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

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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: (CO₂: *cP12*, *Pa*–3, *a* = 5.624(2) Å, 150 K, C–O 1.151(2) Å; HNCO: *oP16*, *Pca*₂₁, *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, –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

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2 isosterism.¹ If compounds with the same number of atoms have also the same total number of
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4 electrons, the electrons may arrange themselves in the same manner.¹ In this case the compounds or
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6 groups of atoms are said to be isosteric.¹ For CO₂ and N₂O there are three atoms and 22 total or 16
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8 valence electrons (e). Langmuir's concept is extraordinary useful in predicting properties of
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10 isosteric molecular species. About 26 isosteric species to CO₂, either neutral or charged, are known
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12 today.¹⁻⁷

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14 Both, the three-atomic heterocumulenic cyanate and azide anions possess 22 total e, corresponding
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16 to the weak acids isocyanic acid HNCO⁸ and hydrazoic acid HN₃,⁹ respectively. In 1919 Langmuir
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18 gave a first indication to their isosterism.¹ Isocyanic acid was first prepared by Liebig and Wöhler¹⁰
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20 in 1830. However, information on the molecular geometry on HNCO was obtained about 100 years
21
22 later in the decade 1940–1950 by electron diffraction,¹¹ by microwave¹² and infra-red
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24 spectroscopy,^{13,14} all performed in the gas phase. As a result from those studies, the C–O, N–C and
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26 N–H distances were determined to 1.17, 1.21 and 0.99 Å, respectively, with the hydrogen atom
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28 being connected to nitrogen with an H–N–C angle of 128°. More recent studies regarding synthesis
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30 and properties of HNCO were reported in our laboratory.¹⁵

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

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49 Apart from the interests of theoretical and synthetic chemistry for isocyanic acid, special
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51 importance arises now due to its role in urban air pollution and possible toxicity. Cars with gasoline
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53 and diesel engines are known to emit HNCO, especially if selective catalytic reduction systems are
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55 used to reduce the emission of nitrogen oxides NO_x. In this case an aqueous solution of urea
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1
2 ((NH₂)₂CO) is added to the exhausts of the engine. In the catalytic reduction system urea is
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4 thermally decomposed into ammonia (NH₃) and isocyanic acid (HNCO). The last compound is
5
6 rapidly decomposed with water on the catalyst surface into ammonia and carbon dioxide. However,
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8 there remains emission of HNCO in the range between 30 and 50 mg HNCO/kg-fuel¹⁷ which is the
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10 found in the urban air pollution and could affect negatively human health.
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15 Of special interest is the comparison of the crystal structures of the isosteric acids HNCO and HN₃.
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17 The structure of HN₃ was recently solved by X-ray single crystal investigation at 100(2) K¹⁸ and
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19 shows a very interesting two-dimensional net, formed by bifurcated hydrogen bonds, in which
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21 tetramers (HN₃)₄ were found in a nearly plane net of four-, eight- and sixteen-membered rings.
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23 Now, a structural investigation of HNCO in the space group *Pca*2₁ is reported, including refinement
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25 of the positional parameters by DFT calculations with the program WIEN2k.¹⁹
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31 **2. EXPERIMENTAL SECTION**

32 **2.1. General Information**

33
34 Isocyanic acid HNCO was prepared from potassium cyanate KOCN and stearic acid as previously
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36 reported.¹⁵ Both educts were intensively ground and filled in a Duran reactor which had at one side
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38 a thin-walled X-ray capillary. The reactor with the starting materials was dried at a high vacuum
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40 line while cooling with liquid nitrogen traps.
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49 **2.2. X-Ray Crystallography**

