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Molecular Structure of Hydrazoic Acid with Hydrogen-Bonded Tetramers in Nearly Planar Layers

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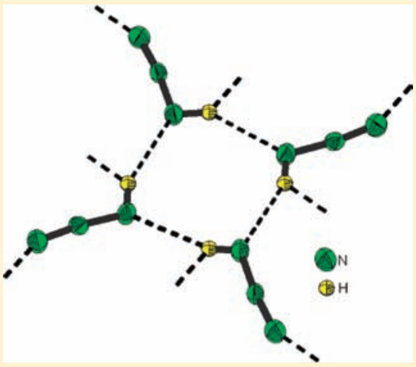
Supporting Information

ABSTRACT: Hydrazoic acid (HN_3)—potentially explosive, highly toxic, and very hygroscopic—is the simplest covalent azide and contains 97.7 wt % nitrogen. Although its molecular structure was established decades ago, its crystal structure has now been solved by X-ray diffraction for the first time. Molecules of HN_3 are connected to each other by hydrogen bonds in nearly planar layers parallel to (001) with stacking sequence A, B, ... The layer distance, at 2.950(1) Å, is shorter than that in 2H-graphite [3.355(2) Å]. The hydrogen bonds N−H···N are of great interest, since the azido group consists of three homonuclear atoms with identical electronegativity, but different formal charges. These hydrogen bonds are bifurcated into moderate ones with ≈2.0 Å and into weak ones with ≈2.6 Å. The moderate ones build up tetramers $(HN_3)_4$ in a nearly planar net of eight-membered rings. To the best of our knowledge, such a network of tetramers of a simple molecule is unique.



INTRODUCTION

The set of physical and chemical properties of inorganic azides determines their wide applications in preparative chemistry as precursors for synthesis of nitrogen compounds that cannot be synthesized in other ways because of their thermal instability, as industrial chemicals, particularly as a source of chemically pure nitrogen, as initial explosives, etc. From a cognitive viewpoint, as substances with simple elementary composition, these solids make it possible to use characteristics found experimentally for the verification of theoretical models of molecular bonding, crystalline structure, and dynamics and regularities of chemical reactions. Inorganic azides exhibit a broad range of crystal stabilities with respect to explosive decomposition. It is believed that there are subtle differences in the bonding of the azides, which are at the origin of different stability and decomposition behavior observed. Thus detailed knowledge of the crystalline structure of azide crystals is of great importance for testing these ideas.

The simplest covalent azide is hydrazoic acid (HN_3), which contains 97.7 wt % nitrogen. With only four atoms, this compound is an ideal model object for theoretical calculations. Although the molecular geometry of HN_3 is now well established, both experimentally and theoretically, the structural and bonding properties of condensed phases of hydrazoic acid remain unknown. The hydrogen-bond geometry and strength in HN_3 is of special interest since its azido group consists of three homonuclear nitrogen atoms with identical electronegativity but different formal charges. Moreover, due to multiple N−N−N bonds in the azido group, the question arises if, by applying very high pressure, polymerization of hydrazoic acid to a nonmolecular and in a final step to a metallic material is possible.

Hydrazoic acid was first prepared in 1890 by Curtius[1] and the first information on the molecular geometry was obtained in 1940 by infrared (IR) spectra.[2] The molecular data were improved by electron diffraction in 1942,[3] by microwave (MW) rotational spectra in 1950,[4] and by ab initio theoretical studies in 1979 by Lievin et al.[5] and in 1980 by Sevin et al.[6] Although, 30 years later, the molecular geometry of HN_3 is now well established, important data on the neat liquid and solid are still missing. This is to be attributed to many difficulties in handling hydrazoic acid. It is an endothermic compound and, therefore, potentially explosive. In addition, it is strongly toxic, very volatile (boiling point 36 °C), low melting (melting point −80 °C), and very hygroscopic.[7]

RESULTS AND DISCUSSION

Therefore, recording of NMR spectra of neat liquid HN_3 would represent a challenge on its own, but turned out here to be successful. A view of the molecular geometry and definition of the nitrogen atoms are shown in Figure 1. In Table 1, the ^{14}N NMR data of neat liquid HN_3 are reported and compared with those of an ethereal solution of HN_3 and also with a solution of NaN_3

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in D_2O. The ^{14}N NMR spectrum of liquid neat HN_3 at 25 °C (Table 1) shows two resonances at an approximate ratio of 1:2.

