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Single-Crystal Neutron Diffraction Study on Guanidine, CN_3H_5

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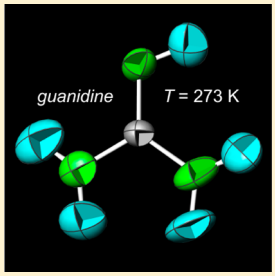
Supporting Information

ABSTRACT: Pure guanidine crystallizes in the orthorhombic space group *Pbca* (no. 61) and a = 8.5022(2) Å, b = 9.0863(2) Å, c = 15.6786(4) Å at 100 K, Z = 16, with two Y-shaped molecules in the asymmetric unit. The compound features a three-dimensional network of classical N−H···N hydrogen bonds. Here, we present the results of a single-crystal neutron diffraction study, performed at two different temperatures (100 and 273 K). The data quality obtained at the HEiDi instrument (FRM II, Munich) allowed to derive accurate positional and anisotropic displacement parameters (ADP) for all the atoms, including H. The experimental hydrogen positions confirm a model derived from theory. On the basis of the displacement parameters, a TLS analysis of thermal motion proves that the guanidine molecules behave in good approximation as rigid bodies and essentially undergo libration. The unusual temperature behavior of one C−N bond found in a preceding single-crystal X-ray study is an artifact going back to this rigid-body movement. The existence of various hydrogen bonds also manifests from a well-resolved IR spectrum, which was analyzed in terms of individual vibrations on the basis of quasi-harmonic ab initio phonon calculations.



INTRODUCTION

Molecular guanidine, just as the anionic and cationic salts (i.e., $NaCN_3H_4$ and CN_3H_6Cl) of the fundamental biomolecule, is a perfect model substance to study hydrogen-bonded networks and the influence of charges and counterions on these networks. While cationic salts of guanidine have been known for many decades and are commercially available, the anionic compounds were synthesized just recently and offer fascinating new structures.[1,2]

The mother compound, guanidine, was first synthesized by Strecker in 1861.[3] While the crystal structure of pure guanidine remained unknown for a long time, several groups have tried to clarify it either using theoretical methods[4] or by co-crystallization experiments.[5] Eventually, the crystal structure of guanidine was determined in 2009 using single-crystal X-ray diffraction (XRD).[6]

Molecular guanidine crystallizes in the orthorhombic space group *Pbca* (no. 61) with two molecules in the asymmetric unit. At 100 K, the lattice parameters arrive at a = 8.5022(2) Å, b = 9.0863(2) Å, and c = 15.6786(4) Å. The rather intricate hydrogen-bonded network was already analyzed by Yamada et al., and a numbering scheme to distinguish a total of eight specific hydrogen bonds was introduced.[6] In particular, the strengths of these hydrogen bonds were estimated from geometrical criteria, namely, from the nitrogen−nitrogen distances (between 2.98 and 3.32 Å at T = 100 K).

In 2012, the hydrogen-bonded network of guanidine was studied in more detail using theoretical PAW−PBE−DFT methods.[7] The C and N atomic positions as well as the cell parameters determined in the previous work by Yamada et al. were kept fixed but all the H positions were quantum-mechanically optimized; such computational H optimization was recently validated against reliable neutron diffraction data.[8] For the guanidine crystal structure, the strengths of the hydrogen bonds were evaluated using two different strategies, namely, from the behavior of isolated molecular dimers and from the theoretical elongation of the entire crystal along the crystallographic directions. For example, the weakest hydrogen bond was calculated as 6.8 kJ mol^{-1} and the strongest as 33.8 kJ mol^{-1}.[7] The weaker bonds feature an amino-nitrogen both as a donor and as an acceptor, but the stronger bonds are composed of an amino-nitrogen as a donor and an imino-nitrogen as an acceptor. Only one hydrogen bond assigned from geometrical criteria turned out as being repulsive in nature, a combination of an imino-nitrogen (donor) and an amino-nitrogen (acceptor).

