N(1)	174(3)
O(1) · · · H(5)	1.94(3)	O(1)–H(5)–N(4)	169(3)
O(1) · · · H(15)	1.96(3)	O(1)–H(15)–N(10)	175(3)
O(2) · · · H(3)	2.15(4)	O(2)–H(3)–N(2)	179(4)
O(2) · · · H(4)	2.18(3)	O(2)–H(4)–N(2)	169(3)
O(2) · · · H(9)	1.87(3)	O(2)–H(9)–N(6)	170(3)
O(2) · · · H(14)	1.85(4)	O(2)–H(14)–N(9)	177(3)
O(3) · · · H(7)	2.03(4)	O(3)–H(7)–N(5)	161(3)
O(3) · · · H(11)	1.84(3)	O(3)–H(11)–N(7)	168(3)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

angle at the bridging nitrogen atom. This difference in behaviour is caused by the weakening of the bridge bonds due to the lowered basicity of the bridge atom on protonation. This weakening is also manifested by the longer C–N bridge bond (1.377 *vs.* 1.344 Å), and the shorter terminal C–N bonds (1.306 *vs.* 1.329 Å). In contrast to the neutral bg, all the terminal nitrogen atoms are planar and sp^2 in character.

TABLE 5

Bond lengths (Å) and angles (°) for $[\mathrm{Hbg}]_2[\mathrm{SO}_4]\cdot 2\mathrm{H}_2\mathrm{O}$ with standard deviations in parentheses

(*a*) Molecule 1

C(1)–N(1)	1.329(4)	N(1)–H(2)	0.90(3)
C(1)–N(2)	1.331(4)	N(2)–H(3)	0.78(3)
C(1)–N(3)	1.337(4)	N(2)–H(4)	0.96(3)
C(2)–N(3)	1.354(3)	N(4)–H(5)	0.86(3)
C(2)–N(4)	1.320(4)	N(4)–H(6)	0.98(3)
C(2)–N(5)	1.331(4)	N(5)–H(7)	0.92(4)
N(1)–H(1)	0.89(3)	N(5)–H(8)	0.94(3)
N(1)–C(1)–N(2)	117.0(3)	C(1)–N(2)–H(4)	123(2)
N(1)–C(1)–N(3)	117.6(3)	H(3)–N(2)–H(4)	119(3)
N(2)–C(1)–N(3)	125.4(3)	C(1)–N(3)–C(2)	121.2(2)
N(3)–C(2)–N(4)	117.1(3)	C(2)–N(4)–H(5)	117(2)
N(3)–C(2)–N(5)	124.3(3)	C(2)–N(4)–H(6)	117(2)
N(4)–C(2)–N(5)	118.4(2)	H(5)–N(4)–H(6)	124(3)
C(1)–N(1)–H(1)	119(2)	C(2)–N(5)–H(7)	125(2)
C(1)–N(1)–H(2)	122(2)	C(2)–N(5)–H(8)	122(2)
H(1)–N(1)–H(2)	119(3)	H(7)–N(5)–H(8)	111(3)
C(1)–N(2)–H(3)	118(2)		

(*b*) Molecule 2

C(3)–N(6)	1.334(4)	N(6)–H(10)	0.85(3)
C(3)–N(7)	1.332(4)	N(7)–H(11)	0.92(3)
C(3)–N(8)	1.337(3)	N(7)–H(12)	0.89(3)
C(4)–N(8)	1.357(4)	N(9)–H(13)	0.97(4)
C(4)–N(9)	1.321(4)	N(9)–H(14)	0.95(3)
C(4)–N(10)	1.325(4)	N(10)–H(15)	0.89(3)
N(6)–H(9)	0.88(3)	N(10)–H(16)	0.92(4)
N(6)–C(3)–N(7)	117.6(2)	C(3)–N(7)–H(12)	121(2)
N(6)–C(3)–N(8)	117.1(3)	H(11)–N(7)–H(12)	118(3)
N(7)–C(3)–N(8)	125.2(3)	C(3)–N(8)–C(4)	121.2(2)
N(8)–C(4)–N(9)	117.7(3)	C(4)–N(9)–H(13)	115(2)
N(8)–C(4)–N(10)	122.4(2)	C(4)–N(9)–H(14)	119(2)
N(9)–C(4)–N(10)	119.9(3)	H(13)–N(9)–H(14)	125(3)
C(3)–N(6)–H(9)	118(2)	C(4)–N(10)–H(15)	125(2)
C(3)–N(6)–H(10)	117(2)	C(4)–N(10)–H(16)	122(2)
H(9)–N(6)–H(10)	122(3)	H(15)–N(10)–H(16)	113(3)
C(3)–N(7)–H(11)	121(2)		