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51 After several days of drying, the reactor was sealed from the vacuum line and then slowly heated to
52
53 60 °C. Stearic acid melts near this temperature and then the formation of gaseous HNCO starts.
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55 Isocyanic acid condenses at the capillary, which is cooled with liquid nitrogen and then sealed.
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2 From each heating experiment three capillaries filled with HNCO were obtained, which were stored
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4 in liquid nitrogen.
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8 Single crystals of HNCO for the structure determination were grown *in situ* in the capillary adjusted
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10 to the Oxford Xcalibur diffractometer. Several cooling and heating cycles are required to obtain a
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12 single crystal in order to check the diffraction pattern. The structure was determined at 123(2) K.
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14 The *hkl* ranges of the measured reflections were: *h* from -8 to 7, *k* from -8 to 8, *l* from -8 to 8.
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16 Within a 24 h cooling and heating procedure from 100(5) to 185(5) K searching for the
17
18 orthorhombic phase of von Dohlen and Carpenter¹⁶ was negative. Structural calculations on HNCO
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20 (*Pca2*₁) were performed with SHELXL-2014.²⁰ The investigated crystal was disordered and
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22 contained two individuals with 55% and 45%. The individuals were rotated against each other with
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24 oxygen and nitrogen atoms nearly lying above each other. Therefore hydrogen atoms could not be
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26 detected from a difference Fourier analysis. In addition, with the position derived by SHELXL-
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28 2014 unrealistic short C-O and unrealistic long C-N distances had been obtained.
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35 **2.3. Density Functional Theory (DFT) Calculations**

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37 The theoretical calculations are based on density functional theory (DFT) and were performed with
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39 the augmented plane wave + local orbital method as implemented in the WIEN2k¹⁹ program. We
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41 utilized the generalized gradient approximation of Perdew et al.²¹ and treated the weak but
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43 important van der Waals interactions using DFT-D3.²² The atomic sphere radii R_{MT} were chosen as
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45 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
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47 wave functions, R^*K_{MAX} was set to 4 and the charge density and potential was expanded in plane
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49 waves up to $G_{MAX}=20$. For the calculations with *Pca2*₁ a 4x4x4 mesh was used, for that with *Pnma* a
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51 2x4x8 mesh. We used experimental lattice parameters in all cases, but refined the positional
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53 parameters of all atoms until the forces were well below 1 mRy/bohr. Since the position of the H
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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. HNCO crystallizes in the orthorhombic acentric space group $Pca2_1$ with 4 formula units in the unit cell. The positional parameters determined from the X-ray diffraction structure analysis by the program SHELXL-2014²⁰ 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 it is in space group $Pca2_1$ difficult to grow polarity pure single crystals.

Table 1: Crystallographic data of solid HNCO, determined at 123(2) K by X-ray single crystal investigation. Structural analysis with the SHELXL-2014²⁰ 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.

Crystal system	orthorhombic
Space group	$Pca2_1$
$a(\text{Å})$	5.6176(9)
$b(\text{Å})$	5.6236(8)
$c(\text{Å})$	5.6231(7)
$T(\text{K})$	123(2)
$V(\text{Å}^3)$	177.64(4)
Z	4
4 H, 4 N, 4 C, 4 O	4 a
$\rho_{\text{calc}}(\text{g}\cdot\text{cm}^{-3})$	1.609(4)
Reflections measured	1390

Reflections unique	339
$R(\sigma)$	0.0260
$R1$	0.0352
$wR2$	0.0887
GOF	1.175
Highest residual electron density ($e/\text{\AA}^{-3}$)	+0.10/-0.17

3.2. DFT Results

Therefore, it was decided to perform DFT calculations with the program WIEN2k.¹⁹ In Table 2 the calculated positional parameters of solid isocyanic acid HNCO in the polar space group $Pca2_1$ are summarized.

Table 2: Positional parameters x , y , z of solid isocyanic acid HNCO in space group $Pca2_1$ derived by DFT calculations with the program WIEN2k.¹⁹ The C-, N- and O-atoms have been all located in Wyckoff position $4a$. Starting parameters were those obtained by the program SHELXL-2014.²⁰ These atomic positions were then refined with WIEN2k.¹⁹ The positions of the H-atoms were derived *ab-initio*. Details of the calculations are given in the Experimental Section.