Because of the limitations of X-ray crystallography, the first structural characterization of guanidine only featured four atoms (C and 3 × N) for which anisotropic displacement parameters (ADPs) could be reliably refined. This small number of experimentally observed ADPs was insufficient to allow for a TLS correction (translational, librational, and screw modes of motion of the whole molecule),[9] very unfortunately. Nonetheless, the thermal behavior of some bond lengths as observed from X-ray diffraction indicated that the guanidine molecules might move as rigid entities.[6] Hence, applying a TLS correction is recommended since it will result in more accurate bond lengths. Here, we present the anisotropic displacement

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parameters of all atoms, based on single-crystal neutron diffraction, and the associated TLS correction. This is intended to validate the calculated values for the spatial parameters and to present a new model for further theoretical studies. Another goal is to find out if there is a correlation between the ADP of a particular hydrogen atom and the strength of a hydrogen bond of which this atom is a part.

EXPERIMENTAL SECTION

Pure guanidine was synthesized as described before.[6] The mother liquor for crystallization was stored in a Schlenk tube for approximately half a year. Afterward, a block-shaped crystal was obtained, with dimensions ($6 \times 6 \times 2$ mm^3) suitable for single-crystal neutron diffraction. A tiny fraction of that sample was checked using powder X-ray diffraction to confirm that this crystal consisted of the desired compound.

The crystal was placed into a sealed aluminum container to prevent any contact with humidity. Then the container was mounted in the closed-cycle cryostat of the single-crystal neutron diffractometer HEiDi where the data were collected at a neutron wavelength of 0.7937 Å. Rocking scans on different reflections confirmed the good quality of the crystal showing Gaussian-like profiles and no evidence for more than one grain. During the two hours of cooling to 100 K, the intensities of four chosen reflections were continuously monitored but did not show any discontinuity. The Bragg data collection at 100 K was done in several steps. Initially, between 7 and 30° in 2θ, a full half shell ($\pm h$, $+k$, $\pm l$) was measured. This set included also reflections systematically extinct in *Pbca* and proved, by their absence, that all reflections follow the reflection conditions for this space group. Then, between 30 and 70° in 2θ, a quarter shell ($+h$, $+k$, $\pm l$) was recorded. To optimize data quality and further stabilize the data refinement, a symmetry-equivalent set of the strongest 500 reflections ($I > 2\sigma$) in this 2θ range with ($-h$, $+k$, $+l$) was measured. In total 2709 reflections were collected. The excellent quality of the data allowed the determination of the anisotropic displacement parameters (ADPs) of all the atoms, including the hydrogen atoms. A second Bragg data set was obtained at 273 K. In order to measure the data more quickly, only those reflections with significant intensities ($I > 3\sigma$) of the measurement at 100 K were collected, in total 1949 reflections. This data set also allowed the refinement of the ADPs of the hydrogen atoms.

Because of the weak interaction of neutrons with the elements in guanidine, absorption phenomena are not relevant for the obtained neutron diffraction data ($\mu < 0.0005$ mm^{-1}). Despite the significantly larger background caused by the incoherent scattering of the hydrogen atoms, the single reflections are well resolved with a good signal-to-noise ratio. The starting values of the atomic positions were taken from the X-ray single-crystal structure refinement.[6] The full-matrix least-squares crystal-structure refinement on F^2 was done using the SHELXL-97 and SHELXTL (including the XP routines) program packages and by applying an extinction correction, which lowered the residual values but did not change the bond lengths.[10] The TLS correction was accomplished utilizing the algorithms implemented in the XP computer code. Geometrical calculations were performed using the PLATON program.[11] CCDC-921526 and CCDC-921527 contain the supplementary crystallographic data for the neutron diffraction at 100 and 273 K. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

The results of both single-crystal neutron diffraction experiments and the corresponding refinements are listed in Table 1. The refinements were conducted without any noticeable problems, and they impressively support the preceding XRD single-crystal study. For illustration, ORTEP drawings of the two symmetry-independent guanidine molecules measured at

