

# Molecular Structure of Isocyanic Acid, HNCO, the Imide of Carbon Dioxide

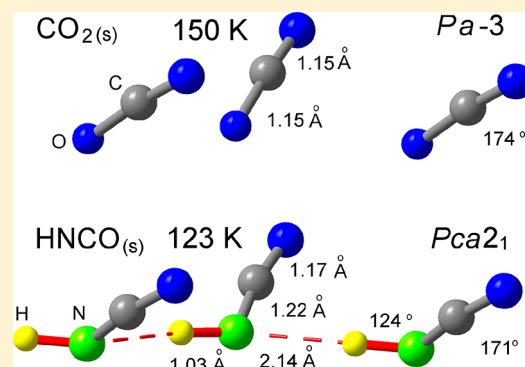
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## Supporting Information

**ABSTRACT:** Isocyanic acid, HNCO, the imide of carbon dioxide, was prepared by reaction of stearic acid and potassium cyanate (KOCN) at 60 °C in a sealed, thoroughly dried reactor. Interestingly, its crystal structure, solved by X-ray single crystal diffraction at 123(2) K, shows a group–subgroup relation for the NCO<sup>−</sup> anion to carbon dioxide: (for CO<sub>2</sub>, *cP12*, *Pa3*, *a* = 5.624(2) Å, 150 K, C–O 1.151(2) Å; for HNCO, *oP16*, *Pca2*<sub>1</sub>, *a* = 5.6176(9), *b* = 5.6236(8), *c* = 5.6231(7) Å, 123(2) K). Precise positions of H, N, C, and O were determined by DFT calculations with WIEN2k leading to interatomic distances C–O 1.17, C–N 1.22, N–H 1.03, and –N–H···N 2.14 Å, and the interatomic angle N–C–O 171°.



## 1. INTRODUCTION AND SYNTHESIS

In 1919 Irving Langmuir pointed out the extraordinary agreement between the physical properties of carbon dioxide (CO<sub>2</sub>) and dinitrogen monoxide (N<sub>2</sub>O), including e.g. critical temperatures and pressures, densities of the liquids, viscosities, and refractive indexes, and introduced the principle of isosterism.<sup>1</sup> If compounds with the same number of atoms also have the same total number of electrons, the electrons may arrange themselves in the same manner.<sup>1</sup> In this case, the compounds or groups of atoms are said to be isosteric.<sup>1</sup> For CO<sub>2</sub> and N<sub>2</sub>O there are three atoms and 22 total or 16 valence electrons (e). Langmuir's concept is extraordinarily useful in predicting properties of isosteric molecular species. About 26 species isosteric to CO<sub>2</sub>, either neutral or charged, are known today.<sup>1–7</sup>

Both the three-atom heterocumulenic cyanate and azide anions possess 22 total e, corresponding to the weak acids isocyanic acid HNCO<sup>8</sup> and hydrazoic acid HN<sub>3</sub>,<sup>9</sup> respectively. In 1919 Langmuir gave a first indication of their isosterism.<sup>1</sup> Isocyanic acid was first prepared by Liebig and Wöhler<sup>10</sup> in 1830. However, information on the molecular geometry on HNCO was obtained about 100 years later in the decade 1940–1950 by electron diffraction,<sup>11</sup> by microwave,<sup>12</sup> and by infrared spectroscopy,<sup>13,14</sup> all performed in the gas phase. As a result from those studies, the C–O, N–C, and N–H distances were determined to 1.17, 1.21, and 0.99 Å, respectively, with the hydrogen atom being connected to nitrogen with an H–N–C angle of 128°. More recent studies regarding synthesis and properties of HNCO were reported in our laboratory.<sup>15</sup>

In 1955 von Dohlen and Carpenter performed the first X-ray single crystal investigation. In their work, HNCO crystallized at –125 °C in an orthorhombic lattice, probably with space group *Pnma*.<sup>16</sup> The resulting distances C–O and N–C (1.18(2) Å, 2×) are in rough agreement with the earlier investigations in the gas phase. However, the quality of the crystal was not sufficient to localize the hydrogen atoms by difference Fourier analysis.