Atom	x	y	z
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

3.3. Group-Subgroup Relations

Solid carbon dioxide CO_2 ²³ crystallizes at ambient pressure in the cubic space group $Pa-3$ with four molecules in the unit cell. The lattice parameter is $a = 5.624(2) \text{ \AA}$ ²³ at 150 K leading to a unit-cell volume $V = 177.88(20) \text{ \AA}^3$. Solid isocyanic acid HNCO (Table 1) crystallizes in the orthorhombic space group $Pca2_1$ with pseudo-cubic lattice parameters $a = 5.6176(9)$, $b = 5.6236(8)$, $c = 5.6231(7) \text{ \AA}$ at 150 K. Hence, HNCO easily suggests a structural comparison of CO_2 and HNCO in a group-subgroup relation²⁴⁻³² (Figure 1).³³

Coming from cubic CO₂ ($P2_1/a-3$, No.205) the first step leads to a *translationengleich*²⁴⁻³¹ (t) step of index 3 (t3) to the maximal non-isomorphic subgroup $Pcab$ ($P 2_1/c 2_1/a 2_1/b$, 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 index2 (t2) and an origin change with $(0, -1/4, 0)$ to the maximal non-isomorphic subgroup $Pca2_1$. Here, position $8c$ in No.61 is changed into twice $4a$ in No.29 with changing the coordinates into x , $y+1/4$, z . In Figure 1 the group-subgroup relation is shown.

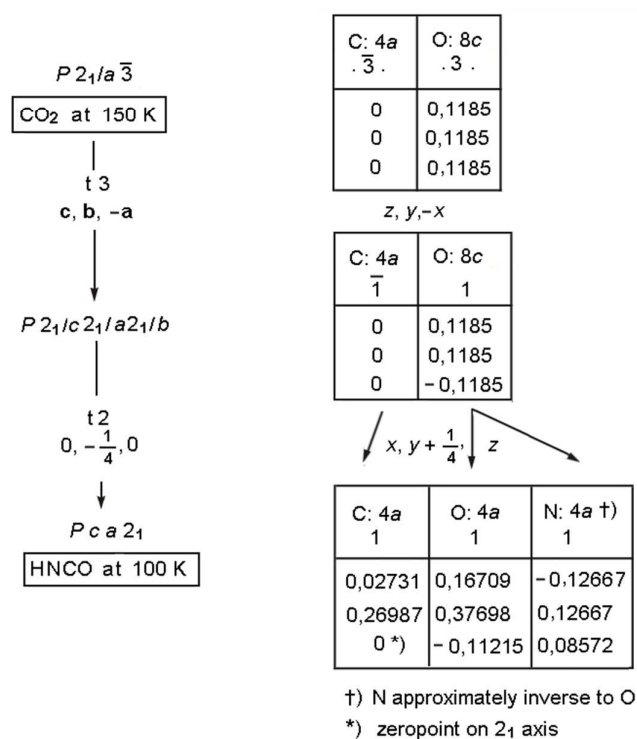


Figure 1. Group-subgroup relation²⁴⁻³¹ showing the symmetry reduction for CO₂ in the centrosymmetric cubic space group $P2_1/a-3$ (No.205) to $Pcab$ ($P2_1/c2_1/a 2_1/b$, No.61) and then for HNCO to the acentric polar orthorhombic space group $Pca2_1$ (No 29).

In CO₂ 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 $Pa-3$ to (0.1185, 0.1185, -0.1185) in $P2_1/c 2_1/a 2_1/b$. For CO₂ in $Pca2_1$ the C atoms have the coordinates (0, 1/4, 0), the O atom (0.1185, 0.3685, -0.1185) and the Oⁱ atom (-0.1185, 0.1315, 0.1185).