(*c*) Hydrogen bonds

O(1) · · · H(8)	2.08(4)	O(1)–H(8)–N(5)	147(3)
O(1) · · · H(12)	1.99(3)	O(1)–H(12)–N(7)	170(4)
O(2) · · · H(10)	2.21(2)	O(1)–H(10)–N(6)	172(3)
O(2) · · · H(14)	2.10(3)	O(2)–H(14)–N(9)	154(3)
O(2) · · · H(20)	1.76(4)	O(2)–H(20)–O(6)	173(3)
O(3) · · · H(2)	2.02(3)	O(3)–H(2)–N(1)	170(4)
O(3) · · · H(5)	2.17(3)	O(3)–H(5)–N(4)	162(4)
O(3) · · · H(6)	2.11(4)	O(3)–H(6)–N(4)	154(3)
O(4) · · · H(4)	1.96(3)	O(4)–H(4)–N(2)	167(3)
O(4) · · · H(18)	1.77(6)	O(4)–H(18)–O(5)	172(4)
O(5) · · · H(11)	2.09(3)	O(5)–H(11)–N(7)	147(3)
O(5) · · · H(16)	1.97(4)	O(5)–H(16)–N(10)	178(3)
O(6) · · · H(17)	2.07(3)	O(6)–H(17)–O(5)	172(4)

The structure of the dication $[\mathrm{H}_2\mathrm{maldm}]^{2+}$ (Figure 4) determined as the sulphate is similar to the two previous structures, but with the important difference that there is no π-bonding contribution to the bridge in this case. The two planar halves of the molecule have the same bond lengths as $[\mathrm{H}_2\mathrm{bg}]^{2+}$, and the nitrogen atoms are clearly sp^2. The lack of strain due to a multiply bonded bridge is evidenced by the torsion angle of 74.1° coupled with the normal bond length of 1.499 Å. These observations also contribute to the assignment of

TABLE 6

Bond lengths (Å) and angles (°) for $[\mathrm{H}_2\mathrm{bg}][\mathrm{SO}_4]\cdot\mathrm{H}_2\mathrm{O}$ with standard deviations in parentheses

C(1)–N(1)	1.308(6)	N(2)–H(3)	0.94(4)
C(1)–N(2)	1.302(5)	N(2)–H(4)	0.73(4)
C(1)–N(3)	1.383(5)	N(3)–H(5)	0.88(4)
C(2)–N(3)	1.373(5)	N(4)–H(6)	0.90(4)
C(2)–N(4)	1.303(5)	N(4)–H(7)	0.86(4)
C(2)–N(5)	1.313(5)	N(5)–H(8)	0.90(4)
N(1)–H(1)	0.75(4)	N(5)–H(9)	0.87(4)
N(1)–H(2)	0.96(4)		
N(1)–C(1)–N(2)	123.9(4)	H(3)–N(2)–H(4)	128(4)
N(1)–C(1)–N(3)	116.4(4)	C(1)–N(3)–C(2)	126.2(3)
N(2)–C(1)–N(3)	119.6(4)	C(1)–N(3)–H(5)	114(2)
N(3)–C(2)–N(4)	121.5(4)	C(2)–N(3)–H(5)	119(2)
N(3)–C(2)–N(5)	116.4(3)	C(2)–N(4)–H(6)	120(3)
N(4)–C(2)–N(5)	122.1(4)	C(2)–N(4)–H(7)	120(3)
C(1)–N(1)–H(1)	119(3)	H(6)–N(4)–H(7)	114(4)
C(1)–N(1)–H(2)	119(3)	C(2)–N(5)–H(8)	113(3)
H(1)–N(1)–H(2)	121(4)	C(2)–N(5)–H(9)	120(3)
C(1)–N(2)–H(3)	118(3)	H(8)–N(5)–H(9)	126(4)
C(1)–N(2)–H(4)	111(3)		

