Crystal Structure and Spectroscopic Analyses of Guanylurea Hydrochloride. Evidence of the Influence of Hydrogen Bonding on the π-Electron Delocalization

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The crystal structure, and a complete vibrational analysis by FTIR and Raman spectra, of guanylurea hydrochloride are presented. The crystallographic results show a pronounced π-electron delocalization on the cation and the presence of strong intra- and inter-molecular hydrogen bonding interactions between amino groups belonging to the guanidine moiety and the carbonyl oxygen of the ureic group. This arrangement gives rise to a polymer-like structure, in which the guanylurea cation chains are laterally hydrogen bonded by Cl^- anions and water molecules. The UV–VIS reflectance spectra are in agreement with the hypothesis of the existence of hydrogen bonding charge transfer complexes in the solid state. Other spectroscopic techniques, such as FTIR and Raman, have been employed to support the crystal data and to investigate the vibrational assignments for this compound.

Guanidinium ion, $[C(NH_2)_3]^+$, and its related compounds have much interested biochemists due to their presence as functional groups in the amino acid arginine and in other biologically active molecules. The importance of crystal structure determination of this kind of compound has been stressed in relation to their ability to act as anion recognition sites in many metalloenzymes.[1] As far as spectroscopic data are concerned, since these compounds exist only in aqueous solution (or in other polar solvents) or as crystals, there are no detailed IR studies on guanylurea hydrochloride.[2,3] On the other hand, because water does not interfere with Raman spectroscopy, several Raman studies are reported in the literature.[4] Spectroscopic and crystallographic studies show the 'Y-delocalization' of guanidinium ion derivatives, which is essential in the stabilisation of molecules of biological importance. From a purely physicochemical point of view, the interest comes from their characteristics, such as the resonance stabilisation of the π-system and the 'Y-aromatic' character associated with both the intra- and inter-molecular hydrogen bonds.

Our contribution reports the results of the crystal structure and of the vibrational analyses (FTIR and Raman) of guanylurea hydrochloride.

An important structural feature is the presence of the ureic groups, which, by formation of strong bifurcated hydrogen bonds, give rise to polymer-like structures in the crystal. UV–VIS reflectance and FTIR and Raman spectroscopy support these results and confirm the importance of a cooperative effect, due to charge transfer along the hydrogen-bonded chains, in the stabilisation of the overall hydrogen bonding system.

Nowadays this class of compound is also used as flame retardant additives in plastic materials[5] and as accelerator agents in thermal curing of epoxy resins.[6] Accordingly, the study presented in this paper is motivated by two independent considerations. The first consideration is the continuation of the investigation of the electronic structure and vibrational assignments of guanylurea hydrochloride with reference to the early studies. The second one is the acquisition of chemical physical properties as an aid in understanding the photothermal stability and the fire retarding capabilities when this compound is present as an additive in bulk polymers.

Experimental

Materials.—All solvents and reagents were purchased from Aldrich and used as received. Guanylurea hydrochloride was obtained by addition of hydrochloric acid (37%) to a stirred solution of 2-cyanoguanidine. After slow cooling the obtained white powder was washed with light petroleum (b.p. 40–60 °C) and dried at 70 °C under vacuum. Recrystallization was performed by dissolution with a mixture of ethanol–methanol (1:1). The elemental analysis suggests the following formula: $C_2H_7ClON_4\cdot0.5H_2O$. (Found: C, 16.50; H, 5.00; N, 39.10. Calc. for $C_2H_7ClN_4O\cdot0.5H_2O$: C, 16.50; H, 5.00; N, 39.1%.) Many attempts were made to prepare a deuteriated solid compound, but incomplete and unstable deuteriation was observed in all cases.

Crystal Data.—$[C_2H_7N_4O]^+Cl^-\cdot0.5H_2O$, $M = 147.57$. Monoclinic $a = 6.556(3)$, $b = 29.923(4)$, $c = 6.651(1)$ Å, $\beta = 96.39(3)^\circ$, $V = 1296.7(6)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections in the range $10 \leqslant \theta \leqslant 13^\circ$), space group $P2_1/n$ (alt. $P2_1/c$ No. 14), $Z = 8$, $D_c = 1.511$ g cm^{-3}. Colourless prismatic crystal of dimensions 0.26 × 0.38 × 0.50 mm. μ(Mo-Kα) = 5.12 cm^{-1}, $F(000) = 616$, $T = 295$ K.