This finding clearly indicates the presence of an ionic azide moiety, as opposed to an ethereal solution of HN_3, which shows three resonances due to covalent nature. However, the chemical shift of the terminal nitrogens in liquid HN_3 ($\delta = -248$ ppm) differs significantly from that of (ionic) sodium azide ($\delta = -283$ ppm), and those from (ionic) chalcogenium azides $[R_3Ch]N_3$ ($\delta = -260$ to -282 ppm for Ch = S, Se, or Te and R = Me or Ph).[8] The ^1H NMR spectrum of liquid HN_3 shows three partially overlapping broad resonances at 6.55, 6.35, and 6.20 ppm, which indicate the presence of different hydrogen-bridged HN_3 oligomers. As visible from the arrangement of HN_3 moieties of the crystal structure (see later in Figures 3 and 4), the two resonances found in the liquid state of ^{14}N NMR spectrum confirm the bridging nature of the γ-N atom of HN_3 in the crystal.

The results of a single-crystal X-ray structure investigation at 100(2) K are summarized in Table 2. HN_3 crystallizes in the monoclinic acentric space group *Cc* with 16 formula units in the unit cell. The H and N atoms have been all located in Wyckoff position 4*a*. The bond distances (angstroms) and bond angles (degrees) in the four HN_3 molecules are given in Table 3.

It is remarkable to compare the data on HN_3 listed in Table 3 with known literature data on the related aminodiazonium cation (protonated HN_3) $H_2N_3^+$ and the hydrogen diazide anion $[N{-}N{-}N\cdots H{-}N{-}N{-}N]^-$. For the $H_2N_3^+$ cation, Christe et al.[9] determined, by X-ray single-crystal investigation, interatomic distances $N_\alpha{-}N_\beta$ 1.295(5) Å and $N_\beta{-}N_\gamma$ 1.101(6) Å and angles $N_\alpha{-}N_\beta{-}N_\gamma$ 175.3(5)°, $H{-}N_\alpha{-}N_\beta$ 107(6)°, and $H{-}N_\alpha{-}N_\beta$ 118(8)°. In the hydrogen diazide anion $[N{-}N{-}N\cdots H{-}N{-}N\text{-}N]^-$, Dehnicke and co-workers[10] obtained, by X-ray single-crystal investigation, in the HN_3 part bond distances $N_\alpha{-}N_\beta$ 1.21(1) Å, $N_\beta{-}N_\gamma$ 1.14(1) Å, and $H{-}N_\alpha$ 1.18(7) Å and bond angles $N_\alpha{-}N_\beta{-}N_\gamma$ 175(1)° and $H{-}N_\alpha{-}N_\beta$ 102(4)°.

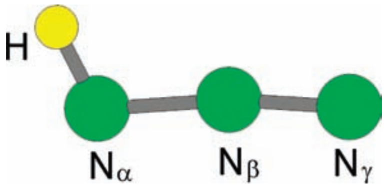
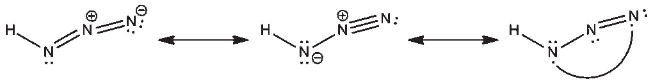


Figure 1. View of the molecular geometry of HN_3 and definition of the nitrogen atoms.

From three mesomeric resonance structures **1**, **2**, and **3**, the second is the more important one. The averaged $N_\alpha{-}N_\beta$ bond distance of 1.233(5) Å suggests a higher bond order than shown in structure **2**.