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2 The symmetry reduction of $Pa-3$ via $Pcab$ to $Pca2_1$ (Figure 1) leads to two polar structures. The
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4 polar structure 1 is obtained with the z parameters (Table 2, $z = -0.6121$ and $z = -0.9142$) for the O
5
6 and the N atom, respectively). In the polar structure 2 the z parameters are inverted to
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8 $z = 0.6121$ and $z = 0.9142$ for O and N, respectively. The polar structure 2 is obtained from polar
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10 structure 1 by reflection with a mirror.
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14 During the synthesis of HNCO with stearic acid and potassium cyanate (KOCN) and cooling to 100
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16 K, the obtained sample will contain approximately the same number of crystals with polarity 1 and
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18 with polarity 2. This could be a reason that the single crystal of HNCO used for the X-ray
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20 diffraction investigation was obtained only with low quality. In principle, the absolute configuration
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22 of a single crystal in space group $Pca2_1$ with good quality, investigated by X-ray diffraction, could
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24 be determined by anomalous dispersion.³² However, for elements with low scattering power as H, C, N
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26 and O, the contribution is only low and therefore it is not an easy procedure to distinguish then
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28 between such crystals.
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32 In Figure 2 a *Diamond view*³³ of the polar HNCO structure is shown with polarity 1 with negative
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34 positional parameters z for the N, O and H atoms (Table 1). In this case the $-N-H$ bonds with 1.026
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36 Å in slightly zigzag chains have the direction “up” parallel to c . In the HNCO structure with
37
38 polarity 2 with positive positional parameters z for the O, N and H atoms the $N-H$ bonds have the
39
40 direction “down”. In both polarities the z parameter of the C atoms is fixed to $z = 0$. Interestingly, in
41
42 HNCO short hydrogen distances of the type $N-H\cdots N$ exist with 2.136 Å but none of $N-H\cdots O$,
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44 although oxygen is more electronegative than nitrogen. The $N-H-$ and the $N-H\cdots N$ bonds create
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46 hydrogen bonds as one-dimensional zigzag shaped chains along [001].
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50 **3.4. Crystal Chemical Properties**

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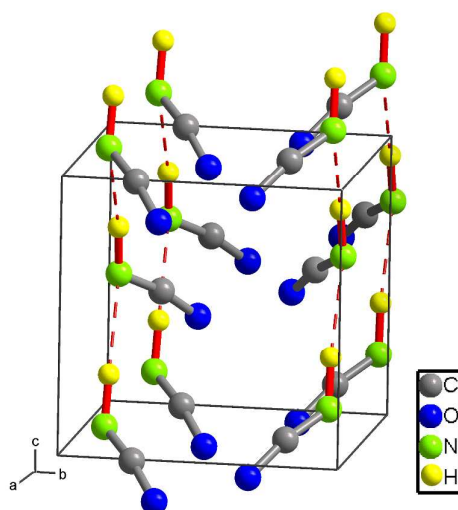


Figure 2. *Diamond view*³³ along [100] for the polar structure of HNCO in $Pca2_1$ is shown with polarity 1 (negative positional parameters z for the O, N and H atoms (Table 1). The red N–H bonds have the direction “up”. In the structure with polarity 2 (positive positional parameters z for such atoms),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

Interatomic distances (\AA) and angles ($^\circ$) for HNCO of previous investigations^{10,11,14} and those obtained by this investigation with DFT calculations (WIEN2k¹⁹) are summarized in Table 3.

Table 3. Interatomic distances (\AA) and angles ($^\circ$) determined by previous investigations in HNCO by electron diffraction¹¹, microwave and infra-red¹² in the gas phase and X-ray diffraction¹⁶ in the solid state and those obtained by DFT calculations with WIEN2k.¹⁹

Experimental Technique	H–N	N–C	C–O	H–N–C	C–N–O	–N–H \cdots N	–N–H \cdots N / H–N \cdots H–
electron diffraction ¹¹ (gas phase)	1.01(est.)*	1.19	1.19	125 (est.)			
microwave, infra-red ¹² (gas phase)	0.99(1)	1.21(1)	1.17(1)	128(1)			
X-ray diffraction ¹⁶ (solid state)	–	1.18(2)	1.18(2)	–			
this study, DFT, WIEN2k ¹⁹	1.03	1.22	1.17	124	171	2.14	164 / 133

* estimated

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 infra-red investigations in the gas phase. In the previous X-ray diffraction investigation¹⁶ the hydrogen atoms could not be detected due to the low