Table 1. Single-Crystal Neutron Diffraction Data and Structure Refinement Details of CN_3H_5

temperature (K)	100	273
formula	CN_3H_5	
formula mass (amu)	59.07	
space group	*Pbca* (no. 61)	
a (Å)	8.5022(2)	8.5568(2)
b (Å)	9.0863(2)	9.1952(2)
c (Å)	15.6786(4)	15.7495(4)
V (Å^3)	1211.23(5)	1239.19(5)
Z	16	
ρ_{calcd} (g cm^{-3})	1.296	1.267
crystal dimensions (mm)	$6 \times 6 \times 2$	
radiation	neutrons; $\lambda = 0.7937$ Å	
2θ limits (deg)	7.88−70.08	7.82−69.72
data collected	$-12 \le h \le 12$	$-11 \le h \le 12$
	$-12 \le k \le 13$	$-12 \le k \le 12$
	$-8 \le l \le 22$	$-8 \le l \le 22$
no. of reflections collected/unique reflections	2709/1910	1949/1249
internal R indices: R_{int}(obs)/R_{int}(all)	0.0302/0.0310	0.0359/0.0379
no. of variables/restraints	164/0	164/0
final R indices: R_1/wR_2 (all data)	0.0414/0.1033	0.0514/0.1008
goodness of fit	1.208	1.088
residuals (fm Å^{-3})	−1.18/1.13	−0.90/0.91

100 K are presented in Figure 1. The guanidine molecule is composed of a central carbon and three nitrogen atoms, forming a Y-shaped carbon−nitrogen backbone, which is planar within a single standard deviation. The molecule consists of two different functional groups, one imino and two amino functions. Even without prior knowledge about the hydrogen positions, amino and imino functions may readily be distinguished by comparing their bond lengths. The shortest C−N distance (typically around 1.29−1.31 Å) is assigned to the imino function (bond order = 2) and the longer C−N distances (ca. 1.35−1.36 Å) are assigned to the amino functions (bond order = 1). This bond-length differentiation is also valid and quite useful in the case of the guanidinate anions.[1,2] Figure 1 reveals that N1 and N4 are the imino and N2, N3, N5, and N6 are the amino functions. The N−H distances vary between 1.00 and 1.03 Å (see also discussion below).

It is worth mentioning that some N−C−N angles differ from the ideal 120° value. In fact, these angles depend on the hydrogen positions. Because the atoms H1 and H4 are located in the carbon−nitrogen plane, the corresponding N1−C1−N2 and N4−C2−N5 angles are widened by about 5°. However, the hydrogen atoms of the amino functions are arranged in an *anti* configuration such that they are situated above and below the carbon−nitrogen plane, and this lets the N2−C1−N3 and N5−C1−N6 angles arrive at 114.6° and 115.1°, respectively. Only the N1−C1−N3 and N4−C2−N6 angles are close to 120°. The four amino groups are slightly pyramidal with all C−N−H angles larger than the ideal tetrahedral one; the C−N−H angles range around 115−116°, except for the amino function at N2 where they adopt values close to 120° (119.8° and 118.0°). The N2-centered amino function is therefore almost planar, most likely due to hydrogen-bonding. In general, all the thermal ellipsoids look perfectly reasonable, indicating the excellent crystal quality and the absence of serious absorption or twinning problems.

Figure 2 shows an ORTEP representation of the anisotropic displacement parameters at 273 K. As expected, these ADPs are

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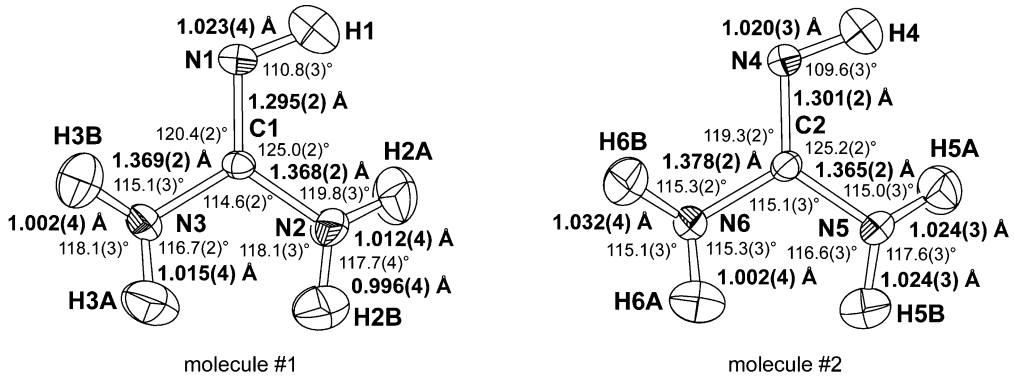

Figure 1. ORTEP drawings of the two symmetry-independent molecules of guanidine at 100 K. The ellipsoids are drawn at the 50% probability level.