Data Collection and Processing.—CAD4 diffractometer, $\omega/2\theta$ scan technique, graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å); 2824 unique reflections measured ($2 \leq \theta \leq 27^\circ$; $+h$, $+k$, $+l$), out of which 2250 having $I \leq 3\,\sigma(I)$ used in the refinement.

Structure Analysis and Refinement.—Solution by direct methods (MULTAN 82).[7] Full matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic. The weighting scheme $\omega = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$, with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Final R and R_w values are 0.035,0.054; max. shift/error = 0.05; largest ΔF peak 0.15 e Å^3; S (esd of an observation of unit weight) = 1.958.

All the calculations performed by the CAD4 SPD[8] and PARST[9] systems of programs; scattering factors from ref. 10.

Table 1 Positional parameters (× 10^4) with esds in parentheses

Atom	*x*	*y*	*z*
O(1A)	−744(2)	10 033.8(5)	2 358(3)
C(1A)	3 355(3)	10 328.9(7)	2 230(3)
C(2A)	697(3)	9 776.8(7)	2 721(3)
N(1A)	2 721(2)	9 908.7(6)	2 602(3)
N(2A)	5 338(3)	10 391.2(6)	2 137(3)
N(3A)	2 055(3)	10 663.2(6)	1 965(3)
N(4A)	523(3)	9 351.3(7)	3 230(3)
O(1B)	1 150(3)	7 567.5(5)	3 171(2)
C(1B)	1 120(3)	7 317.2(7)	−951(3)
C(2B)	1 092(3)	7 850.9(7)	1 837(3)
N(1B)	1 080(3)	7 737.7(5)	−197(2)
N(2B)	1 066(3)	7 279.3(7)	−2 930(2)
N(3B)	1 211(3)	6 967.3(6)	225(3)
N(4B)	1 035(4)	8 248.8(7)	2 173(3)
Cl(1)	1 501.3(9)	8 598.7(2)	7 157.1(8)
Cl(2)	5 599.0(8)	9 052.6(2)	3 293.2(8)
O(w)	5 930(3)	8 522.7(6)	9 392(3)

Table 2 Bond distances/Å and bond angles/° with esds in parentheses

C(1A)–N(1A)	1.356(3)	C(1B)–N(1B)	1.356(3)
C(1A)–N(2A)	1.322(3)	C(1B)–N(2B)	1.318(2)
C(1A)–N(3A)	1.313(3)	C(1B)–N(3B)	1.304(3)
C(2A)–O(1A)	1.221(2)	C(2B)–O(1B)	1.225(2)
C(2A)–N(1A)	1.395(2)	C(2B)–N(1B)	1.394(2)
C(2A)–N(4A)	1.326(3)	C(2B)–N(4B)	1.319(3)
N(1A)–C(1A)–N(2A)	117.6(2)	N(1B)–C(1B)–N(2B)	116.7(2)
N(1A)–C(1A)–N(3A)	121.6(2)	N(1B)–C(1B)–N(3B)	121.6(2)
N(2A)–C(1A)–N(3A)	120.9(2)	N(2B)–C(1B)–N(3B)	121.6(2)
O(1A)–C(2A)–N(1A)	122.0(2)	O(1B)–C(2B)–N(1B)	122.1(2)
O(1A)–C(2A)–N(4A)	124.7(2)	O(1B)–C(2B)–N(4B)	123.9(2)
N(1A)–C(2A)–N(4A)	113.3(2)	N(1B)–C(2B)–N(4B)	114.0(2)
C(1A)–N(1A)–C(2A)	125.8(2)	C(1B)–N(1B)–C(2B)	125.9(2)

Spectroscopic Measurements.—The Raman spectra of powders were measured in a rotating cell by using a Jobin-Yvon HG2S spectrophotometer equipped with a Spectra-Physics 165 Ar^+ laser source. The laser line used was at 514.5 nm and spectral resolution was set at 4 cm^{-1} throughout. The reflections of other laser lines were eliminated by an interference filter and fluorescence emission was subtracted by a fitting of the spectrum baseline with a polynomial function. The Raman spectra of deuterium oxide solutions (20% w/w) were recorded in Pyrex glass tube in the same conditions.

The FTIR spectra in KBr pellets were obtained on a Bruker IFS88 spectrometer with a resolution of 2 cm^{-1} and at least 300 scans, while the solutions (20% w/w) were analysed by a Specac overhead ATR on a ZnSe crystal (transmittance 4000–670 cm^{-1}) at 45° (6 reflections) using water and the deuterium oxide as references, a resolution of 6 cm^{-1} and at least 1000 scans. The reported spectra were corrected for the different penetration of radiation with the incident wavelength[11] applying a software routine of Bruker ATS.

