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Communication

Nitrocarbamoyl Azide $O_2NN(H)C(O)N_3$: A Stable but Highly Energetic Member of the Carbonyl Azide Family

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ABSTRACT: The diazotization of nitrosemicarbazide (**1**) resulted in the formation and isolation of nitrocarbamoyl azide (**2**), which was thoroughly characterized by spectroscopic and structural methods. This compound shows surprising stability but also high reactivity and sensitivity, with a melting point of 72 °C and a detonative decomposition point at 83 °C. In addition, five selected salts were synthesized by careful deprotonation. The decomposition mechanism of **2** in solution was investigated and could be clarified by performing experiments using methanol and hydrazine as trapping reagents. The energetic and physicochemical properties of all these compounds were investigated and classified.

Although in most cases they are short-lived, carbonyl azides ($RC(O)N_3$) have been known for more than a century.[1,2] Especially their decomposition to form isocyanates, named after Curtius, makes them interesting and indispensable from a synthetic point of view.[3−5] Nevertheless, there are only a small number of well-characterized low-molecular-weight representatives. Synthesis and proper analysis are complicated by the low stability and often by the explosive nature of acyl azides.[6] Nevertheless, over the past few years it has been possible to completely analyze some simple carbonyl azides such as formyl azide and carbonyl diazide.[7−9] Other simple carbonyl azides such as carbamoyl azide or oxalyl diazide have been described in the literature, but their structures and properties are not yet fully understood (Figure 1).[10−14]

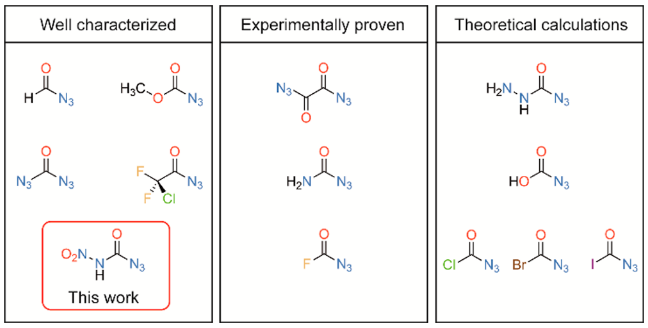

Figure 1. Smallest representatives of the carbonyl azide family.

Nitrocarbamoyl azide (HNCA, **2**) is another representative of this substance class that is interesting from many perspectives. Above all, this compound is characterized by the fact that with azide and nitramine functions it should have good energetic potential. This was also recognized by Bottaro et al., who attempted to synthesize NCA^- salts by nitration of carbamoyl azides.[15] However, the claimed ionic materials were examined only by IR spectroscopy.[15]

In addition, several questions regarding the molecule arise from an academic point of view. On one hand, the acidic proton of the nitramine unit offers many possibilities for functionalization of this site, but on the other hand, it is also uncertain to what extent the decomposition mechanism is affected. By following the Curtius rearrangement for the decomposition of carbonyl azides, HNCA would provide a platform for further chemistry with various nucleophiles. Furthermore, reactions with energetic building blocks could generate an innovative access to future energetic materials. In this contribution, the synthesis, properties, and crystal structures of pure nitrocarbamoyl azide and several of its salts and decomposition products are reported.

HNCA (**2**) can be synthesized by diazotization of nitrosemicarbazide (**1**)[16,17] with a slight excess of sodium nitrite in 2 M HCl at 0 °C. Yields of up to 76% can be achieved by rapid extraction of the reaction solution with diethyl ether and quick removal of the solvent under a nitrogen stream. These conditions proved to be particularly practicable and favorable, as direct access to neutral **2** was gained. (*Caution: it is strongly recommended that full body protection be worn during work with any compound discussed here.*) HNCA crystallizes in the form of colorless needle-shaped crystals and is stable under ambient conditions for several weeks. Salts were obtained by dissolving **2** in cold methanol and then adding 1 equiv of the respective bases (Scheme 1).