1
2 crystal quality. Regarding the interatomic distances N–C and C–O, identical values of 1.18(2) Å
3
4 were obtained for both. However, in this study the C–O distance (1.17 Å) is smaller than the N–C
5
6 distance (1.22 Å), as also observed by microwave and infra–red spectroscopic investigations in the
7
8 gas phase 1.17(1) and 1.21(1) Å, respectively, by Jones et al.¹²
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10
11 In this investigation no evidence of an orthorhombic phase was found, which was observed by von
12
13 Dohlen and Carpenter.¹⁶ In addition to the structural investigation at 123(2) K (Table 1), a search
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15 within 24 h for an orthorhombic phase was performed by measurements at 100(5), 120(5), 140(5),
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17 160(5), 165(5), 170(5), 175(5), 180(5) and 185(5) K. In all cases only the slightly varying
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19 orthorhombic lattice parameters in the range of 5.62 to 5.68 Å were obtained. Therefore, it must be
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21 concluded that the phase of von Dohlen and Carpenter¹⁶ is metastable, if obtained by
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23 depolymerization of cyanuric acid and not by protonation of cyanate by stearic acid. Also from
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25 WIEN2k¹⁹ calculations it is evident that the total energy of the HNCO phase of von Dohlen and
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27 Carpenter¹⁶ is about a few kJ/mole higher than that of the HNCO phase related to CO₂.
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29 Interestingly, a refinement of von Dohlen's positional parameters¹⁶ by DFT calculations³⁴ with
30
31 WIEN2k¹⁹ showed that in this phase N–H···O hydrogen bonds are present.
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37 As already mentioned, the anions OCN/NCO[−] and N₃[−] are isosteric, but the crystal structures of
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39 HNCO and HN₃¹⁸ differ significantly. In HNCO only one short N–H···N hydrogen bond of 2.14 Å
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41 is observed connecting the HNCO molecules to one–dimensional zig zag chains along [001].
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43 Hydrazoic acid contains 16 formula units in the unit–cell, space group *C1c1*, and four
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45 crystallographic independent HN₃ molecules. Here, the N–H···N hydrogen bonds are bifurcated into
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47 shorter distances (Table 4, N–H···N_{short} 2.24(20) Å) and longer distances (Table 4, N–H···N_{long}
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49 2.78(20) Å). With this connection a two–dimensional layer structure is created, with four–, eight–
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51 and sixteen–membered rings are formed by (HN₃)₄ tetramers. Displacement ellipsoids show their
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53 highest values perpendicular to the layers, indicating only weak van–der–Waals forces between
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55 them. In Table 4 the average distances and angles in solid HN₃ are summarized with labeling as H–
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59
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$N_I-N_{II}-N_{III}$.¹⁸

Table 4. Average interatomic distances (Å) in HN_3 for $H-N_I$, N_I-N_{II} , $N_{II}-N_{III}$, $N-H\cdots N_{short}$, $N-H\cdots N_{long}$ and average angles ($^\circ$) $H-N_I-N_{II}$, $N_I-N_{II}-N_{III}$, as determined by X-ray single crystal investigation.¹⁸

$H-N_I(\text{Å})$	$N_I-N_{II}(\text{Å})$	$N_{II}-N_{III}(\text{Å})$	$H-N_I-N_{II}(^\circ)$	$N_I-N_{II}-N_{III}(^\circ)$	$N-H\cdots N_{short}(\text{Å})$	$N-H\cdots N_{long}(\text{Å})$
0.82(20)	1.233(4)	1.121(4)	109(4)	172.8(3)	2.24(20)	2.78(20)

Upon comparison of the H-N interatomic distances in HNCO and HN_3 according Tables 4 and 5, it is obvious that the N-C distance with 1.22 Å in HNCO is comparable to the N_I-N_{II} distance with 1.233(4) Å in HN_3 . However, the C-O distance with 1.17 Å in HNCO is remarkably longer than the $N_{II}-N_{III}$ distance with 1.121(4) Å in HN_3 . The angles N-C-O with 171° in HNCO and $N_I-N_{II}-N_{III}$ with $172.8(3)^\circ$ in HN_3 deviate only by 2° . The strongest deviation is found for N-H distances. In HNCO it was calculated by DFT to 1.03 Å, but in HN_3 , 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_3 does not have a core electron.³⁵ Therefore the N-H distance is determined too short by X-rays.³⁵ A N-H distance of approximately 1.03 Å, as calculated by WIEN2k¹⁹ in HNCO, can also be approximately assumed for HN_3 .

Although HNCO and HN_3 are isosteric acids, there are small, but significant differences for the melting and boiling points, as well as the acid constants pK_a , as displayed in Table 5.