The aqueous solution transmission UV–VIS spectra and the powder reflectance spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer set with a resolution of 2 nm and equipped with integrating sphere.

Results and Discussions

Crystallographic Data.—Final atomic positional parameters are reported in Table 1. Bonds distances and angles are given in Table 2. Tables of hydrogen atom co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.* The asymmetric unit consists of two independent guanylurea cations, two anions and a water molecule; the crystal is composed of guanylurea cations, Cl^- anions and water molecules, in the ratio 2:2:1, linked by a three dimensional network of hydrogen bonds.

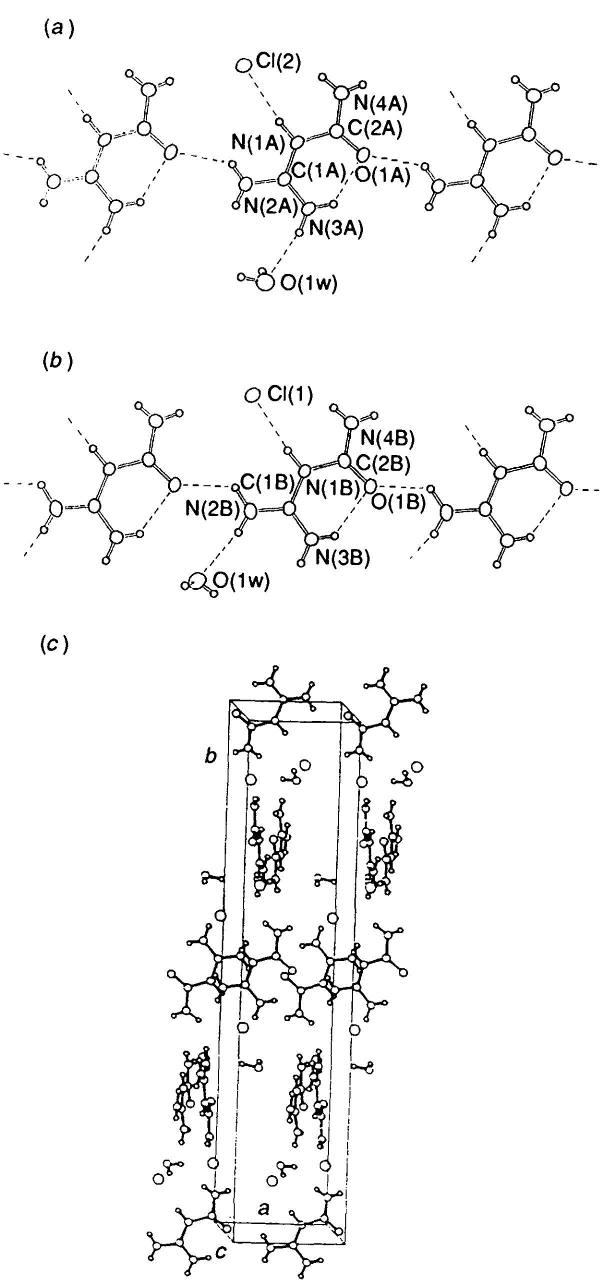

Fig. 1 Crystal views of the two independent chains formed by the A and B cations, (*a*) and (*b*) respectively. The two projections show the cations linked head-to-tail by means of hydrogen bonds and laterally hydrogen bonded by Cl^- anions and water molecule. (*c*) Unit cell and its contents.

Figs. 1(*a*) and 1(*b*) show the two independent chains formed by the cations A and B, respectively, linked head-to-tail by hydrogen bonds and laterally hydrogen-bonded by Cl^- anions and water molecules. Fig. 1(*c*) shows the unit cell and its contents. From a geometrical point of view, the two cations are statistically indistinguishable, differing only in the intermolecular contacts. Both cations are essentially planar, all the nitrogen and carbon atoms are sp^2 hybridized and the conformation around N(1)–C(2) bond is *Z* (or *trans*). These features play an

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* For details of the deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