Apart from the interests of theoretical and synthetic chemistry for isocyanic acid, a special importance arises now due to its role in urban air pollution and possible toxicity. Cars with gasoline and diesel engines are known to emit HNCO, especially if selective catalytic reduction systems are used to reduce the emission of nitrogen oxides NO<sub>x</sub>. In this case an aqueous solution of urea ((NH<sub>2</sub>)<sub>2</sub>CO) is added to the exhausts of the engine. In the catalytic reduction system, urea is thermally decomposed into ammonia (NH<sub>3</sub>) and isocyanic acid (HNCO). The last compound is rapidly decomposed with water on the catalyst surface into ammonia and carbon dioxide. However, there remains emission of HNCO in the range between 30 and 50 mg HNCO/kg fuel,<sup>17</sup> which is found in urban air pollution and could negatively affect human health.

Of special interest is the comparison of the crystal structures of the isosteric acids HNCO and HN<sub>3</sub>. The structure of HN<sub>3</sub> was recently solved by an X-ray single crystal investigation at

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100(2) K<sup>18</sup> and shows a very interesting two-dimensional net, formed by bifurcated hydrogen bonds, in which tetramers (HN<sub>3</sub>)<sub>4</sub> were found in a nearly planar net of 4-, 8-, and 16-membered rings. Now, a structural investigation of HNCO in the space group *Pca*2<sub>1</sub> is reported, including refinement of the positional parameters by DFT calculations with the program WIEN2k.<sup>19</sup>

## 2. EXPERIMENTAL SECTION

**2.1. General Information.** Isocyanic acid HNCO was prepared from potassium cyanate KOCN and stearic acid as previously reported.<sup>15</sup> Both educts were intensively ground and filled into a Duran reactor, having attached at one side a thin-walled X-ray capillary. The reactor with the starting materials was dried on a high vacuum line while cooling with liquid nitrogen traps.

**2.2. X-ray Crystallography.** After several days of drying, the reactor was sealed from the vacuum line and then slowly heated to 60 °C. Stearic acid melts near this temperature, and then, the formation of gaseous HNCO starts. Isocyanic acid condenses at the capillary, which is cooled with liquid nitrogen and then sealed. From each heating experiment, three capillaries filled with HNCO were obtained, and were stored in liquid nitrogen.

Single crystals of HNCO for the structure determination were grown *in situ* in the capillary adjusted to the Oxford Xcalibur diffractometer. Several cooling and heating cycles are required to obtain a single crystal in order to check the diffraction pattern. The structure was determined at 123(2) K. The *hkl* ranges of the measured reflections were the following: *h* from −8 to 7, *k* from −8 to 8, and *l* from −8 to 8. Within a 24 h cooling and heating procedure from 100(5) to 185(5) K, searching for the orthorhombic phase of von Dohlen and Carpenter<sup>16</sup> was negative. Structural calculations on HNCO (*Pca*2<sub>1</sub>) were performed with SHELXL-2014.<sup>20</sup> The investigated crystal was disordered and contained two individuals with 55% and 45%. The individuals were rotated against each other with oxygen and nitrogen atoms nearly lying above each other. Therefore, hydrogen atoms could not be detected from a difference Fourier analysis. In addition, with the position derived by SHELXL-2014 unrealistic short C–O and unrealistic long C–N distances had been obtained.