(1) **(2)** **(3)**

The increased valence bond (VB) theory[11] explains in **2** and **3** with an increased VB structure both the short $N_\alpha{-}N_\beta$ and $N_\beta{-}N_\gamma$ bonds.

The averaged structural data of the molecular geometry of HN_3 in the solid state (Table 4) agrees well for the N−N distances and angles with data obtained in the last decades by IR[2] and MW[12] investigations on molecules, whereas significant disagreement (approximately 0.20 Å) is revealed for the $H{-}N_\alpha$ distance. Determined from single-crystal X-ray investigation, the averaged $H{-}N_\alpha$ bond distance of 0.82(20) Å is unrealistically short (Table 4).

However, in the single-crystal X-ray investigation of the aminodiazonium cation $H_2N_3^+$, Christe et al.[9] determined also a very short N−H bond length of 0.76(7) Å, although "on the basis of ab initio calculation a realistic N−H-bond distance $H_2N_3^+$ is 1.01 Å".[9] "The observed N−H bond length of 0.76(7) Å is unrealistic short due to the fact that hydrogen does not possess any core electrons, and therefore, the X-rays are being diffracted by the binding electrons".[9] In the present X-ray study, the N−H bond length is also found too short for the very same reason. As mentioned earlier, the $N_\alpha{-}H$ polar covalent bond distance in HN_3 determined with X-ray diffraction is unrealistic, but this can be corrected. The N−D bond distance in ND_3 is 1.039(20) Å (neutron diffraction at 77 K)[13] and the N−H bond distance in $H_2N_3^+$ is 1.01 Å (ab initio calculation)[9].

Table 1. ^{14}N NMR Data for HN_3 and NaN_3 at 25 °C

sample	N_α (ppm)	N_β (ppm)	N_γ (ppm)
HN_3, neat liquid	−248	−136	−248
HN_3, solution in ether	−320	−129	−174
NaN_3 in D_2O	−283	−133	−283

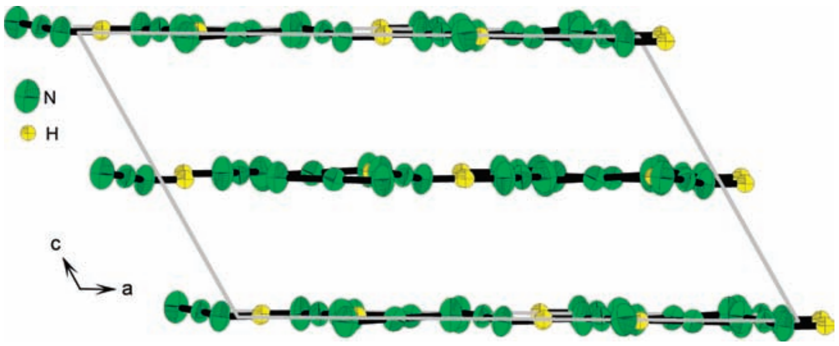


Figure 2. Diamond2 view[15] of HN_3 at 100(2) K along the negative *b*-axis on the two-layer structure A, B, ..., with displacement ellipsoids of 50% probability, anisotropic for nitrogen, isotropic for hydrogen with $U_H = 0.0150$ Å^2. Such a layer stacking is also found in 2H-graphite. The layer distance in HN_3 is 2.950 Å at 100(2) K; in 2H-graphite it is 3.356(2) Å.[16] In both layer structures the displacement ellipsoids show their highest displacements perpendicular to the layers, indicating only weak van der Waals forces between the layers.