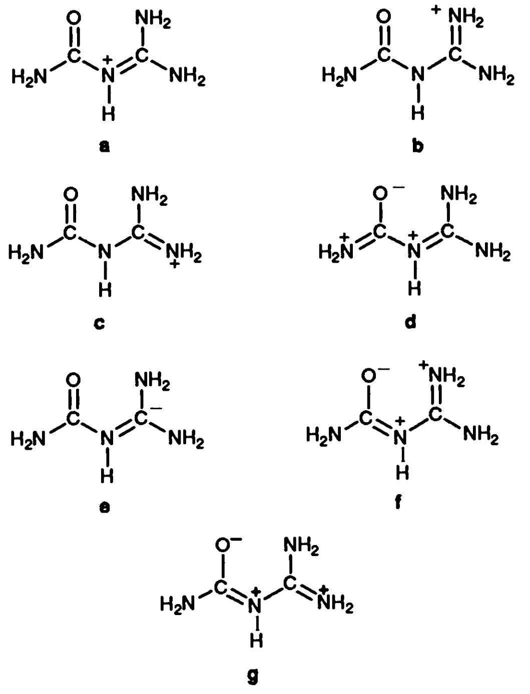

Fig. 2 Possible canonical forms of guanylurea cation contributing to the overall resonance

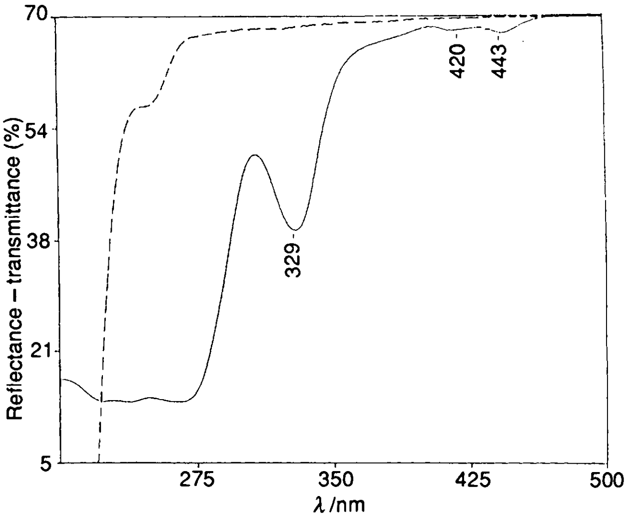

Fig. 3 UV–VIS reflectance and transmittance spectra of guanylurea hydrochloride for: crystalline powder in reflectance (%), ——, and aqueous solution in transmittance (%), - - - -

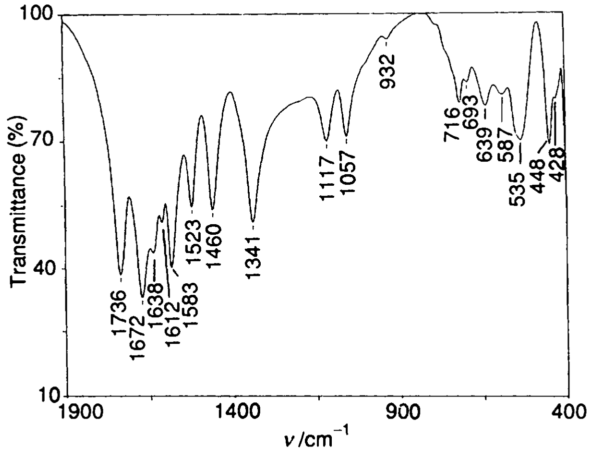

Fig. 4 FTIR spectrum of the crystalline solid of guanylurea hydrochloride in a KBr pellet