Table 5. Melting/boiling points and acid constants pK_a for HNCO and HN_3 .

	melting point ($^\circ\text{C}$)	boiling point ($^\circ\text{C}$)	acid constant pK_a
HNCO	$-86.8^8, -86^{36}$	$23.5^8, 23^{36}$	$3.9^8, 3.7^{36}$
HN_3	$\sim -80^9, -80^{36}$	$35.7^9, 35.7^{36}$	$4.8^9, 4.6^{36}$

The bonding in HNCO is to a small degree slightly weaker than in HN_3 . Therefore, the melting

1
2 point for the first is approximately 6 °C lower (Table 6). This tendency holds also for the boiling
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4 point of HNCO which is approximately 12 °C lower than in HN₃. The one-dimensional chains in
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6 HNCO (Figure 3) seem to be slightly weaker than the two-dimensional net in HN₃ with a layer
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8 structure formed by bifurcated hydrogen bonds.
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11 These structural facts are also reflected in the acid-base properties of HNCO and HN₃. The pK acid
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13 constant for HNCO is nearly one order of magnitude lower than in HN₃, indicating a weaker
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15 -N-H...N bond and therefore weakly stronger acid properties for HNCO.
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19 Although HNCO is slightly weaker hydrogen-bonded than HN₃, the cell-volume for one formula
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21 unit of HNCO at 1 bar (44.35 Å³, 123(2) K) is approximately 11 % lower than that for HN₃ (49.68
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23 Å³, 100(2) K). In this case the sizes of molecules with different composition are compared to each
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25 other. However, one N-atom is also present in HNCO and the sizes of the remaining two atoms C
26
27 and O with covalent radii r for the $r_C = 0.77$ Å and $r_O = 0.66$ Å (with a sum of $0.77 + 0.66 = 1.43$
28
29 Å)³⁷ can be approximately substituted by two N-atoms with $r_N = 0.70$ Å (with a sum of $0.70 + 0.70$
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31 = 1.40 Å).³⁷ Since the layers in HN₃ containing four-, eight- and sixteen-membered rings create
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33 large voids, it can be expected that squeezing of HN₃ (with HN₃ structure) could probably lead to a
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35 transformation into a more densely packed polymorph with HNCO structure.
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40 However, as our own experimental experience shows, filling a high pressure diamond cell with
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42 liquid HN₃ at ambient pressure in a cooling room at $T = -20$ °C is not an easy experimental task.
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44 HN₃ is a strong poison, very sensitive against moisture and has a high vapor pressure. The
45
46 difference of the boiling temperatures of diethylether (Et₂O) and hydrazoic acid (HN₃) is about
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48 1°C.³⁸ However, probably obtaining isotopic structures for HNCO at 1 bar and for HN₃ at -86 °C,
49
50 squeezed in a diamond cell, electrons may arrange themselves in the same manner, thus clearly
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52 fulfilling Langmuir's criterion for isosterism¹ also for these solids.
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4. CONCLUSION

Isocyanic acid (space group $Pca2_1$), the imide of carbon dioxide ($Pa/2_1-3$), shows strong structural relations to CO_2 . The lattice parameters of orthorhombic HNCO (123(2) K) are pseudo-cubic ($Pca2_1$) and deviate only on the second digit from that of cubic CO_2 . In solid 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 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 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 \cdots N hydrogen bonds (2.14 Å) 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 N-H bond showing upwards in the chain, and the other one downwards.

The comparison of the two isosteric acids shows that HNCO with chains of one-dimensional hydrogen bonds is slightly weaker bonded than 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.

4. ACKNOWLEDGEMENTS

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Supporting Information. The cif-file from the X-ray diffraction investigation for HNCO (*Pca2*₁), cif-files from the DFT calculations for HNCO (*Pca2*₁) and for HNCO (*Pnma*), and the topological projection of the crystal structure of CO₂ on the crystal structure of HNCO, are available free of charge via the Internet at <http://pubs.acs.org>.

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53 Et_2O is 34.6 °C compared to 35.7 °C for HN_3 (Table 5).

6. Table of Contents

51 Isocyanic acid HNCO is the imide of carbon dioxide, prepared by reaction of stearic acid and
52 potassium cyanate (KOCN) at 60 °C in a sealed, thoroughly dried reactor. Interestingly, the crystal
53 structure, solved by X-ray single crystal diffraction at 123(2) K, shows a group–subgroup relation
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2 for the NCO^- anion to carbon dioxide.
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7. Figure Table of Contents

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