Hydrogen bonds

O(1) · · · H(7)	2.24(4)	O(1)–H(7)–N(4)	160(4)
O(1) · · · H(9)	2.00(4)	O(1)–H(9)–N(5)	175(4)
O(1) · · · H(10)	2.13(5)	O(1)–H(10)–O(5)	160(4)
O(2) · · · H(5)	1.84(4)	O(2)–H(5)–N(3)	177(4)
O(2) · · · H(6)	1.99(4)	O(2)–H(6)–N(4)	170(4)
O(3) · · · H(8)	1.89(4)	O(3)–H(8)–N(5)	170(4)
O(3) · · · H(11)	1.90(6)	O(3)–H(11)–O(5)	161(6)
O(4) · · · H(3)	1.92(4)	O(4)–H(3)–N(2)	168(4)
O(4) · · · H(4)	2.12(4)	O(4)–H(4)–N(2)	171(5)
O(5) · · · H(2)	1.93(5)	O(5)–H(2)–N(1)	160(4)

TABLE 7

Bond lengths (Å) and angles (°) for $[\mathrm{H}_2\mathrm{maldm}][\mathrm{SO}_4]$ with standard deviations in parentheses

C(1)–N(1)	1.297(4)	N(2)–H(3)	0.87(3)
C(1)–N(2)	1.308(4)	N(2)–H(4)	0.83(4)
C(1)–C(2)	1.499(4)	C(2)–H(5)	0.94(3)
C(2)–C(3)	1.498(4)	C(2)–H(6)	0.89(3)
C(3)–N(3)	1.305(4)	N(3)–H(7)	0.91(3)
C(3)–N(4)	1.306(4)	N(3)–H(8)	0.86(3)
N(1)–H(1)	0.83(3)	N(4)–H(9)	0.93(3)
N(1)–H(2)	0.92(3)	N(4)–H(10)	0.84(3)
N(1)–C(1)–N(2)	121.1(3)	C(1)–N(1)–H(1)	125(2)
N(1)–C(1)–C(2)	121.2(3)	C(1)–N(1)–H(2)	120(2)
N(2)–C(1)–C(2)	117.7(3)	H(1)–N(1)–H(2)	114(3)
C(1)–C(2)–C(3)	116.2(3)	C(1)–N(2)–H(3)	121(2)
C(1)–C(2)–H(5)	108(1)	C(1)–N(2)–H(4)	118(2)
C(1)–C(2)–H(6)	107(1)	H(3)–N(2)–H(4)	120(3)
C(3)–C(2)–H(5)	108(2)	C(3)–N(3)–H(7)	122(2)
C(3)–C(2)–H(6)	108(2)	C(3)–N(3)–H(8)	117(2)
H(5)–C(2)–H(6)	109(3)	H(7)–N(3)–H(8)	120(3)
C(2)–C(3)–N(3)	118.9(3)	C(3)–N(4)–H(9)	121(2)
C(2)–C(3)–N(4)	118.7(3)	C(3)–N(4)–H(10)	121(2)
N(3)–C(3)–N(4)	122.4(3)	H(9)–N(4)–H(10)	118(3)

Hydrogen bonds

O(1) · · · H(2)	1.85(3)	O(1)–H(2)–N(1)	176(3)
O(1) · · · H(4)	2.01(4)	O(1)–H(4)–N(2)	164(3)
O(2) · · · H(1)	2.20(3)	O(2)–H(1)–N(1)	165(2)
O(2) · · · H(10)	2.02(3)	O(2)–H(10)–N(4)	171(3)
O(3) · · · H(7)	1.95(3)	O(3)–H(7)–N(3)	165(3)
O(4) · · · H(3)	2.04(3)	O(4)–H(3)–N(2)	172(3)
O(4) · · · H(8)	2.03(3)	O(4)–H(8)–N(3)	174(3)
O(4) · · · H(9)	1.98(3)	O(4)–H(9)–N(4)	170(3)

multiple-bond character in the biguanidinium ions described above.

TABLE 8

Average bond lengths and angles for free and complexed ligands [a]

	$[Hbg]^+$	$[H_2bg]^{2+}$	[M(bg – H)] [b]	[M(bg)] [b]	$[H_2maldm]^{2+}$	[M(maldm)] [c]
C–N(bridge)/Å	1.344	1.377	1.353	1.373	1.499	1.507
$C{-}NH_2$/Å	1.329	1.306	1.370	1.344	1.304	1.333
C–NHM/Å			1.313	1.305		1.289
C–N–C/°	121.6	126.2	120.7	126.9	116.2	115.5
N–C–N(ring)/°	124.9	120.5	126.8	121	120.0	119.4

[a] [M(bg – H)] represents $[\overline{M\{NHC(NH_2)NC(NH_2)N}H\}]$, [M(bg)] represents $[\overline{M\{NHC(NH_2)NHC(NH_2)N}H\}]$, and [M(maldm)] represents $[\overline{M\{NHC(NH_2)CH_2C(NH_2)N}H\}]$. [b] Average values from ref. 11. [c] Average values from ref. 12.