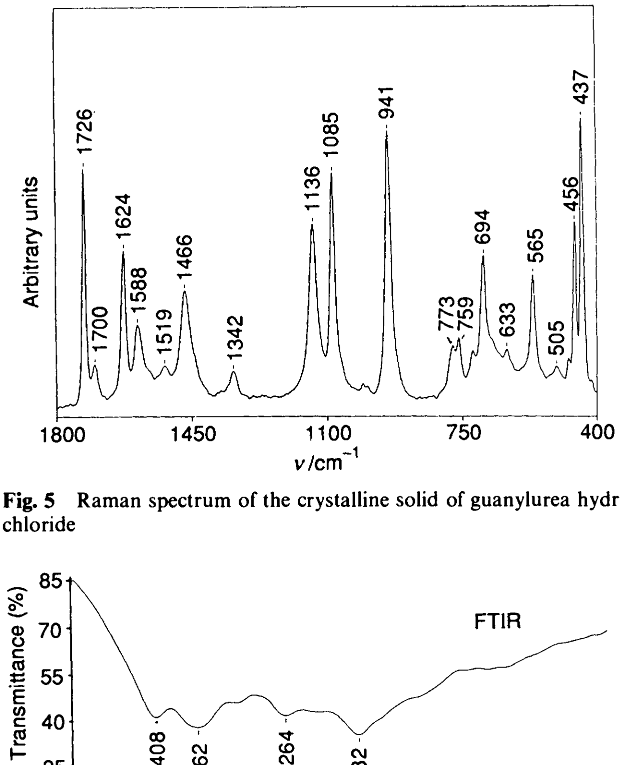

Fig. 5 Raman spectrum of the crystalline solid of guanylurea hydrochloride

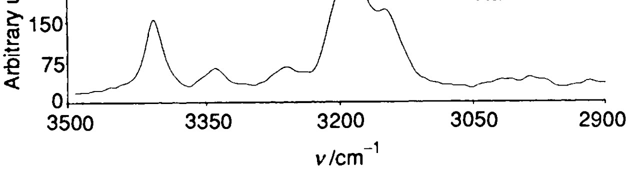

Fig. 6 FTIR and Raman spectra of solid guanylurea in the N–H stretching region

important role in the stabilization of the whole cation by means of π-electron delocalization associated with a strong intramolecular $N(3)-H\cdots O(1)$ hydrogen bond. At the same time, the resulting positive partial charges on hydrogens favour the involvement of NH and NH_2 groups in intermolecular hydrogen bond interactions.

Among the possible canonical forms contributing to the fundamental state of the structure of the cations the most important seem to be the **a**–**d** forms, while the contribution of the **e**–**g** forms is not determinant (Fig. 2). These conclusions arise from bond distance analysis and from their comparison with those found in other strictly similar molecules or cations. Amide conjugation along the ureic fragment $O(1)=C(2)-N(1)H$ is poor, $C(2)-O(1)$ bonds [1.221(2) and 1.225(5) Å] being not far from a pure double bond distance of 1.200 Å and the little C=O elongation has to be chiefly imputed to the delocalization through the other ureic fragment $O(1)=C(2)-N(4)H_2$. This hypothesis is supported by the $C(2)-N(1)$ bond distances [1.395(2) and 1.394(2) Å] which are not statistically different from the non-conjugated amidic C–N bonds of 1.400(3) and 1.388(3) Å, found in the bis(2,2-dimethylpropionyl)amine crystal structure[12] and of 1.402 Å in the (*E*, *Z*) diacetamide structure obtained by gas-phase electron diffraction data.[13] On the other hand, the values of $N(1)-C(1)$ bond distances, [1.356(3) Å in both cations] are consistent with the presence of

Table 3 Hydrogen bond parameters. Distances/Å and angles/°.

D–H ··· A	Symmetry operator[a]	D–H	D ··· A	H ··· A	D–H ··· A
N(1A)–H(1A) ··· Cl(2)	I	0.94(2)	3.184(2)	2.26(2)	171(2)
N(2A)–H(22A) ··· O(1A)	III	0.83(3)	2.771(3)	2.13(3)	133(2)
N(3A)–H(32A) ··· O(1A)	I	0.86(3)	2.663(2)	2.02(3)	130(2)
N(3A)–H(31A) ··· O(1W)	IV	0.87(2)	2.960(3)	2.13(2)	158(2)
N(1B)–H(1B) ··· Cl(1)	VI	0.89(2)	3.149(2)	2.27(2)	172(2)
N(2B)–H(22B) ··· O(1B)	VI	0.97(3)	2.739(2)	2.06(3)	125(2)
N(2B)–H(21B) ··· O(1W)	VII	0.82(2)	2.984(3)	2.17(2)	168(2)
N(3B)–H(32B) ··· O(1B)	I	0.79(3)	2.662(2)	2.05(2)	133(2)
O(1w)–H(1w) ··· Cl(1)	I	0.92(2)	3.119(2)	2.20(2)	175(2)
O(1w)–H(2w) ··· Cl(2)	II	0.72(3)	3.069(2)	2.35(3)	172(3)
Short contacts or weak hydrogen bonds[b]					
N(4A)–H(42A) ··· Cl(1)	I	0.85(3)	3.454(2)	2.95(3)	119(2)
N(4A)–H(42A) ··· Cl(2)	I	0.85(3)	3.442(3)	2.70(3)	146(2)
N(4A)–H(41A) ··· Cl(2)	V	0.78(2)	3.354(3)	2.59(2)	167(2)
N(3B)–H(31B) ··· Cl(2)	VIII	0.87(2)	3.318(2)	2.45(2)	177(2)
N(3B)–H(32B) ··· O(1w)	VIII	0.79(3)	3.159(3)	2.58(3)	132(2)
N(4B)–H(41B) ··· O(1)	I	0.85(3)	3.426(2)	2.59(3)	170(2)