In order to obtain insight into the structure and bonding of HNCA, the molecular orbital (MO) energies were calculated for three different potential tautomers using the G09W code and various resonance structures using the VB2000 code

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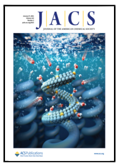

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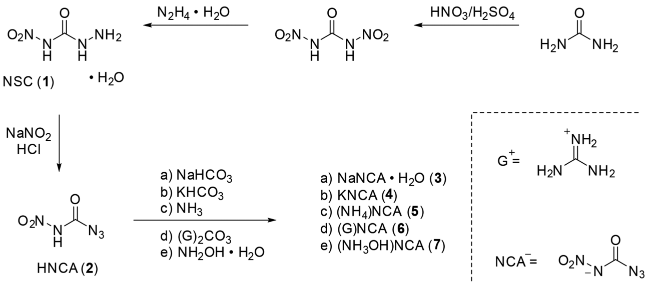
Scheme 1. Synthetic Pathway toward HNCA (2) and Its Salts 3−7



(version 2.8) (further details and results are provided in the Supporting Information). Of particular interest were the proton location as well as whether there was some indication supporting the presence of the closed tetrazole tautomer. The MO energies of the three tautomers in Figure 2 were calculated at the B3LYP/cc-pVDZ level. The energies of conformations **B** and **C** relative to the amide form **A** are 10.3 and 4.8 kcal mol^{-1}, respectively. The equilibrium is therefore strongly in favor of tautomer **A**.

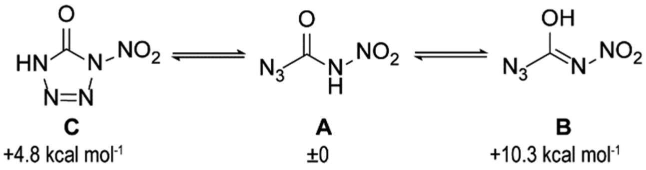


Figure 2. Tautomers of HNCA (**2**): **A**, amide form; **B**, iminol form; **C**, 1-nitrotetrazolone form. Energies relative to **A** are shown.

To confirm the theoretical findings, the focus was set on low-temperature single-crystal X-ray diffraction measurements. The crystal structures of compounds **1**−**8** were successfully determined. All of the data and structures are shown in the Supporting Information. Despite their high sensitivity toward external stimuli, crystalline **2** is fine to handle, and crystals suitable for X-ray measurements were obtained directly from the crude product. HNCA crystallizes in the monoclinic space group $P2_1/c$ with four molecular units per unit cell (Figure 3).

Similar to other comparable carbonyl azides, the azide group is syn to the carbonyl function with respect to the C−N$_\alpha$ bond.[8,18,19] The molecule itself is nearly planar. Although the azide group is almost in a plane with respect to C=O (N3−N2−N1−C1, 2.1(15)°; N2−N1−C1−O1, 178.62(15)°), the nitro group of the nitramine is twisted out of this plane (O1−C1−N1) by about 10°. As expected, the azide functionality shows an angle of 174.03(13)° due to negative hyperconjugation and long bonding effects. This is in accordance with the angle in $HC(O)N_3$ (174.49(17)°) and only slightly larger than those in $OC(N_3)_2$ (172.1(5)°, 172.6(6)°). The N1−N2 (1.2685(18) Å) and N2−N3 (1.233(5) Å) bond lengths show no divergence toward other members of the carbonyl azide family (Figure 1).[8,9]

The sufficient stability and solubility of the parent molecule **2** allowed characterization not only by ^{13}C NMR spectroscopy (δ = 152.1 ppm, ^{1}H resonance not observed) but also by ^{15}N NMR spectroscopy. Since significant decomposition was observed at room temperature, the ^{15}N spectrum was recorded at 0 °C in methanol-d_4. All five resonances were observed, with assignments as displayed in Figure 4 (δ = −45.6, −140.0,