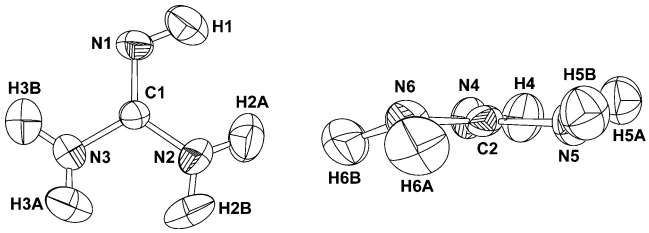

Figure 2. Perspective ORTEP drawing of the guanidine molecule #1 at 273 K (left), with the ellipsoids drawn at a 50% probability level, and perspective view parallel to the carbon−nitrogen plane of the guanidine molecule #2, also at 273 K (right).

consistently larger since the measuring temperature is only 50 K below guanidine's melting point. The very large anisotropic displacement parameters of the hydrogen atoms suggest that the conformation of the pyramidal amide functionalities may be subject to inversion in the case of sufficiently small activation barriers. Nonetheless, the amino groups are still pyramidal, even at 273 K, and they are still in an *anti* configuration. We recall that a theoretical study on guanidine revealed the planar form being 23.8 kJ mol^{-1} higher in energy than the nonplanar structure; also, the *anti* conformation is slightly favored by approximately 9 kJ mol^{-1}.[4c] This finding is clearly corroborated by the experimental data. As seen from Figures 1 and 2, guanidine does not adopt the unfavorable *syn* configuration.

In order to compare the bond lengths derived by the two diffraction methods, all corresponding values are given in Table 2. The carbon−nitrogen bond lengths at both temperatures differ by not more than 0.8%, underlining the ability of both X-ray and neutron diffraction to correctly localize such heavy atoms. The well-known difficulties of localizing H atoms by means of X-ray diffraction are also visible from the table. The XRD H−N bond lengths are notoriously too short (0.86−0.92 Å), whereas by using neutron diffraction the resulting hydrogen−nitrogen bond lengths arrive at much more reasonable values around 1.00−1.03 Å. This corresponds perfectly to the well-known fact that X-ray radiation interacts with *electron* densities, while neutron radiation interacts with *nuclear* densities. The results of the TLS correction are also included in the table.[9] As expected, this very correction leads to (very slightly) elongated bond lengths. At 100 K, all bonds are elongated by 0.01 Å on average. At 273 K, the C1−N1 and C1−N2 bonds widen by 0.02 and 0.03 Å, all other C−N bonds

Table 2. Comparison of the Bond Lengths (Å) of the Two Symmetry-Inequivalent Guanidine Molecules Derived by Different Methods at Temperatures of 100 and 270/273 K (SC-XRD, Single-Crystal X-ray Diffraction; SC-ND, Single-Crystal Neutron Diffraction; TLS, Rigid-Body-Motion Correction[9])

bond	100 K, SC-XRD	100 K, SC-ND	100 K, SC-ND + TLS	270 K, SC-XRD	273 K, SC-ND	273 K, SC-ND + TLS
Molecule #1						
C1−N1	1.3002(9)	1.295(2)	1.305	1.2872(15)	1.297(4)	1.317
C1−N2	1.3663(10)	1.368(2)	1.380	1.3456(17)	1.340(4)	1.365
C1−N3	1.3618(9)	1.369(2)	1.377	1.3519(15)	1.356(4)	1.369
N1−H1	0.914(11)	1.023(4)	1.029	0.890(15)	1.012(8)	1.023
N2−H2A	0.913(13)	1.012(4)	1.018	0.838(15)	1.013(8)	1.025
N2−H2B	0.882(14)	0.996(4)	1.003	0.825(17)	0.994(8)	1.008
N3−H3A	0.858(12)	1.015(4)	1.024	0.869(16)	1.004(8)	1.020
N3−H3B	0.862(12)	1.002(4)	1.011	0.867(16)	0.992(9)	1.010
Molecule #2						
C2−N4	1.3024(9)	1.301(2)	1.309	1.2917(14)	1.298(3)	1.309
C2−N5	1.3635(9)	1.365(2)	1.371	1.3559(14)	1.356(3)	1.364
C2−N6	1.3757(9)	1.378(2)	1.386	1.3709(15)	1.370(4)	1.381
N4−H4	0.914(12)	1.020(3)	1.026	0.884(14)	1.022(8)	1.030
N5−H5A	0.880(11)	1.024(3)	1.030	0.861(13)	1.023(8)	1.032
N5−H5B	0.856(13)	1.024(3)	1.031	0.875(14)	1.017(8)	1.026
N6−H6A	0.884(13)	1.002(4)	1.009	0.855(15)	1.005(6)	1.014
N6−H6B	0.922(12)	1.032(4)	1.037	0.889(14)	1.029(6)	1.036