[a] I: x, y, z; II: $x, y, z + 1$; III: $x + 1, y, z$; IV: $-x + 1, -y + 2, -z + 1$; V: $x - 1, y, z$; VI: $x, y, z - 1$; VII: $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{3}{2}$; VIII: $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$. [b] Short contacts characterized by D ··· A distances slightly greater and H ··· A distances slightly shorter than the sums of Van der Waals radii taken from ref. 21 (1.75, 1.52, 1.55 and 1.20 Å for Cl, O, N and H, respectively).

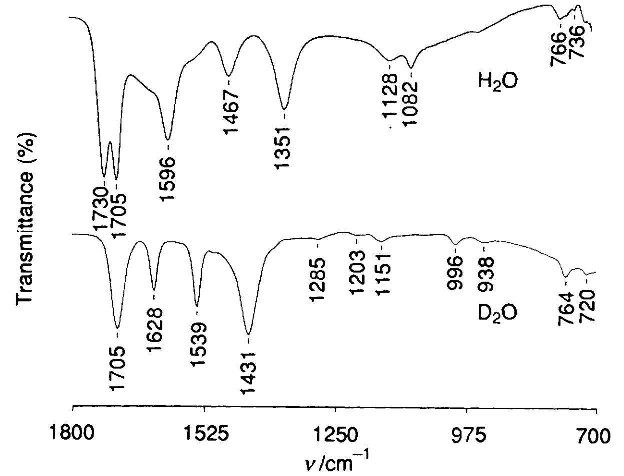

Fig. 7 FTIR–ATR spectra in a solution (20% w/w) of guanylurea hydrochloride: in D_2O (lower) and H_2O (upper)

some π-conjugation and are comparable to that found in the similar structure of bis(N^1-2,2-dimethylpropionyl)-2,2-dimethylpropionamidine,[12] where the C–N distance is 1.361(4) Å. These data show the importance of the canonical form **a** in describing the delocalization on the cations.

The fragments C–NH_2 present the shortest C–N bond distances found in this compound. In order to determine the contribution of canonical forms **b–d**, it is useful to compare the present bond situation with that found in the crystal structures of related cations, where bond orders are easy to calculate, for symmetry reasons. For instance, in the structures of guanidinium cation[1] and its amidic derivatives[14,15] C–NH_2 bond distances (1.324 Å on average) correspond to a π-bond order of 1/3, while in the *N,N*-dimethylbisguanidinium cation[16] the bond distances (1.333 Å on average) correspond to a π-bond order of 1/4. (The π-bond order values have been calculated from the consideration that in symmetric molecules the canonical forms used to describe the ground state are equivalent). The C–NH_2 bond lengths in both guanylurea cations (1.317 Å on average) are, therefore, indicative of a fundamental contribution of the three canonical forms **b–d** to the overall delocalization. The π-electron delocalizations have been found to be related to intra- and inter-molecular hydrogen bond formation in the crystals, as shown by comparing bond distances obtained by theoretical *ab initio* calculations on small isolated molecules (*i.e.*, formamide, acetamide, *N*-formyl formohydrazide, glyoxime *etc.*) with those determined by accurate structural data from neutron or X-ray diffraction on the same molecules upon formation of hydrogen bonds.[17–20]

The structure reported here is characterized by an excess of hydrogen-bond donors with respect to hydrogen-bond acceptors (Table 3). In order to maximize the hydrogen bond energy contribution to the crystal lattice energy and to involve all the possible hydrogen-bond donors in the intermolecular interactions, the packing is characterized by a large number of competitive hydrogen bonds, some of them being bifurcated and others weak.[22] An additional gain in energy comes from the co-operative effect due to the ribbons formed by the cations linked head-to-tail by hydrogen bonds. The A cations adopt the packing arrangement shown in Fig. 1(*a*). They are situated approximately on the *xy* plane and run along the *a* axis, while the B cations [Fig. 1(*b*)] are situated on the *yz* plane running along the *c* axis. The hydrogen bond co-operative effect, established from theoretical studies on water polymers,[23] seems to be associated with charge transfer, whose presence is observed in the UV–VIS reflectance spectrum of the crystals as reported in Fig. 3. The spectra show the presence of absorption bands at 329, 420 and 443 nm for the crystalline powders which disappeared in aqueous solution (20% w/w). This shows the formation, in crystals, of strong interactions involving the ureic and amino guanidine moieties in charge-transfer complexes, where electronic effects can be propagated along polymer-like structures as in a mixture of polyconjugated compounds with different lengths.[24]