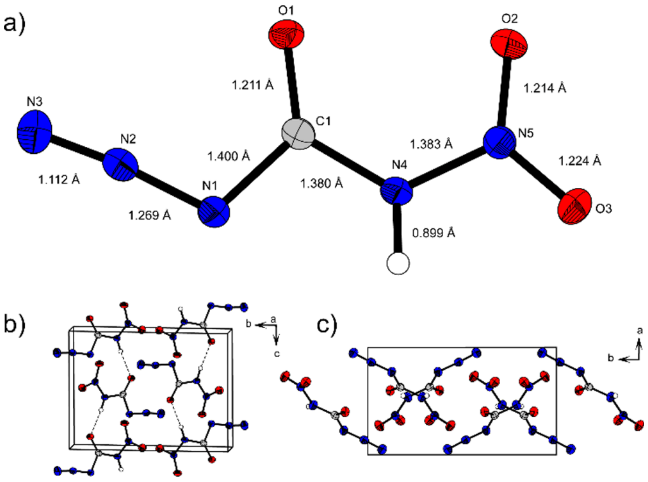


Figure 3. (a) Molecular structure and bond lengths of **2** as determined by low-temperature X-ray diffraction with thermal ellipsoids drawn at the 50% probability level. (b, c) Views of the packing of **2** (b) slightly twisted along the *a* axis and (c) along the *c* axis. Intramolecular H···O interactions are shown as dotted lines.

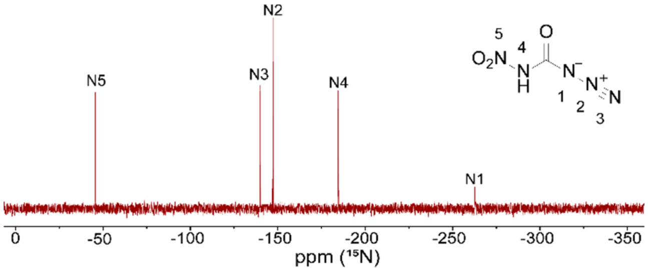
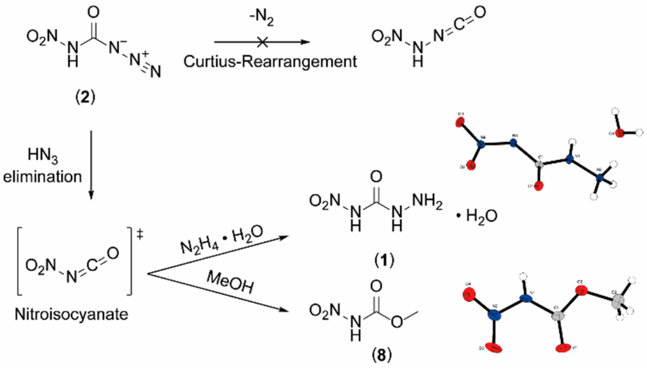


Figure 4. ^{15}N NMR spectrum of **2** in CD_3OD at 0 °C.

−147.2, −184.6, and −262.7 ppm). The resonance of the α-nitrogen atom (N-1) of the azido moiety is significantly shifted to lower field compared with those of organic azides, which is typical for carbonyl azides.[20] In a similar fashion, the resonance of the γ-nitrogen atom (N-3) is also shifted to lower field and detected “left” of that of the β-nitrogen atom (N-2). The assignments of N$_\beta$ ($\Delta\nu_{1/2}$ = 50 Hz) and N$_\gamma$ ($\Delta\nu_{1/2}$ = 140 Hz) were based on the line widths of the resonances in the corresponding ^{14}N NMR spectrum. The resonances of the nitramine moiety are found in the typical regions, with the nitro group at −45.6 ppm and the amine resonance at −184.6 ppm.[19,21] Because of the low solubility and quick decomposition even in cold methanol, only ^{14}N NMR data for the NCA$^-$ anion are available. With ammonium salt **5** as a representative example, in addition to the ammonium signal (−367 ppm, $\Delta\nu_{1/2}$ = 6 Hz), four further resonances are detectable for the NCA$^-$ anion. The signals for the azide nitrogen atoms at −135 ppm ($\Delta\nu_{1/2}$ = 45 Hz), −143 ppm ($\Delta\nu_{1/2}$ = 112 Hz), and −267 ppm ($\Delta\nu_{1/2}$= 162 Hz) are similar to those of the neutral compound. However, the signal of the nitro group is significantly downfield-shifted to −10 ppm ($\Delta\nu_{1/2}$ = 42 Hz) upon deprotonation (the nitramide nitrogen resonance was not observed in the ^{14}N NMR spectrum because of the extremely large line width).