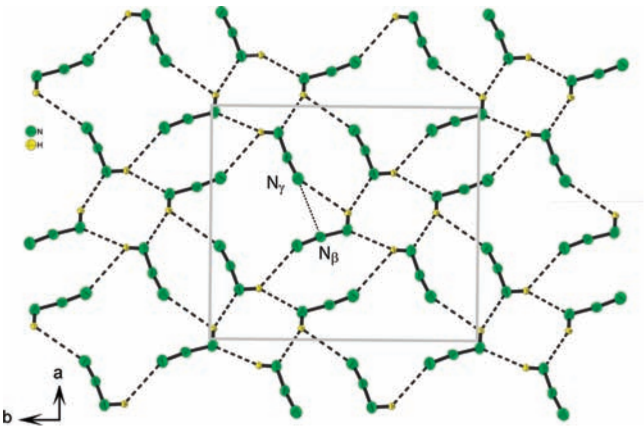


Figure 3. Diamond2 view[15] of HN_3 at 100(2) K along the negative *c*-axis on the nearly planar layer at $z \approx 0$ (displacement ellipsoids of 50% probability, anisotropic for nitrogen, isotropic for hydrogen with U_H = 0.0150 $Å^2$). The planar layer at $z \approx {}^1/_2$ is obtained from that at $z \approx 0$, for example, with a glide *c* at $y = 0$ (applying at first a mirror plane at $y = 0$, followed by a shift with $c/2$). Hydrazoic acid molecules form in both layers nearly planar nets of tetramers $(HN_3)_4$ as eight-membered rings consisting of four short hydrogen $N_\alpha{-}H\cdots N_\alpha$ and four $N_\alpha{-}H$ polar covalent bonds. In the centers of these eight-membered rings, nearly 4-fold rotation axes are found. In addition, two short and two long hydrogen bonds and four covalent azido bonds form eight-membered rings, and four long hydrogen bonds and 12 covalent azido bonds form 16-membered rings. Interestingly, next-neighbor azido groups to a tetramer are arranged nearly perpendicular to them. One such contacts is shown here. Such contacts allow nearly parallel alignment of the tetramers in two perpendicular directions within the layers.

With an averaged value of 1.02 Å from these investigations, the polar covalent $N_\alpha{-}H$ bond distance in HN_3 is corrected by adding 0.20 Å to the averaged distance of 0.82(20) Å [X-ray diffraction (Table 3)], resulting in a distance of ≈1.02 Å. The corrected $N_\alpha{-}H$ bond (≈ 1.02 Å) has been confirmed by density functional theory (DFT) calculations with the program WIEN2k.[14]

Nothing was known until now about the arrangement of HN_3 molecules in the solid. Figure 2 shows a Diamond2 view[15] of HN_3 at 100 K along the negative *b*-axis.

Hydrazoic acid crystallizes in a two-layer structure with stacking parallel (001) layers at $z \approx 0$ and $z \approx {}^1/_2$, as is also found in 2H-graphite (here with $z = 0$ and $z = {}^1/_2$, respectively).[16] The layer distance in HN_3 is 2.950(1) Å at 100 K, shorter than in 2H-graphite, where the distance is 3.355(2) Å at 300 K.[16] Between such layers only weak van der Waals forces are present. Therefore, the thermal displacement ellipsoids show for both layer structures their highest displacements perpendicular to (001): in HN_3, for N1−N12 between U_{33} = 0.0252(6) and 0.0550(10) $Å^2$, and in 2H-graphite, for C1 and C2 U_{33} = 0.0160(20) $Å^2$.[16]