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Table 3. Bond Lengths (Å) and Angles of the Eight Hydrogen Bonds in Crystalline Guanidine at T = 100 K[a]

		No.	D−H···A[b]	d (D−H)	d(H···A)	d(D···A)	angle D−H···A
SC-XRD	molecule #1	1	N1−H1···N5^{I}	0.914(11)	2.383(11)	3.2657(9)	162.4(10)
		2	N2−H2A···N6^{II}	0.913(13)	2.246(13)	3.1203(10)	160.1(12)
		3	N2−H2B···N1^{III}	0.882(14)	2.458(14)	3.1965(10)	141.6(12)
		4	N3−H3A···N1^{III}	0.858(12)	2.208(11)	3.0426(9)	164.2(10)
		5	N3−H3B···N2^{IV}	0.862(12)	2.485(12)	3.3228(10)	163.9(10)
	molecule #2	6	N5−H5A···N1^{V}	0.880(11)	2.106(11)	2.9838(9)	176.0(11)
		7	N5−H5B···N4^{VI}	0.856(13)	2.155(13)	3.0013(9)	169.9(11)
		8	N6−H6B···N4^{VII}	0.922(12)	2.080(12)	2.9988(9)	174.4(10)
SC-ND	molecule #1	1	N1−H1···N5^{I}	1.023(4)	2.274(4)	3.265(2)	162.5(1)
		2	N2−H2A···N6^{II}	1.012(4)	2.142(4)	3.120(2)	162.0(1)
		3	N2−H2B···N1^{III}	0.996(4)	2.350(4)	3.197(2)	142.5(1)
		4	N3−H3A···N1^{III}	1.015(4)	2.071(4)	3.044(2)	160.0(1)
		5	N3−H3B···N2^{IV}	1.002(4)	2.346(4)	3.321(2)	164.1(1)
	molecule #2	6	N5−H5A···N1^{V}	1.024(3)	1.963(4)	2.985(2)	176.5(1)
		7	N5−H5B···N4^{VI}	1.024(3)	1.992(4)	3.004(2)	169.2(1)
		8	N6−H6B···N4^{VII}	1.032(4)	1.975(4)	3.004(2)	175.5(1)

[a]The first data set (SC-XRD) has been taken from Yamada et al., while the second data set (SC-ND) was obtained from single-crystal neutron diffraction. D and A represent donor and acceptor functions building up the hydrogen bonds. [b]Symmetry codes: I, −1 + x, y, z; II, −1/2 + x, 1/2 − y, − z; III, 1/2 + x, y, 1/2 − z; IV, − x, −1/2 + y, 1/2 − z; V, 1/2 − x, 1/2 + y, z; VI, 1/2 + x, 1/2 − y, − z; VII, 1 − x, − y, − z.

by 0.01 Å. The N−H bonds are elongated by 0.01 Å, too, whereas N3−H3A and N3−H3B widen by 0.02 Å. It is worth mentioning that the TLS algorithm leads to reasonable centers of gravity for the molecules (#1, 0.158 Å, and #2, 0.155 Å from the central carbon atom at 100 K, and #1, 0.345 Å, and #2, 0.327 Å at 273 K) and internal TLS residual values (R_G = 0.16 and 0.17 for T = 100 K, and R_G = 0.11 and 0.10 for T = 273 K). As expected, the rigid-body movement intensifies with rising temperature, and the centers of gravity shift away from the C atoms. Likewise, the R_G values shrink because it is easier to model the movement into the larger anisotropic ellipsoids. A closer look at the final TLS matrixes exhibits the presence of librational modes only but no translational and screw modes of motion whose values are close to zero.