Vibrational Analysis.—Guanylurea cations are approximately planar in the crystal, but they do not lie on crystallographic symmetry planes. It seems reasonable to assume, as far as spectroscopic analyses are concerned, that they have no symmetry in the solid state. On the other hand, we suggest that this compound in solution could have a plane of symmetry containing the molecule and thus belong to the point group C_s. On this basis, all fundamental modes of vibration for guanylurea hydrochloride should be active, as reported in Table 4 and as shown in the FTIR and Raman spectra (Figs. 4–7).

Table 4 Vibrational assignments of guanylurea hydrochloride

2-Cyanoguanidine		Guanylurea hydrochloride					
IR[a] solid	Raman solid	IR[a] solid	Raman solid	IR[b] aq. soln.	Raman[c] D_2O soln.	IR[d] D_2O soln.	Assignments
3430vs	3340vw	3408vs	3407w				$\nu_a(NH_2)$
3382vs	3330wb	3362vs	3354sh				
3334vs		3320vs	3308vw				
3240vs		3264vs	3260w				$\nu_s(NH_2)$
3185vs		3230vs	3240sh				
3149vs	3138wb	3182vs	3186w				
		3152sh	3148w				
2209vs	2206m						$\nu(C\equiv N)$
2164vs	2158vs						
1665vs		1736s	1726s	1730vs	1279w	1285w	$\delta(NH_2)$guanidine
1642vs	1642w						
		1672vs	1700mw	1705vs	1703m	1705vs	$\nu(CO)$Amide
1576vs		1638m	1624ms	1620sh	1625w	1628m	$\nu(C=N)$
		1612m					
		1583s	1588m	1596ms	1148w	1151w	$\delta(NH_2)$Amide
1505s	1530w	1523m	1519w	1550sh	1532m	1539ms	$\nu_a(NCN)$
		1460m	1466mb	1467m	1417m	1431vs	$\nu(CN)$Amide
			1440sh				
			1382vw				941 + 437
		1341mb	1342mw	1351m	1005mw	996w	$\delta(NH)$
	1102m	1117mw	1136s	1128wb	860sh		$\rho(NH_2)$
1090m		1057mw	1085vs	1082w	811w		
			1002vw				565 + 437
930ms	936s	932vw	941vs	941vw	942vs	938w	$\nu_s(NCN)$
					925s		
727m			773m	766vw	768w	764w	$\omega(NCN)$
		756sh	759m	736vw	752w		
		728sh					
		716mw	716w	719sh	719w	720vw	
669m	669m		694ms	694m	683sh	690sh	$\delta(NCN)$
		693w	674sh		651ms		
		639mb	633w				
555mb		587mw	565m				$\omega(NH_2)$
525m	525s				424s		
517m		535mb	505w				
500mw	500m	448m	456s		492s		$\rho(NCN)$
465mb	465vw	428mw	437vs		455s		

Legend of intensities: s = strong; m = medium; w = weak; v = very and b = broad. [a] Solid in KBr pellets. [b] Determination with the overhead ATR using H_2O as reference. [c] A 20% guanylurea hydrochloride solution in D_2O. [d] Determination with the overhead ATR using D_2O as reference.

All assignments are based on the spectra of reference compounds[2–4] and on Raman and FTIR–ATR spectra recorded in aqueous and deuterium oxide solution, because we have not obtained a stable and wholly deuteriated solid compound.

The FTIR strong vibration bands centred at 3362 and 3182 cm^{-1} and the corresponding Raman bands have been attributed to the stretching vibrations of the $-NH_2$ groups (Fig. 6). The higher frequency has been assigned to asymmetric stretching, $\nu_a(NH_2)$, and the lower frequency to the symmetric one, $\nu_s(NH_2)$. The very broad nature of these bands demonstrates the strong hydrogen-bond interactions involving the amino groups. In this spectral region the comparison with the FTIR spectrum of 2-cyanoguanidine (Table 4) shows the disappearance of the stretching band of the cyano group at 2209 cm^{-1}, indicating the formation of the ureic group.