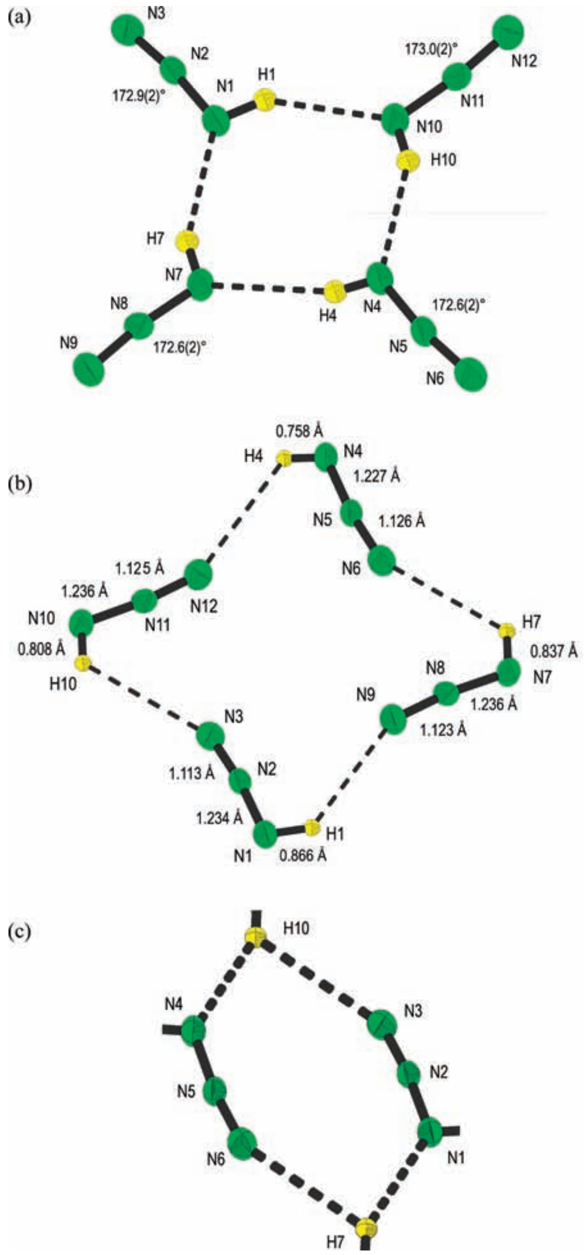


Figure 4. Diamond2 plots[15] of hydrazoic acid forming three different nearly planar rings within the layers are shown (displacement ellipsoids of 50% probability, anisotropic for nitrogen, isotropic for hydrogen with U_H = 0.0150 $Å^2$). (a) An eight-membered ring is obtained if the connection is performed via four short hydrogen bonds (≈ 2.0 Å) and four polar covalent $N_\alpha{-}H$ bonds (≈1.0 Å). (b) A 16-membered ring is obtained if the connection is performed by four long hydrogen bonds (≈2.6 Å), four polar covalent $N_\alpha{-}H$ bonds (≈1.0 Å), and eight covalent N−N bonds (≈1.1−1.2 Å). (c) An eight-membered ring is obtained if the connection is performed via two short hydrogen bonds (≈2.0 Å), two long hydrogen bonds (≈2.6 Å), and two polar covalent $N_\alpha{-}H$ bonds (≈1.0 Å).

Figure 3 shows a Diamond2 plot[15] along the negative *c*-axis on the acentric unit cell of solid HN_3 with the layer at $z \approx 0$. The layer at $z \approx {}^1/_2$ is obtained, for example, with a glide *c* at *y* = 0. Every four molecules are connected to tetramers $(HN_3)_4$ as eight-membered rings consisting of four small edges formed by $N_\alpha{-}H$ polar covalent chemical bonds (≈1.0 Å) and four long edges formed by short $N_\alpha{-}H\cdots N_\gamma$ hydrogen bonds. The hydrogen bonds are bifurcated. Two short and two long $N_\alpha{-}H\cdots N_\gamma$ hydrogen bonds and four covalent azido bonds form eight-membered rings, and four long $N_\alpha{-}H\cdots N_\gamma$ hydrogen bonds and 12 covalent azido bonds form 16-membered rings. The donor (D)−acceptor (A) geometries for the short hydrogen bonds in solid HN_3 at 100 K are summarized in Table 5, and for the long hydrogen bonds, in Table 6.