**2.3. Density Functional Theory (DFT) Calculations.** The theoretical calculations are based on density functional theory (DFT) and were performed with the augmented plane wave + local orbital method as implemented in the WIEN2k<sup>19</sup> program. We utilized the generalized gradient approximation of Perdew et al.<sup>21</sup> and treated the weak but important van der Waals interactions using DFT-D3.<sup>22</sup> The atomic sphere radii  $R_{\text{MT}}$  were chosen as 0.545 Å for C, 0.598 Å for N and O, and 0.333 Å for H. The plane wave cutoff parameter for the wave functions,  $R^*K_{\text{MAX}}$ , was set to 4 and the charge density and potential was expanded in plane waves up to  $G_{\text{MAX}} = 20$ . For the calculations with *Pca*2<sub>1</sub>, a  $4 \times 4 \times 4$  mesh was used, and for that with *Pnma*, there is a  $2 \times 4 \times 8$  mesh. We used experimental lattice parameters in all cases, but refined the positional parameters of all atoms until the forces were well below 1 mRy/bohr. Since the positions of the H atoms are unknown in many cases, we started from several educated guesses and refined to the next local minimum. Clearly, the structure with H attached to N and bridging to another N atom has the lowest total energy. The calculations were performed at the mpp2 cluster of the Leibniz-Rechenzentrum, Garching

(Bavarian Academy of Science), and the Vienna Scientific Cluster (VSC3).

## 3. RESULTS AND DISCUSSION

**3.1. X-ray Diffraction Results.** The results of a single crystal X-ray structure investigation are summarized in Table 1.

**Table 1. Crystallographic Data of Solid HNCO, Determined at 123(2) K by X-ray Single Crystal Investigation<sup>a</sup>**

crystal syst	orthorhombic
space group	<i>Pca</i> 2 <sub>1</sub>
<i>a</i> (Å)	5.6176(9)
<i>b</i> (Å)	5.6236(8)
<i>c</i> (Å)	5.6231(7)
<i>T</i> (K)	123(2)
<i>V</i> (Å <sup>3</sup> )	177.64(4)
<i>Z</i>	4
4 H, 4 N, 4 C, 4 O	4a
$\rho_{\text{calc}}$ (g cm <sup>−3</sup> )	1.609
reflms measured	1390
reflms unique	339
<i>R</i> ( $\sigma$ )	0.0260
<i>R</i> 1	0.0352
<i>wR</i> 2	0.0887
GOF	1.175
highest residual electron density (e/Å <sup>−3</sup> )	+0.10/−0.17

<sup>a</sup>Structural analysis with the SHELXL-2014<sup>20</sup> program showed that the investigated crystal consists of two crystals (1, 55%; 2, 45%), stacked above each other. Therefore, hydrogen positions could not be precisely determined by a difference Fourier analysis.

HNCO crystallizes in the orthorhombic acentric space group *Pca*2<sub>1</sub> with 4 formula units in the unit cell. The positional parameters determined from the X-ray diffraction structure analysis by the program SHELXL-2014<sup>20</sup> lead to both very short C–O ((0.99(1), 1.04(1) Å) and very long C–N ((1.30(1) and 1.36(1)) distances, since in space group *Pca*2<sub>1</sub> it is difficult to grow polarity pure single crystals.

**3.2. DFT Results.** Therefore, it was decided to perform DFT calculations with the program WIEN2k.<sup>19</sup> In Table 2 the calculated positional parameters of solid isocyanic acid HNCO in the polar space group *Pca*2<sub>1</sub> are summarized.

