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 anion to carbon dioxide: (for CO2, cP12, Pa3, a = 5.624(2) Å, 150 K, C−O 1.151(2) Å; for HNCO, cP16, Pca21, 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 (CO2) and dinitrogen monoxide (N2O), including e.g. critical temperatures and pressures, densities of the liquids, viscosities, and refractive indexes, and introduced the principle of isosterism.1 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.1 In this case, the compounds or groups of atoms are said to be isosteric.2 For CO2 and N2O 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 CO2, either neutral or charged, are known today.3−7

Both the three-atom heterocumulenic cyanate and azide anions possess 22 total e, corresponding to the weak acids isocyanic acid HNCO8 and hydrazoic acid HN3,9 respectively. In 1919 Langmuir gave a first indication of their isosterism.8 Isocyanic acid was first prepared by Liebig and Wöhler10 in 1830. However, information on the molecular geometry on HNCO was obtained about 100 years later in the decade 1940−1950 by electron diffraction,11 by microwave,12 and by infrared spectroscopy,13,14 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.15

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.16 The resulting distances C−O and N−C (1.18(2) Å, 2x) 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 NOx. In this case an aqueous solution of urea ((NH2)2CO) is added to the exhausts of the engine. In the catalytic reduction system, urea is thermally decomposed into ammonia (NH3) 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,17 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 HN3. The structure of HN3 was recently solved by an X-ray single crystal investigation at
100(2) K\textsuperscript{18} and shows a very interesting two-dimensional net, formed by bifurcated hydrogen bonds, in which tetramers (HN\textsubscript{4})\textsubscript{4} were found in a nearly planar net of 4+, 8-, and 16-membered rings. Now, a structural investigation of HNCO in the space group \textit{Pca\textsubscript{2}1}, is reported, including refinement of the positional parameters by DFT calculations with the program WIEN2k\textsuperscript{19}.

### 2. EXPERIMENTAL SECTION

#### 2.1. General Information

Isocyanic acid HNCO was prepared from potassium cyanate KOCN and stearic acid as previously reported.\textsuperscript{15} 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.

#### 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 diachronometer. 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 \textit{hkl} ranges of the measured reflections were the following: \textit{h} from −8 to 7, \textit{k} from −8 to 8, and \textit{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\textsuperscript{16} was negative. Structural calculations on HNCO (\textit{Pca\textsubscript{2}1}) were performed with SHELXL-2014.\textsuperscript{20} 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\textsuperscript{19} program. We utilized the generalized gradient approximation of Perdew et al.\textsuperscript{21} and treated the weak but important van der Waals interactions using DFT-D\textsuperscript{3}.\textsuperscript{22} The atomic sphere radii \textit{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, \textit{R}_{\text{KMAX}} was set to 4 and the charge density and potential was expanded in plane waves up to \textit{GMAX} = 20. For the calculations with \textit{Pca\textsubscript{2}1}, a \(4 \times 4 \times 4\) mesh was used, and for that with \textit{Pnma}, there is a \(2 \times 2 \times 8\) 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>
<thead>
<tr>
<th>crystal syst</th>
<th>orthorhombic</th>
</tr>
</thead>
<tbody>
<tr>
<td>space group</td>
<td>\textit{Pca\textsubscript{2}1}</td>
</tr>
<tr>
<td>\textit{a} (Å)</td>
<td>5.6176(9)</td>
</tr>
<tr>
<td>\textit{b} (Å)</td>
<td>5.6236(8)</td>
</tr>
<tr>
<td>\textit{c} (Å)</td>
<td>5.6231(7)</td>
</tr>
<tr>
<td>\textit{T} (K)</td>
<td>123(2)</td>
</tr>
<tr>
<td>\textit{V} (Å\textsuperscript{3})</td>
<td>177.64(4)</td>
</tr>
<tr>
<td>\textit{Z}</td>
<td>4</td>
</tr>
<tr>
<td>4 H, 4 N, 4 C, 4 O</td>
<td>4a</td>
</tr>
<tr>
<td>\textit{ρ}_{\text{calc}} (g cm\textsuperscript{-3})</td>
<td>1.609</td>
</tr>
<tr>
<td>reflns measured</td>
<td>1390</td>
</tr>
<tr>
<td>reflns unique</td>
<td>339</td>
</tr>
<tr>
<td>\textit{R}(\sigma)</td>
<td>0.0260</td>
</tr>
<tr>
<td>\textit{R}1</td>
<td>0.0352</td>
</tr>
<tr>
<td>\textit{wR}2</td>
<td>0.0887</td>
</tr>
<tr>
<td>GOF</td>
<td>1.175</td>
</tr>
</tbody>
</table>