The average value of the short $H\cdots A$ distance is 2.24(20) Å with an average angle $D{-}H\cdots A$ of 151(5)°, and for the long $H\cdots A$ distance average values of 2.78(20) Å and 127(5)° are obtained, respectively. With an increased $N_\alpha{-}H$ bond distance of ≈1.02 Å in HN_3 (determined by infrared spectroscopy[2] and microwave;[12] Table 4), the average short $N_\alpha{-}H\cdots N_\alpha$ hydrogen bond of 2.24(20) Å (Table 5) can be corrected to ≈2.0 Å and the average long $N_\alpha{-}H\cdots N_\gamma$ hydrogen bond of 2.78(20) Å (Table 6) can be corrected to ≈2.6 Å. The short hydrogen bond of ≈2.0 Å can be classified as moderate, as they are typically observed in acids;[17] the long $N_\alpha{-}H\cdots N_\gamma$ hydrogen bond of ≈2.6 Å can be classified as weak.[17]

One tetramer of hydrazoic acid $(HN_3)_4$, one 16-membered ring, and one eight-membered ring are shown in Figure 4.

The eight-membered tetramer rings can be considered as truncated squares, if the corners of a slightly distorted square are cut off. The centers of these rings are two-dimensionally nearly centrosymmetric and have slightly distorted 4-fold rotation axes. The average deviation from such ideal positions is 0.040 Å for the N_α atoms, 0.013 Å for the N_β atoms, and 0.013 Å for the N_γ atoms, but for the H atoms the average deviation can be as much as 0.065 Å. In addition, parallel alignment of the eight-membered rings is supported by $N_\gamma\cdots N_\beta$ contacts of 3.0−3.1 Å. between two different tetramers These contacts are slightly shorter than 2 times the van der Waals radius of nitrogen (1.6 Å).[18] Further stabilization of these contacts could be achieved by the attraction of the N_γ and N_β atoms with formally negative and positive charges, respectively (see mesomeric form **1**). One such contact for each layer is shown in Figure 3 as dotted line.

Table 2. Crystallographic Data for HN_3 at 100(2) K, Determined by X-ray Single-Crystal Investigation[a]

crystal system	monoclinic
space group	*Cc*
a (Å)	11.6070(20)
b (Å)	11.6091(12)
c (Å)	6.7825(14)
β (deg)	119.57(3)
V	794.8(2)
Z	16
16 H in 4 x	4*a*
48 N in 12 x	4*a*
D_{calc} ($g\cdot cm^{-3}$)	1.4384(4)
reflections measured	3973
reflections unique	828
$R(\sigma)$	0.0277
*R*1	0.0244
w*R*2	0.0504
GOF	1.033
highest res. elec. dens. ($Å^{-3}$)	+0.124/−0.108

[a] Experimental uncertainties are given in parentheses.

Interestingly, neighbored azido groups belonging to the same eight- or 16-membered rings are nearly perpendicular to each other (Figure 3). Also, the 16-membered rings are in two dimensions nearly centrosymmetric and contain a slightly distorted 4-fold rotation axis. Repeating the structural motifs of the eight- and 16-membered rings in the layers seems to be easier in a slightly distorted centrosymmetric arrangement, although the three-dimensional structure is overall acentric with only a glide *c* (Figure 3).

In ND_3 at 77 K, the hydrogen bonds $N{-}D\cdots N$ within the tetrahedral three-dimensional net are 2.393(9) Å (neutron diffraction[13]), classified as weak.[17] However, in the eight-membered rings of HN_3 tetramers, the $N_\alpha{-}H\cdots N_\alpha$ bonds are moderate with ≈2.0 Å,[17] approximately 0.4 Å shorter than those in ND_3. Therefore, this may be an indication that this decrease may be influenced by resonance-assisted hydrogen bonds (RAHBs). RAHB is a result of π-delocalization that involves hydrogen.[19−22] Such interaction could be also present in solid ammonium azide (NH_4N_3). By neutron diffraction, short $N{-}H\cdots N$ hydrogen bonds of 1.930(9) and 1.974(9) Å have been determined here in nearly planar 10-membered rings (N_α, N_β, two N_γ, two N_{NH4+}, and four H atoms).[23]