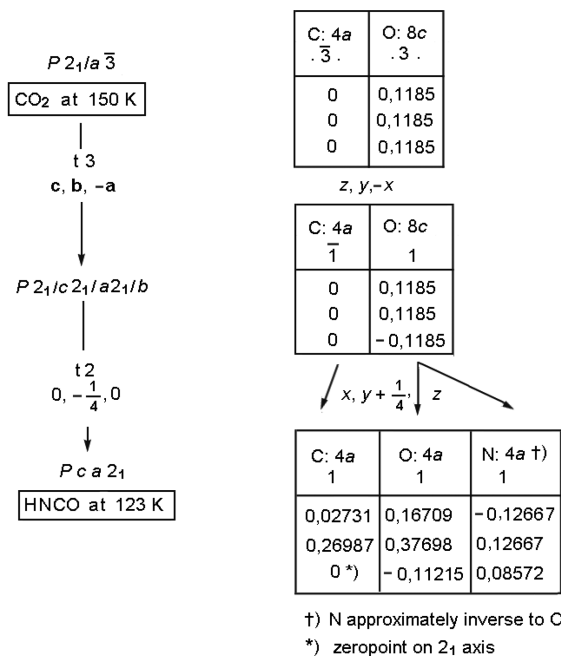
**3.3. Group–Subgroup Relations.** Solid carbon dioxide CO<sub>2</sub><sup>23</sup> crystallizes at ambient pressure in the cubic space group *Pa* $\bar{3}$  with four molecules in the unit cell. The lattice parameter is  $a = 5.624(2)$  Å<sup>23</sup> at 150 K leading to a unit-cell volume  $V = 177.88(20)$  Å<sup>3</sup>. Solid isocyanic acid HNCO (Table 1)

**Table 2. Positional Parameters *x*, *y*, *z* of Solid Isocyanic Acid HNCO in Space Group *Pca*2<sub>1</sub>, Derived by DFT Calculations with the Program WIEN2k<sup>19,a</sup>**

atom	<i>x</i>	<i>y</i>	<i>z</i>
C	0.0273	0.2699	0.0000
O	0.3329	0.3770	−0.6121
N	0.8733	0.1437	−0.9142
H	0.1755	0.8520	−0.2386

<sup>a</sup>The C-, N-, and O-atoms have been all located in Wyckoff position 4a. Starting parameters were those obtained by the program SHELXL-2014.<sup>20</sup> These atomic positions were then refined with WIEN2k.<sup>19</sup> The positions of the H-atoms were derived *ab initio*. Details of the calculations are given in the Experimental Section.

crystallizes in the orthorhombic space group  $Pca2_1$  with pseudocubic lattice parameters  $a = 5.6176(9)$  Å,  $b = 5.6236(8)$  Å,  $c = 5.6231(7)$  Å at 123 K. Hence, HNCO easily suggests a structural comparison of  $\text{CO}_2$  and HNCO in a group–subgroup relation<sup>24–31</sup> (Figure 1).



**Figure 1.** Group–subgroup relation<sup>24–31</sup> showing the symmetry reduction for  $\text{CO}_2$  in the centrosymmetric cubic space group  $P2_1/a\bar{3}$  (No. 205) to  $Pcab$  ( $P2_1/c2_1/a2_1/b$ , No. 61) and then for HNCO to the acentric polar orthorhombic space group  $Pca2_1$  (No. 29).

Coming from cubic  $\text{CO}_2$  ( $P2_1/a\bar{3}$ , No. 205) the first step leads to a translationengleich<sup>24–31</sup> (t) step of index 3 (t3) to the maximal nonisomorphic subgroup  $Pcab$  ( $P2_1/c2_1/a2_1/b$ , No. 61). The position  $24d$  in No. 205 is here reduced to  $8c$  in No. 61 while the axes have to be changed into  $c, b, -a$  and the coordinates into  $z, y, -x$ . Further symmetry reduction is achieved in a translationengleich step of index 2 (t2) and an origin change with  $(0, -1/4, 0)$  to the maximal nonisomorphic subgroup  $Pca2_1$ . Here, position  $8c$  in No. 61 is changed into twice  $4a$  in No. 29 upon changing the coordinates into  $x, y + 1/4, z$ . In Figure 1 the group–subgroup relation is shown.