All the ionic structures are extensively hydrogen bonded. The oxygen atoms of the anions accept multiple hydrogen bonds, one {O(2) in $[Hbg]_2[CO_3]$} being bonded to four different hydrogen atoms giving a distorted trigonal-bipyramidal arrangement. The shortest O · · · H(N) distance is 1.84 Å, and the average OHN angle is 168°. In the same way that the intramolecular hydrogen bond in bg is a determining factor in its planar structure, the intermolecular hydrogen bonds in the ionic structures could have an important effect on the cation geometries. In fact, the only significant effect is the change in the out-of-plane distortion in $[Hbg]^+$. The angles between the two

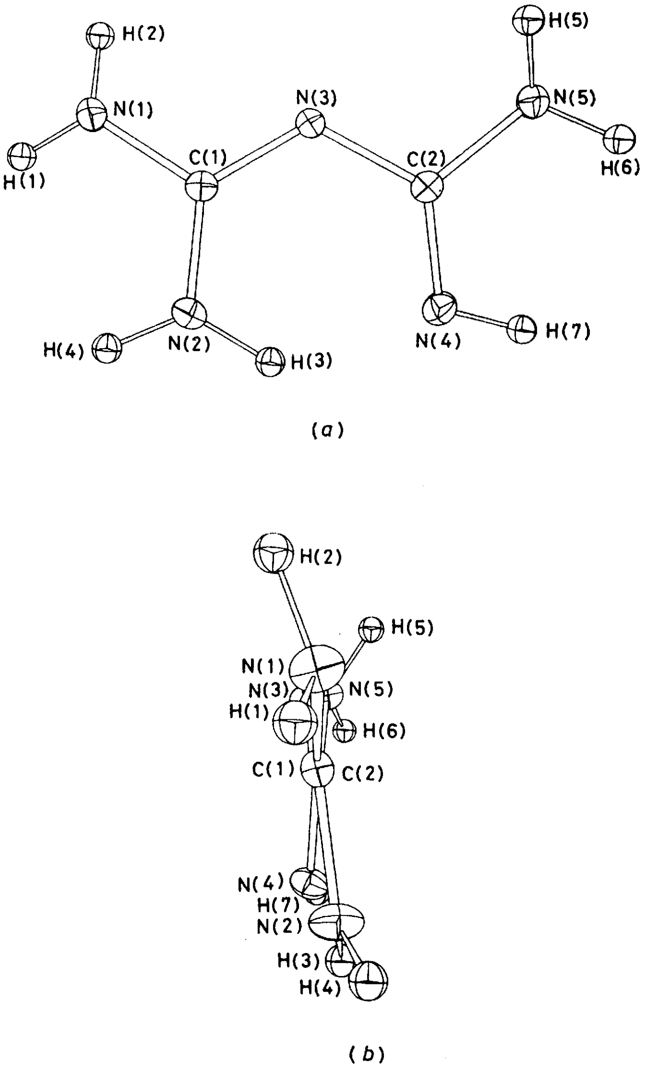


FIGURE 1 Neutral biguanide

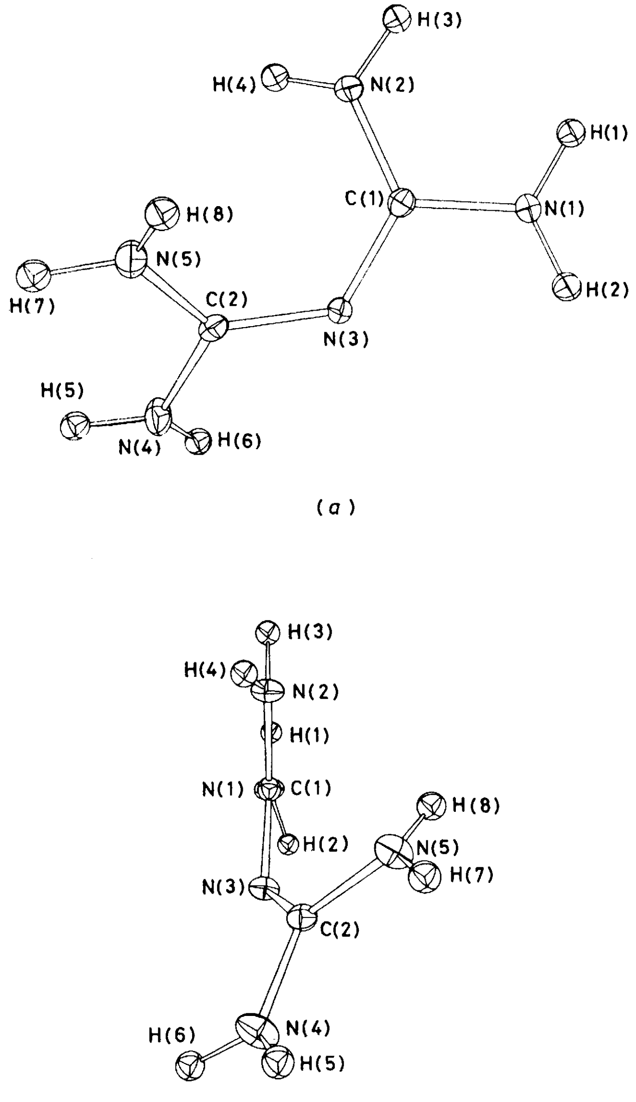