The class of azides can formally be divided into organic and inorganic ones.[24−27] Most organic azides of the type R-N_3 as well as many non-metal inorganic azides XN_3 (X = F, Cl, Br, or I) are predominantly covalent in nature and contain an asymmetric and slightly bent azide group. In contrast, purely ionic metal azides of the type $M^+N_3^-$ (e.g., M = Li to Cs) contain a linear and symmetrical azide anion. Their crystal structures can be compared for the smaller cations with the NaCl-type and for the larger ones with the CsCl-type structure.[28] For methyl, silyl, and germyl azides only, the

Table 3. Bond Distances and Bond Angles in Solid HN_3 at 100(2) K, Determined by X-ray Single-Crystal Investigation[a]

molecule	$H{-}N_\alpha$ (Å)	$N_\alpha{-}N_\beta$ (Å)	$N_\beta{-}N_\gamma$ (Å)	$H{-}N_\alpha{-}N_\beta$ (deg)	$N_\alpha{-}N_\beta{-}N_\gamma$ (deg)
1	0.87(20)	1.234(2)	1.113(3)	103(2)	172.9(2)
2	0.76(20)	1.227(2)	1.126(2)	113(2)	172.6(2)
3	0.84(20)	1.236(2)	1.123(2)	111(2)	172.6(2)
4	0.81(20)	1.236(2)	1.121(2)	109(2)	173.0(2)

[a] Experimental uncertainties are given in parentheses.

Table 4. Bond Distances and Bond Angles in Molecular HN_3 Determined by IR and by Microwave Investigation in Comparison to Averaged Data Obtained by X-ray Single-Crystal Investigation[a]

method	$N_\alpha{-}N_\beta$ (Å)	$N_\beta{-}N_\gamma$ (Å)	$N_\alpha{-}N_\beta{-}N_\gamma$ (deg)	$H{-}N_\alpha$ (Å)	$H{-}N_\alpha{-}N_\beta$ (deg)
IR spectrum[2]	1.241	1.128		1.012	111
microwave[12]	1.243(5)	1.134(2)	171.3(50)	1.015(15)	108.8(40)
X-ray single crystal, averaged	1.233(5)	1.121(5)	172.8(2)	0.82(20)	109(5)

[a] Experimental uncertainties are given in parentheses.

Table 5. Donor−Acceptor Geometries for Short Hydrogen Bonds in Solid HN_3 at 100(2) K, Obtained by Single-Crystal X-ray Investigation[a]

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
N(1)−H(1)···N(10)	0.87(20)	2.23(20)	2.968(5)	143(5)
N(4)−H(4)···N(7)	0.76(20)	2.28(20)	2.989(5)	157(5)
N(7)−H(7)···N(1)	0.84(20)	2.22(20)	2.988(5)	152(5)
N(10)−H(10)···N(4)	0.81(20)	2.21(20)	2.950(5)	152(5)

[a] Experimental uncertainties are given in parentheses.

Table 6. Donor−Acceptor Geometries for Long Hydrogen Bonds in Solid HN_3 at 100(2) K, Obtained by Single-Crystal X-ray Investigation[a]

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
N(1)−H(1)···N(9)	0.87(20)	2.65(20)	3.299(5)	133(5)
N(4)−H(4)···N(12)	0.76(20)	2.88(20)	3.354(5)	123(5)
N(7)−H(7)···N(6)	0.84(20)	2.77(20)	3.327(5)	126(5)
N(10)−H(10)···N(3)	0.81(20)	2.80(20)	3.333(5)	126(5)

[a] Experimental uncertainties are given in parentheses.

molecular structures have been determined, either by electron diffraction or by microwave spectra.[29−31]