The $-NH_2$ bending modes have been found at 1736 and 1726 cm^{-1} and at 1583 and 1588 cm^{-1} in the FTIR and Raman spectra, respectively. In agreement with the observed shifts in the FTIR spectra of the corresponding deuteriated compound occurring at 1285 and 1151 cm^{-1} with a ratio $\nu(NH/ND) =$ *ca.* 1.36, the higher frequency has been assigned to the amino groups belonging to the guanidinium ion fragment, $\delta(NH_2)$-guanidine, and the lower frequency to the primary amide, $\delta(NH_2)$amide belonging to the ureic group. There are three arguments in favour of these assignments. The first involves bond order and delocalization enhancement between the two amino groups and the central nitrogen atom in the guanidine ion, in accordance with the crystal structure, where the presence of a pronounced π-electron delocalization, and of a higher bond order have been suggested. Consequently, it could explain the unexpectedly high intensity of the band at 1736 cm^{-1} in the Raman spectrum (Fig. 5) and the involvement of the whole guanidine fragment in the bending motion. Therefore, the simplified model of independent vibrating units cannot be rigidly applied, rather all atoms in the guanidine fragment must be considered to be in motion. The second argument is related to the presence of two bands at 1730 and 1705 cm^{-1} in aqueous solution as reported in Fig. 7. Their existence in aqueous solution excludes their attribution to hydrogen-bonded and non-hydrogen-bonded carbonyl groups with the surrounding amino groups to form polymer-like compounds in the solid, confirming that the charge-transfer complexes are completely dissociated in aqueous solution as shown in the UV–VIS spectra reported in Fig. 3. The third consideration is related to the disappearance with deuteriation of this band in the FTIR–ATR spectrum as reported in Fig. 7, where the band at 1730 cm^{-1} is undoubtedly shifted to 1285 cm^{-1} in the FTIR–ATR spectrum, while the band at 1705 cm^{-1} remains unshifted. Accordingly the bands at 1672 and 1583 cm^{-1} in the FTIR spectrum and those at 1700 and 1583 cm^{-1} in the Raman spectrum, have been associated with the stretching vibrations of the carbonyl, ν(CO), and with the bending vibrations of the primary amide belonging to the ureic group, $\delta(NH_2)$amide, respectively.

Two amino groups also show two distinguishable bands for the rocking vibrations. In fact, the bands found at 1117 and 1057 cm^{-1} in the FTIR spectrum and at higher intensities at 1136 and 1085 cm^{-1} in the Raman spectrum have been attributed to amino groups of the guanidine moiety and the primary amide, respectively. The attribution to two different amino groups can be confirmed from the FTIR–ATR spectrum of the aqueous solution, where these bands undergo no changes with deuteriation; on the other hand, they move to 860 and 811 cm^{-1} in the Raman spectrum. Besides, in the FTIR and Raman spectra of the solid the band at 1341 cm^{-1}, which is shifted to 996 and to 1005 cm^{-1}, respectively, in deuterium oxide solution has been assigned to the bending vibration, δ(NH), as indicated in the very similar spectrum of guanidine.[3] The band at 1467 cm^{-1} in FTIR, showing a weak intensity in the Raman spectrum and no changes with deuteriation, has been assigned to stretching ν(CN) of the amide group, a characteristic band for primary amides[25] in this spectral region.

The FTIR bands located at 1638, 1612, 1523 and 932 cm^{-1} have been attributed to the characteristic vibrations of guanidine skeletal modes, because they remain unchanged with deuteriation and for the assignments of the reference compounds as extensively reported in the literature.[2–4] However, the doublet occurring at 1638 and 1612 cm^{-1} is usually reduced to a single component at 1628 cm^{-1} in aqueous solution and in a poorly crystalline solid. We have considered that the two bands occurring at 1628 and 1523 cm^{-1} are the analogues of ν(C=N) and ν_a(NCN) of the guanidine ion and the weak band at 932 cm^{-1}, showing a very strong expected peak at 941 cm^{-1} in the corresponding Raman spectrum, has been attributed to ν_s(NCN). By comparison with 2-cyanoguanidine, these results suggest an increase of π-bond order in the guanidine moiety, which is responsible for the higher frequency of C=N stretching. The doublet at 1638 and 1612 cm^{-1} observed in the crystalline solid can be reasonably attributed to the two independent cations (A and B) seen in the crystal structure [Figs. 1(*a*) and (*b*)].

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