*Structural analysis with the SHELXL-2014\textsuperscript{20} 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 \textit{Pca\textsubscript{2}1}, with 4 formula units in the unit cell. The positional parameters determined from the X-ray diffraction structure analysis by the program SHELXL-2014\textsuperscript{20} lead to both very short C–O (ranging from 1.09(1) to 1.04(1) Å) and very long C–N (ranging from 1.30(1) to 1.36(1) Å) distances, since in space group \textit{Pca\textsubscript{2}1}, 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.\textsuperscript{19} In Table 2 the calculated positional parameters of solid isocyanic acid HNCO in the polar space group \textit{Pca\textsubscript{2}1} are summarized.

<table>
<thead>
<tr>
<th>atom</th>
<th>\textit{x}</th>
<th>\textit{y}</th>
<th>\textit{z}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.0273</td>
<td>0.2699</td>
<td>0.0000</td>
</tr>
<tr>
<td>O</td>
<td>0.3329</td>
<td>0.3770</td>
<td>−0.6121</td>
</tr>
<tr>
<td>N</td>
<td>0.8733</td>
<td>0.1437</td>
<td>−0.9142</td>
</tr>
<tr>
<td>H</td>
<td>0.1755</td>
<td>0.8520</td>
<td>−0.2386</td>
</tr>
</tbody>
</table>

*The C-, N-, and O-atoms have been all located in Wyckoff position 4a. Starting parameters were those obtained by the program SHELXL-2014.\textsuperscript{20} These atomic positions were then refined with WIEN2k. The positions of the H-atoms were derived \textit{ab initio}. Details of the calculations are given in the Experimental Section.*
crystallizes in the orthorhombic space group Pca21 with pseudocubic lattice parameters \(a = 5.6176(9) \, \text{Å}, b = 5.6236(8) \, \text{Å}, c = 5.6231(7) \, \text{Å}\) at 123 K. Hence, HNCO easily suggests a structural comparison of CO2 and HNCO in a group—subgroup relation \(^{24−31}\) (Figure 1).

In Figure 2, a Diamond view \(^{33}\) along [100] for the polar structure of HNCO in Pca21 is shown with polarity 1 (negative positional parameters \(z\)) 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 such atoms, the red N−H bonds have the direction “down”. Isotropic displacement spheres of 50% are shown with \(U = 0.0300 \, \text{Å}^2\) for C, O, N and \(U = 0.0200 \, \text{Å}^2\) 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.

### 3.4. Crystal Chemical Properties

Interatomic distances (Å) and angles (deg) for HNCO of previous investigations \(^{10,11,14}\) and those obtained by this investigation with DFT calculations (WIEN2k \(^{19}\)) 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. \(^{12}\) with microwave and infrared investigations in the gas phase. In the previous X-ray diffraction investigation, \(^{16}\) 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
infrared spectroscopic investigations in the gas phase, 1.17(1) and 1.21(1) Å, respectively, by Jones et al.11

In this investigation no evidence of an orthorhombic phase was found, which was observed by von Dohlen and Carpenter.16 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 is metastable, if obtained by depolymerization of cyanuric acid and not by protonation of cyanate by stearic acid. Also, from WIEN2k calculations it is evident that the total energy of the HNCO phase of von Dohlen and Carpenter16 is metastable, if obtained by depolymerization of cyanuric acid and not by protonation of cyanate by stearic acid. Therefore, the determined −N−H distance is too short by X-rays. A N−H distance of approximately 1.03 Å, as calculated by WIEN2k in HNCO, can also be approximately assumed for HN3.

Although HNCO and HN3 are isosteric acids, there are small, but significant differences for the melting and boiling points, as well as the acid constants pKα, as displayed in Table 5.