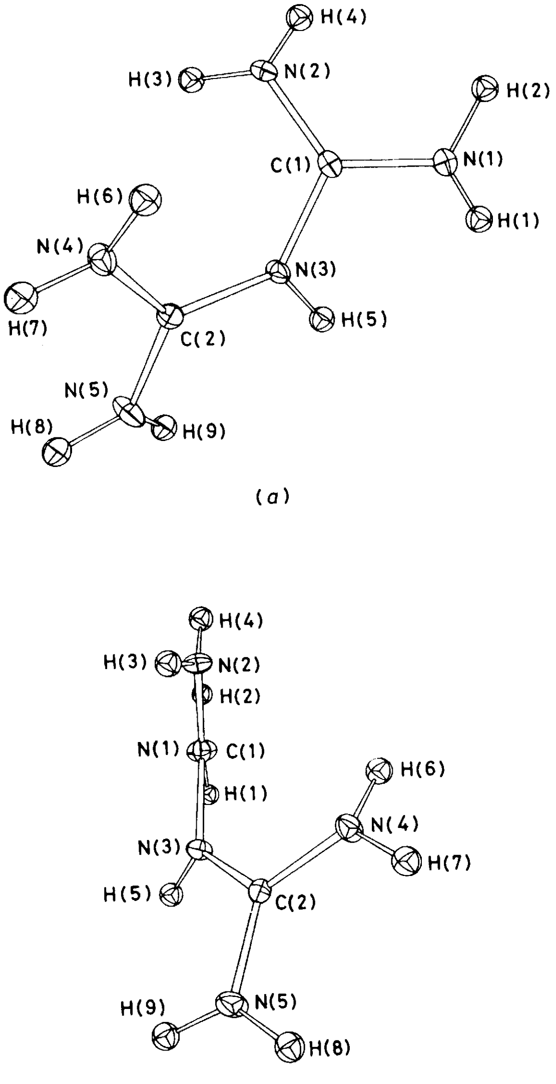


FIGURE 2 Monoprotonated biguanide

planar halves of the cation are 39.5° for the chloride,[4] 41.5 and 42.7° for the carbonate, and 44.0 and 49.1° for the sulphate. This is rather surprising since the increase in the torsion angle should weaken the π contribution to the bridge and lead to longer bond lengths. With the larger torsion angles a lengthening of one of the bridge bonds occurs, but this is barely significant. Perhaps the most important effect produced by the extensive hydrogen bonding is the reduction in the thermal movement of the anions and the hydrogen atoms. This, coupled with the extensive π bonding, gives rigid compact structures as evidenced by their high densities and low temperature factors.