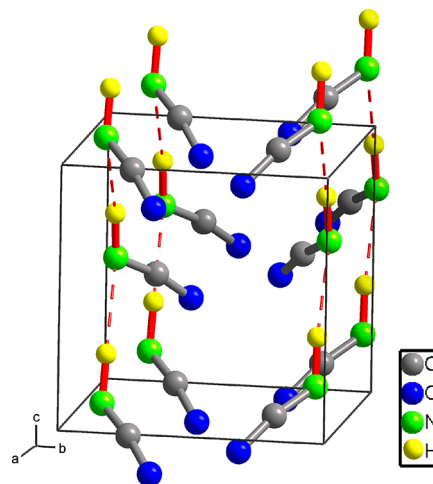
In  $\text{CO}_2$  the coordinates of the C atoms remain in position  $4a$  (0, 0, 0), whereas the oxygen atoms O are shifted from (0.1185, 0.1185, 0.1185) in  $Pa\bar{3}$  to (0.1185, 0.1185, -0.1185) in  $P2_1/c2_1/a2_1/b$ . For  $\text{CO}_2$  in  $Pca2_1$ , the C atoms have the coordinates (0, 1/4, 0), the O atom (0.1185, 0.3685, -0.1185), and the O<sup>i</sup> atom (-0.1185, 0.1315, 0.1185).

The symmetry reduction of  $Pa\bar{3}$  via  $Pcab$  to  $Pca2_1$  (Figure 1) leads to two polar structures. The polar structure 1 is obtained with the  $z$  parameters (Table 2,  $z = -0.6121$  and  $z = -0.9142$ ) for the O and the N atom, respectively. In the polar structure 2 the  $z$  parameters are inverted to  $z = 0.6121$  and  $z = 0.9142$  for O and N, respectively. The polar structure 2 is obtained from polar structure 1 by reflection with a mirror.

During the synthesis of HNCO with stearic acid and potassium cyanate (KOCN) and cooling to 100 K, the obtained sample will contain approximately the same number of crystals with polarity 1 and with polarity 2. This could be a reason that the single crystal of HNCO used for the X-ray diffraction

investigation was obtained only with low quality. In principle, the absolute configuration of a single crystal in space group  $Pca2_1$  with good quality, investigated by X-ray diffraction, could be determined by anomalous dispersion.<sup>32</sup> However, for elements with low scattering power such as H, C, N, and O, the contribution is low, and therefore, it is not an easy procedure to distinguish then between such crystals.

In Figure 2, a Diamond view<sup>33</sup> of the polar HNCO structure is shown with polarity 1 with negative positional parameters  $z$



**Figure 2.** Diamond view<sup>33</sup> along [100] for the polar structure of HNCO in  $Pca2_1$  is shown with polarity 1 (negative positional parameters  $z$  for the O, N, and H atoms, Table 1). The red N–H bonds have the direction “up”. In the structure with polarity 2 (positive positional parameters  $z$  for such atoms), the red N–H bonds have the direction “down”. Isotropic displacement spheres of 50% are shown with  $U = 0.0300$  Å<sup>2</sup> for C, O, N and  $U = 0.0200$  Å<sup>2</sup> for H. The red N–H distances are 1.026 Å. The fragmented red N–H⋯N hydrogen bonds are 2.14 Å. The chains of N–H⋯N contacts are zigzag shaped and run along [001]. The carbon atoms with  $z = 0$  have the same coordinates.

for the N, O, and H atoms (Table 1). In this case the N–H bonds with 1.026 Å in slightly zigzag chains have the direction “up” parallel to  $c$ . In the HNCO structure with polarity 2 with positive positional parameters  $z$  for the O, N, and H atoms, the N–H bonds have the direction “down”. In both polarities the  $z$  parameter of the C atoms is fixed to  $z = 0$ . Interestingly, in HNCO short hydrogen distances of the type N–H⋯N exist with 2.14 Å but none exist for N–H⋯O, although oxygen is more electronegative than nitrogen. The N–H bonds create hydrogen bonds as one-dimensional zigzag shaped chains along [001].

**3.4. Crystal Chemical Properties.** Interatomic distances (Å) and angles (deg) for HNCO of previous investigations<sup>10,11,14</sup> and those obtained by this investigation with DFT calculations (WIEN2k<sup>19</sup>) are summarized in Table 3.