<table>
<thead>
<tr>
<th>H−N (Å)</th>
<th>N−H−N (Å)</th>
<th>H−N−C (Å)</th>
<th>H−N−C (deg)</th>
<th>N−H−N (Å)</th>
<th>N−H−N (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.82(20)</td>
<td>1.233(4)</td>
<td>1.121(4)</td>
<td>109(4)</td>
<td>172.8(3)</td>
<td>2.24(20)</td>
</tr>
</tbody>
</table>

Table 5. Melting/Boiling Points and Acid Constants pKα for HNCO and HN3

<table>
<thead>
<tr>
<th>melting point (°C)</th>
<th>boiling point (°C)</th>
<th>acid constant pKα</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNCO</td>
<td>−86.8,8 −86.56</td>
<td>23.5,8 23.75</td>
</tr>
<tr>
<td>HN3</td>
<td>−80.5,5 −80.56</td>
<td>35.7,5 35.75</td>
</tr>
</tbody>
</table>

The bonding in HNCO is to a small degree slightly weaker than in HN3. 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 HN3. The one-dimensional chains in HNCO (Figure 2) seem to be slightly weaker than the two-dimensional net in HN3 with a layer structure formed by bifurcated hydrogen bonds.

These structural facts are also reflected in the acid—base properties of HNCO and HN3. The pKa acid constant for HNCO is nearly 1 unit of magnitude lower than that in HN3, indicating a weaker N−H−N bond and therefore slightly stronger acid properties for HNCO.

Although HNCO has slightly weaker hydrogen-bonding than HN3, the cell volume for one formula unit of HNCO at 1 bar (44.35 Å³, 123(2) K) is approximately 11% lower than that for HN3 (49.68 Å³, 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 HN3, which is also present in HNCO, and the sizes of the remaining two atoms C and O with covalent radii r for rC = 0.77 Å and rO = 0.66 Å (with a sum of 0.77 + 0.66 = 1.43 Å) can be approximately substituted by two N-atoms with rN = 0.70 Å (with a sum of 0.70 + 0.70 = 1.40 Å). Since the layers in HN3 containing 4-, 8-, and 16-membered rings create large voids, it can be expected that squeezing of HN3 (with HN3 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 HN3 at ambient pressure in a cooling room at T = −20 °C is not an easy experimental
task. HN₃ is a strong poison, highly explosive, and has a high vapor pressure. The difference of the boiling temperatures of diethyl ether (Et₂O) and hydrazoic acid (HN₃) is about 1 °C.³⁸ However, one could obtain isotypic structures for HNCO at 1 bar and at −86 °C and for HN₃ squeezed in a diamond cell. Then, electrons may arrange themselves in the same manner, thus clearly fulfilling Langmuir’s criterion for isosterism also for these solids.

4. CONCLUSION

Isocyanic acid (space group Pca₂ᵢ), the imide of carbon dioxide shows strong structural relations to CO₂ (Pca). The lattice parameters of orthorhombic HNCO (123 K) are pseudocubic (Pca₂) and deviate only on the second digit from that of cubic CO₂. In solid CO₂ 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 CO₂ 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 Å, for the oxygen atoms O with 0.27, and for the Oᵢ and N atoms with −0.18 Å, respectively. In HNCO short N−H−N hydrogen bonds (2.14 Å) connect the molecules to one-dimensional zigzag chains. Due to the polar space group Pca₂, there are two structures for HNCO, e.g. one with the 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 HN₃ with bifurcated hydrogen bonds in plane layers, resulting in lower melting and boiling points for the first and also slightly stronger acid−base properties.

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(25) Bärnighausen, H. Group-Subgroup Relations Between Space-groups. *MATCH, Communications in Mathematical Chemistry* 1980, 9, 139.


(34) Blaha, P. DFT calculation with WIEN2k for HNCO, unpublished results: *Pnma*, \(a = 10.82 \text{ Å}, b = 5.23 \text{ Å}, c = 3.57 \text{ Å}, N (0.4301, 1/4, 0.4041), C (0.3259, 1/4, 0.281), O (0.2192, 1/4, 0.2103), H (0.5128, 1/4, 0.2700).


(38) Beyer, H. *Lehrbuch der Organischen Chemie*; S. Hirzel Verlag: Leipzig, 1967; p 112. The boiling temperature of Et2O is 34.6 °C compared to 35.7 °C for HN3 (Table 5).