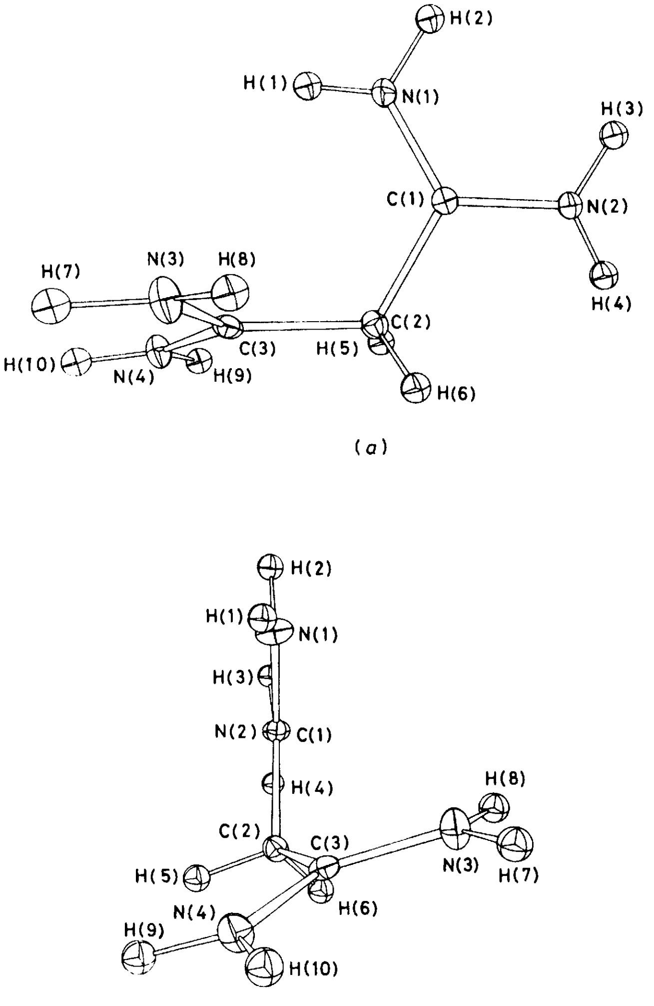
(a)

(b)

FIGURE 3 Diprotonated biguanide

It was previously suggested [1] that the high enthalpy of protonation of biguanide was linked to the formation of a delocalised π system in the cation. The multiple bonds were then thought to render the molecule more rigid and thus account for the negative value for ΔS. It is evident from the above structures that the protonation reactions do indeed form rigid π-bonded species; however, the free base also has a similar, if less symmetric, structure in the solid state. Since the structure of the solid base seems to be largely determined by the presence of an intramolecular bond, it is quite feasible that this is no longer the case in aqueous solution. Indeed, one would expect that a hydrogen bond to nitrogen would be destroyed in favour of a bond to oxygen, which would in turn destroy the planarity of the molecule. If this is the case the lability of the hydrogen atoms might well permit the formation of the originally proposed symmetric diamidine structure with two localised double bonds.

It is instructive to compare the bond lengths and angles reported here with those of transition-metal complexes containing these compounds as ligands,[11,12] since we may consider complex formation as the simple



(a)

(b)

FIGURE 4 Diprotonated malondiamidine

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[11] L. Coghi, M. Nardelli, and G. Pelizzi, *Acta Cryst.*, 1976, **B32**, 842 and refs. therein.

[12] D. Schwarzenbach and R. Schmelczer, *Acta Cryst.*, 1978, **B34**, in the press.

replacement of two protons by a metal ion. In all the cases studied complex formation removes the steric interaction that caused the deformation of the cations and allows the ligands to approach planarity. Despite this drastic change in geometry, other changes are minor. The most important effect is the non-equivalence introduced into the terminal C–N bonds due to the more basic character of the MNH nitrogen atom with respect to the NH_2 group. Apart from this non-equivalence, the bond lengths and angles in analogous species are (Table 8) almost identical. The changes produced on protonation of the bridging nitrogen atom of $[Hbg]^+$ as reported above are seen to be reproduced when the complexed ligand is protonated. The bridge angle increases (121 *vs.* 127°), the bridge bonds are lengthened (1.353 *vs.* 1.373 Å), and the internal angle at sp^2 carbon decreases (127 *vs.* 121°). The most surprising observation is that the bridge bonds in bg complexes do not appear to be any stronger than in the cations. This is so even though the planarity of the complexed ligand must improve the overlap between the *p* orbital of the bridging nitrogen atom and the *p* orbitals of the adjacent carbon atoms.

It is clear that there remain many questions to be answered concerning the bonding in both the free and complexed ligands. To this end we are determining the charge-density distribution in these systems from low-temperature *X*-ray data and from theoretical calculations.

We thank Professor G. Schwarzenbach for his gift of $[H_2maldm]Cl_2$ and for making available his thermodynamic data prior to publication, and the Swiss National Science Foundation for support.

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