The best agreement in Table 3 between the previous results and those obtained by DFT calculations is achieved by Jones et al.<sup>12</sup> with microwave and infrared investigations in the gas phase. In the previous X-ray diffraction investigation,<sup>16</sup> the hydrogen atoms could not be detected due to the low crystal quality. Regarding the interatomic distances N–C and C–O, identical values of 1.18(2) Å were obtained for both. However, in this study the C–O distance (1.17 Å) is smaller than the N–C distance (1.22 Å), as also observed by microwave and

**Table 3. Interatomic Distances (Å) and Angles (deg) Determined by Previous Investigations in HNCO by Electron Diffraction,<sup>11</sup> Microwave, and Infrared Spectroscopy<sup>12</sup> in the Gas Phase and X-ray Diffraction<sup>16</sup> in the Solid State and Those Obtained by DFT Calculations with WIEN2k<sup>19</sup>**

exptl technique	H–N	N–C	C–O	H–N–C	C–N–O	N–H···N	N–H···N/H–N···H
electron diffraction <sup>11</sup> (gas phase)	1.01 (est) <sup>a</sup>	1.19	1.19	125 (est)			
microwave, infrared <sup>12</sup> (gas phase)	0.99(1)	1.21(1)	1.17(1)	128(1)			
X-ray diffraction <sup>16</sup> (solid state)		1.18(2)	1.18(2)				
this study, DFT, WIEN2k <sup>19</sup>	1.03	1.22	1.17	124	171	2.14	164/133

<sup>a</sup>Estimated.

**Table 4. Average Interatomic Distances (Å) in HN<sub>3</sub> for H–N<sub>I</sub>, N<sub>I</sub>–N<sub>II</sub>, N<sub>II</sub>–N<sub>III</sub>, N–H···N<sub>short</sub>, N–H···N<sub>long</sub> and Average Angles (deg) H–N<sub>I</sub>–N<sub>II</sub>, N<sub>I</sub>–N<sub>II</sub>–N<sub>III</sub>, as Determined by X-ray Single Crystal Investigation<sup>18</sup>**

H–N <sub>I</sub> (Å)	N <sub>I</sub> –N <sub>II</sub> (Å)	N <sub>II</sub> –N <sub>III</sub> (Å)	H–N <sub>I</sub> –N <sub>II</sub> (deg)	N <sub>I</sub> –N <sub>II</sub> –N <sub>III</sub> (deg)	N–H···N <sub>short</sub> (Å)	N–H···N <sub>long</sub> (Å)
0.82(20)	1.233(4)	1.121(4)	109(4)	172.8(3)	2.24(20)	2.78(20)

infrared spectroscopic investigations in the gas phase, 1.17(1) and 1.21(1) Å, respectively, by Jones et al.<sup>12</sup>

In this investigation no evidence of an orthorhombic phase was found, which was observed by von Dohlen and Carpenter.<sup>16</sup> In addition to the structural investigation at 123(2) K (Table 1), a search within 24 h for an orthorhombic phase was performed by measurements at 100(5), 120(5), 140(5), 160(5), 165(5), 170(5), 175(5), 180(5), and 185(5) K. In all cases only the slightly varying orthorhombic lattice parameters in the range 5.62–5.68 Å were obtained. Therefore, it must be concluded that the phase of von Dohlen and Carpenter<sup>16</sup> is metastable, if obtained by depolymerization of cyanuric acid and not by protonation of cyanate by stearic acid. Also, from WIEN2k<sup>19</sup> calculations it is evident that the total energy of the HNCO phase of von Dohlen and Carpenter<sup>16</sup> is a few kJ/mol higher than our HNCO phase related to CO<sub>2</sub>. Interestingly, a refinement of von Dohlen's positional parameters<sup>16</sup> by DFT calculations<sup>34</sup> with WIEN2k<sup>19</sup> showed that in this phase N–H···O hydrogen bonds are present.