In the preceding single-crystal X-ray study of guanidine, the thermal behavior of all geometrical data was carefully studied.[6] It turned out that, upon increasing the temperature, the *inter*molecular distances (hydrogen bonds) increase, and that is clearly supported by the present neutron work. As also expected, the *intra*molecular distances (C−N and N−H bonds) seem to shrink with increasing temperature as an artifact because of the stronger thermal motion. Note that the preceding XRD study revealed the largest change in bond length (a decrease of 1.5%, for all other bonds about 0.4−1.0%) for the C1−N2 bond upon rising temperature. Together with the relatively large thermal displacement parameter of the N2 atom, exactly this finding served as a useful hint to check for a rigid-body movement. Indeed, by applying the rigid-body correction for 273 K, the C1−N2 bond arrives at a more common value of 1.37 Å instead of the former 1.34 Å (Table 2). In conclusion and as already speculated by Yamada et al., the guanidine molecule #1 does exhibit a larger thermal motion than molecule #2.[6] After the rigid-body correction, the C−N bonds of both molecules are almost identical. To sum up, the C1−N2 bond was the victim of an artificial bond shorting that went back to the large thermal parameter of the N2 atom but that question could only be solved through the availability of the neutron diffraction data and the resulting ADPs.

Table 3 lists the hydrogen bonds as defined in the previous work.[6] The donor−acceptor nitrogen distances (d(D···A)) derived by either neutron or X-ray single-crystal diffraction agree within three standard deviations. At 100 K, the shortest distances belong to the hydrogen bonds #6, 7, and 8, and the longest N−N distance still considered as a hydrogen bond (#5) is 3.32 Å. This distance was originally chosen for geometrical reasons,[6] and a subsequent theoretical study revealed an energetic stabilization of only 6.8 kJ mol^{-1} for that bond, rather small compared to the strongest H-bond (#8, d(D···A) = 3.00 Å, E = 33.8 kJ mol^{-1}).[7]

On the basis of the neutron data, we may now check previous work that theoretically calculated all N−H bond distances in the guanidine crystal using density functional theory.[7,8] Table 4 compares the measured data (at 100 K) with the calculated ones (at absolute zero temperature) and reveals an excellent agreement. DFT slightly overestimates the N−H bond by only 0.01−0.03 Å, which amounts to a relative error of only 0.6−2.6%. We trust that the single-crystal neutron data of guanidine may contribute for a better understanding of hydrogen bonds, in particular because of the molecule's similarity to important biomolecules.

Table 4. Comparison of the N−H Distances (Å) Derived by DFT Methods[7] and by SC-ND Data at a Temperature of 100 K

	d_{DFT}(N−H)	$d_{SC\text{-}ND}$(N−H)	Δ	Δ (%)
N1−H1	1.029	1.023(4)	0.006	0.6
N2−H2A	1.026	1.012(4)	0.014	1.4
N2−H2B	1.021	0.996(4)	0.025	2.6
N3−H3A	1.033	1.015(4)	0.018	1.8
N3−H3B	1.019	1.002(4)	0.017	1.7
N4−H4	1.027	1.020(3)	0.007	0.7
N5−H5A	1.037	1.024(3)	0.013	1.3
N5−H5B	1.036	1.024(3)	0.012	1.2
N6−H6A	1.019	1.002(4)	0.018	1.7
N6−H6B	1.042	1.032(4)	0.010	1.0

At this point, several crystal-structure comparisons may come to mind, in particular because guanidine, CN_3H_5, is chemically so closely related to ubiquitous molecules such as carbonic acid,

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CO_3H_2, and urea, CON_2H_4. For carbonic acid, such comparison is plainly impossible because of the simple (and sad) fact that its crystal structure is still unknown, despite the groundbreaking phase-pure synthesis of the molecule 13 years ago already.[12]

With respect to urea, we remind the reader that this molecule contains a carbonyl group instead of an imino group found in guanidine. Since this carbonyl O atom is a stronger hydrogen-bond acceptor than the $^{(imino)}$N atom, urea's crystal structure is strongly affected by hydrogen bonds and thus looks very different (space group $P\bar{4}2_1m$) from the one of guanidine. In particular, the rather short distance N−H···O = 2.07 Å found at 123 K underlines the hydrogen-bond strength.[13] Because of the high crystal symmetry, a central carbonyl O atom accepts four simultaneous hydrogen bonds, mirrored by the planarity of the urea molecule and point-group symmetry *mm*2. Various models for the rigid-body motion of the urea molecule have been computationally tested, and the best seems to be the one in which the molecule is assumed to vibrate as a rigid body but with the inclusion of two selected librations for the nonrigid motion of the amino groups.[13] This clearly differs from the guanidine case.