Nevertheless, in the structural chemistry of azides, the tetramers of HN_3 in nearly planar layers forming eight- and 16-membered rings have a unique position. To the best of our knowledge, such tetramers of small molecules connected by hydrogen bonds have not been observed up to now. The N···N distances in hydrogen bonds (Tables 5 and 6) and frequency of N−H stretching modes in Raman spectra are indicative for the strength of hydrogen bonding in solid hydrazoic acid. Since the parameters of hydrogen bonds are known to show systematic variations with changes of the interatomic distances, application of pressure is a natural way to study hydrogen-bonded substances. Indeed, our preliminary Raman spectra at elevated pressure (1 GPa) show considerable red shift of N−H stretching frequencies, indicating strengthening of hydrogen bonds with pressure. Thus the pressure can span the N_α−H···N_α distances also in solid HN_3 all the way from weak to strong, thereby tuning the hydrogen bonds to the symmetric case. However, if steric repulsion can appear in the eight-membered rings, then hydrogen atoms would come close to one another at the compression, leading to a new molecular arrangement (and consequently a new phase) or bonding situation reducing this repulsion. Finally, application of pressure can lead to possible formation of polymeric (nonmolecular) hydrogen−nitrogen solid-ultimate case of energetic material. High-pressure investigations on HN_3 up to the megabar range with this goal are underway.

EXPERIMENTAL SECTION

Hydrazoic acid was prepared from sodium azide and stearic acid,[32,9,33] filled in a Duran glass apparatus and dried intensely for several hours with a high vacuum line with liquid nitrogen-cooled traps. The glass reactor was reduced to an X-ray capillary with low wall thickness and about 0.3 mm diameter, loosing conically the diameter. After the end of the drying procedure, the reactor was sealed from the high vacuum line and then slowly heated to 130 °C,[32] while the X-ray capillary was cooled with liquid nitrogen. After the hydrazoic acid was condensed to a height of about 8 mm, the X-ray capillary was sealed off. With this procedure, contact with air or moisture was strictly excluded from the sample.

This capillary filled with liquid HN_3 at room temperature could be handled without any explosion on a Guinier low-temperature diffractometer at 150 K and a Raman spectrometer at the same temperature and also stored for more than 1 year.

For NMR spectroscopic experiments, this glass capillary was carefully placed into a standard NMR tube and filled with benzene-d_6 as lock substance. The NMR spectra were recorded on a JEOL Eclipse 400 instrument at 25 °C, and chemical shifts were determined with respect to external Me_4Si (^1H, 399.8 MHz) and $MeNO_2$ (^{14}N, 28.9 MHz). The ^1H and ^{14}N NMR spectra for neat liquid HN_3 were recorded on a JEOL Eclipse 400 instrument at 25 °C.

For the structure determination, single crystals were grown in situ in the X-ray capillary by use of the cryojet of an Oxford Diffraction Xcalibur3 diffractometer near the melting point of HN_3 at $\approx$193 K in several melting and crystallizing cycles. The tip of a finger, carefully touching the capillary, was used as the heating source. A single crystal of dimensions $0.2 \times 0.2 \times 0.2$ mm^3 was obtained. The structure was determined at 100(2) K on an Oxford Diffraction Xcalibur3 diffractometer. In total, 3973 reflections in the range h, $k = \pm14$, $l = \pm8$ were measured, leading to 828 unique reflections (Table 2). The structure was solved by use of the SHELXL-97 program.[34] The hydrogen positions were obtained by a difference Fourier synthesis without geometric constraints. The thermal parameters of nitrogen atoms were refined anisotropically, and those of hydrogen, isotropically. Positional and thermal parameters of solid HN_3 at 100(2) K are summarized in Table S1 in the Supporting Information.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Structural information (CIF); additional technical details (PDF); one table listing positional and thermal parameters of solid HN_3 at 100(2) K and one figure showing ^1H and ^{14}N NMR spectra of HN_3 at 25 °C (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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