As already mentioned, the anions OCN/NC<sup>−</sup> and N<sub>3</sub><sup>−</sup> are isosteric, but the crystal structures of HNCO and HN<sub>3</sub><sup>18</sup> differ significantly. In HNCO only one short N–H···N hydrogen bond of 2.14 Å is observed connecting the HNCO molecules to one-dimensional zigzag chains along [001]. Hydrazoic acid contains 16 formula units in the unit cell, space group C1c1, and four crystallographic independent HN<sub>3</sub> molecules. Here, the N–H···N hydrogen bonds are bifurcated into shorter distances (Table 4, N–H···N<sub>short</sub> 2.24(20) Å) and longer distances (Table 4, N–H···N<sub>long</sub> 2.78(20) Å). With this connection a two-dimensional layer structure is created, with 4-, 8-, and 16-membered rings formed by (HN<sub>3</sub>)<sub>4</sub> tetramers. Displacement ellipsoids show their highest values perpendicular to the layers, indicating only weak van der Waals forces between them. In Table 4 the average distances and angles in solid HN<sub>3</sub> are summarized with labeling as H–N<sub>I</sub>–N<sub>II</sub>–N<sub>III</sub>.<sup>18</sup>

Upon comparison of the H–N interatomic distances in HNCO and HN<sub>3</sub> according Tables 3 and 4, it is obvious that the N–C distance with 1.22 Å in HNCO is comparable to the N<sub>I</sub>–N<sub>II</sub> distance with 1.233(4) Å in HN<sub>3</sub>. However, the C–O distance with 1.17 Å in HNCO is remarkably longer than the N<sub>II</sub>–N<sub>III</sub> distance with 1.121(4) Å in HN<sub>3</sub>. The angles N–C–O with 171° in HNCO and N<sub>I</sub>–N<sub>II</sub>–N<sub>III</sub> with 172.8(3)° in HN<sub>3</sub> deviate only by 2°. The strongest deviation is found for the N–H distances. In HNCO it was calculated by DFT to 1.03 Å, but in HN<sub>3</sub>, determined by X-ray diffraction, the averaged distance is 0.82(20) Å which is 0.21 Å smaller than in HNCO. The

smaller value results from the fact that the hydrogen atom in HN<sub>3</sub> does not have a core electron.<sup>35</sup> Therefore, the determined N–H distance is too short by X-rays.<sup>35</sup> A N–H distance of approximately 1.03 Å, as calculated by WIEN2k<sup>19</sup> in HNCO, can also be approximately assumed for HN<sub>3</sub>.

Although HNCO and HN<sub>3</sub> are isosteric acids, there are small, but significant differences for the melting and boiling points, as well as the acid constants pK<sub>a</sub>, as displayed in Table 5.

**Table 5. Melting/Boiling Points and Acid Constants pK<sub>a</sub> for HNCO and HN<sub>3</sub>**

	melting point (°C)	boiling point (°C)	acid constant pK <sub>a</sub>
HNCO	−86.8, <sup>8</sup> −86 <sup>36</sup>	23.5, <sup>8</sup> 23 <sup>36</sup>	3.9, <sup>8</sup> 3.7 <sup>36</sup>
HN <sub>3</sub>	~−80, <sup>9</sup> −80 <sup>36</sup>	35.7, <sup>9</sup> 35.7 <sup>36</sup>	4.8, <sup>9</sup> 4.6 <sup>36</sup>

The bonding in HNCO is to a small degree slightly weaker than in HN<sub>3</sub>. Therefore, the melting point for the first is approximately 6 °C lower (Table 5). This tendency holds also for the boiling point of HNCO which is approximately 12 °C lower than in HN<sub>3</sub>. The one-dimensional chains in HNCO (Figure 2) seem to be slightly weaker than the two-dimensional net in HN<sub>3</sub> with a layer structure formed by bifurcated hydrogen bonds.

These structural facts are also reflected in the acid–base properties of HNCO and HN<sub>3</sub>. The pK<sub>a</sub> acid constant for HNCO is nearly 1 unit of magnitude lower than that in HN<sub>3</sub>, indicating a weaker N–H···N bond and therefore slightly stronger acid properties for HNCO.