Coming back to guanidine's crystal structure itself, another goal is the search for a correlation between the sizes of the ADPs and the DFT-calculated strengths of the hydrogen bonds. All eight H-bonds have been visualized at both temperatures by means of ORTEP drawings, and they are provided as Supporting Information. Trivially, the ADPs at 273 K are much larger than those at 100 K. One is tempted to assume that a more strongly bonded H atom should exhibit smaller ADPs because of being more strongly trapped in that particular hydrogen bond, but surprisingly enough, non-H-bonded atoms such as H1, H4, and H6A exhibit volumes of their thermal ellipsoids very similar to those H atoms that are part of the strongest bonds. Obviously, there is no such simple correlation between hydrogen bonding strengths and the associated ADPs. These displacement parameters of the peripheric H atoms reflect their quite similar distance from the center of libration rather than their individual bonding situation

In addition to the previously described diffraction experiments, we also recorded an IR spectrum of pure guanidine, depicted in Figure 3. In comparison to the pioneering work of Jones,[14] the new spectrum is better resolved, probably because of the metathesis reaction,[6] which yields a high-purity product, especially after an extra sublimation step.[1] In the earlier work, CN_3H_6OH had been dried using phosphorus pentoxide, and it may well be that the broadening of the infrared peaks was most likely caused by water impurities.

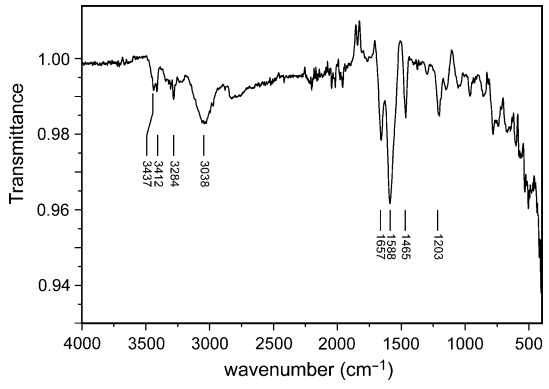

Figure 3. Infrared spectrum of guanidine (CN_3H_5) taken at room temperature.

The spectrum contains very broad absorptions between 3500 and 3000 cm^{-1}, which are assigned to the hydrogen bonds. To ease interpretation of the spectrum, the phonon DOS was calculated using ab initio methods as described earlier.[15] Visual inspections of the simulated phonons were used to analyze the phonons in greater detail. The highest wavenumber at a theoretical 3450 cm^{-1} are found for asymmetric stretching vibrations of amino groups, $^{(amino)}\nu$, followed by stretching vibrations of the imino groups, $^{(imino)}\nu$, about 200 wavenumbers lower. The next vibrations are assigned to symmetric stretching vibrations of the amino groups, $^{(amino)}\nu$, and they fall in a rather broad range between ca. 3250 and 2930 cm^{-1}.

CONCLUSIONS

A single crystal of guanidine suitable for neutron diffraction was measured, and accurate spatial and anisotropic displacement parameters were derived, also for the hydrogen atoms. To account for the rigid-body movement of the two symmetry-independent molecules, a TLS correction was carried out, therefore improving previous XRD bond length data. In particular, the unusual temperature behavior of one C−N bond was elucidated. In addition, previously calculated N−H bond lengths derived from density functional theory were verified, the residual error being smaller than 0.03 Å. Finally, no simple correlation was found between the strength of a particular hydrogen bond and the magnitude of the ADPs of the corresponding hydrogen atom being part of it. Individual vibrations seen in a well-resolved experimental IR spectrum of guanidine were assigned based on ab initio calculations.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data as CIF files and sketches of all hydrogen bonds in guanidine at 100 and 273 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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