Although HNCO has slightly weaker hydrogen-bonding than HN<sub>3</sub>, the cell volume for one formula unit of HNCO at 1 bar (44.35 Å<sup>3</sup>, 123(2) K) is approximately 11% lower than that for HN<sub>3</sub> (49.68 Å<sup>3</sup>, 100(2) K). In this case the sizes of molecules with different composition are compared to each other. However, one N-atom is also present in HNCO, and the sizes of the remaining two atoms C and O with covalent radii *r* for *r*<sub>C</sub> = 0.77 Å and *r*<sub>O</sub> = 0.66 Å (with a sum of 0.77 + 0.66 = 1.43 Å)<sup>37</sup> can be approximately substituted by two N-atoms with *r*<sub>N</sub> = 0.70 Å (with a sum of 0.70 + 0.70 = 1.40 Å).<sup>37</sup> Since the layers in HN<sub>3</sub> containing 4-, 8-, and 16-membered rings create large voids, it can be expected that squeezing of HN<sub>3</sub> (with HN<sub>3</sub> structure) could probably lead to a transformation into a more densely packed polymorph with HNCO structure.

However, as our own experimental experience shows, filling a high pressure diamond cell with liquid HN<sub>3</sub> at ambient pressure in a cooling room at *T* = −20 °C is not an easy experimental

task.  $\text{HN}_3$  is a strong poison, highly explosive, and has a high vapor pressure. The difference of the boiling temperatures of diethyl ether ( $\text{Et}_2\text{O}$ ) and hydrazoic acid ( $\text{HN}_3$ ) is about  $1^\circ\text{C}$ .<sup>38</sup> However, one could obtain isotopic structures for HNCO at 1 bar and at  $-86^\circ\text{C}$  and for  $\text{HN}_3$  squeezed in a diamond cell. Then, electrons may arrange themselves in the same manner, thus clearly fulfilling Langmuir's criterion for isosterism<sup>1</sup> also for these solids.

#### 4. CONCLUSION

Isocyanic acid (space group  $Pca2_1$ ), the imide of carbon dioxide shows strong structural relations to  $\text{CO}_2$  ( $Pa\bar{3}$ ). The lattice parameters of orthorhombic HNCO (123 K) are pseudocubic ( $Pca2_1$ ) and deviate only on the second digit from that of cubic  $\text{CO}_2$ . In solid  $\text{CO}_2$  isolated molecules are bound to each other by only weak van der Waals bonds in a molecular structure.

From a topological projection of the crystal structure of  $\text{CO}_2$  on the crystal structure of HNCO without hydrogen atoms, it is shown that the C, N, and O atoms are only slightly shifted. The strongest shift is found for the carbon atoms with  $0.15\text{ \AA}$ , for the oxygen atoms O with  $0.27$ , and for the O<sup>i</sup> and N atoms with  $-0.18\text{ \AA}$ , respectively. In HNCO, short  $\text{N-H}\cdots\text{N}$  hydrogen bonds ( $2.14\text{ \AA}$ ) connect the molecules to one-dimensional zigzag chains. Due to the polar space group  $Pca2_1$ , there are two structures for HNCO, e.g. one with the  $\text{N-H}$  bond showing upward in the chain, and the other one downward.

The comparison of the two isosteric acids shows that HNCO with chains of one-dimensional hydrogen bonds is slightly weaker bonded than  $\text{HN}_3$  with bifurcated hydrogen bonds in plane layers, resulting in lower melting and boiling points for the first and also slightly stronger acid–base properties.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b00557.

Topological projection of the crystal structure of  $\text{CO}_2$  on the crystal structure of HNCO (PDF)  
 HNCO  $Pca2_1$ , X-ray diffraction (CIF)  
 HNCO  $Pca2_1$ , DFT (CIF)  
 HNCO  $Pnma$ , DFT (CIF)

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##### Notes

The authors declare no competing financial interest.

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