As already mentioned above, **2** is bench-stable but decomposes rapidly in solution at ambient temperature, especially in protic solvents. The decomposition of **2** probably does not proceed via a Curtius rearrangement to the isocyanate, as usually occurs for carbonyl azides.[22−24] However, neither isocyanatonitramine nor derivatives thereof were observed as decomposition products. In our opinion, elimination of HN_3 to form an intermediate nitroisocyanate in solution seems likely. The latter has already been reported and analyzed.[25] This hypothesis is supported by trapping reactions with hydrazine hydrate and methanol as nucleophiles, yielding compounds **1** and **8**. In an attempt to form a hydrazinium salt of **2**, the precursor molecule **1** was obtained and isolated in almost quantitative yield. Furthermore, treatment of **2** in methanol at 60 °C furnished methyl nitrocarbamate (**8**) (Scheme 2).

Scheme 2. Proposed Decomposition Mechanism of 2 and Trapping Reactions of the Intermediate Nitroisocyanate with Methanol and Hydrazine Hydrate As Nucleophiles



Besides the guanidinium salt **6** (115 °C), the most temperature-stable compound is the potassium salt, which decomposes by detonation at 120 °C (Table 1). Therefore, KNCA (**4**) was investigated in a classic initiation capability test using pressed pentaerythritol tetranitrate (PETN) as the main charge. Salt **4** (30 mg) was loosely filled on top of the secondary explosive and ignited using an electrical ignitor, and it was able to cause a positive deflagration-to-detonation transition (DDT) toward the PETN loading (Figure 5). This was indicated by a hole in the copper plate and fragmentation of the shell.

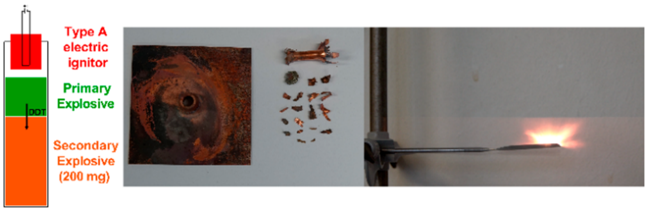


Figure 5. Schematic initiation test setup (left), result of the initiation test of potassium salt **4** toward PETN (center), and flame test of 5 mg of **4** with the moment of detonation (right).

The sensitivities cover almost the entire spectrum and range from the insensitive guanidinium salt **6** (impact sensitivity (IS) = 40 J; friction sensitivity (FS) = 324 N) to the extremely sensitive potassium salt **4** (IS < 1 J; FS < 0.1 N). Neutral HNCA has sensitivities of <1 J toward impact and 0.5 N toward friction, which are in the ranges for a primary explosive. The electrostatic discharge (ESD) sensitivities follow the general sensitivity trend. No ESD sensitivity values are given for **3** and **7** because those salts melted under the electrical load.

For all of the water-free compounds, the detonation parameters were calculated using the EXPLO5 code (further details and results are provided in the Supporting Information). All of the metal-free compounds (**2** and **5**−**7**) show positive enthalpies of formation.[26] The calculated detonation velocity (V_{det}) values range from 7441 m/s^{-1} for the potassium salt **4** to a remarkable value of 9460 m/s for the hydroxylammonium salt **7** (Table 1). Thus, **7** outperforms HMX (V_{det} = 9193 m/s) in terms of detonation velocity and has a value close to that of CL-20 (V_{det} = 9772 m/s). The neutral compound **2** has V_{det} = 8333 m/s and a detonation pressure (P_{CJ}) of 270 kbar, which are similar to those of PETN (V_{det} = 8429 m/s; P_{CJ} = 308 kbar).

In summary, the synthesis and thorough characterization of nitrocarbamoyl azide (HNCA, **2**) and several salts are reported. HNCA is solid at room temperature (because of the strong hydrogen bridge with a length of $d(D{-}H\cdots A)$ = 2.808(2) Å), melts at 72 °C, and decomposes at 83 °C. The predominantly sensitive compounds show interesting results in the calculation of the detonation parameters, especially the hydroxylammonium salt **7** with V_{det} = 9460 m/s. The potassium salt **4** is a high-performing primary explosive that

Table 1. Energetic Properties and Detonation Parameters of 1−7

	1	2	3	4	5	6	7
formula	$CH_4N_4O_3{\cdot}H_2O$	CHN_5O_3	$NaCN_5O_3{\cdot}H_2O$	KCN_5O_3	$CH_4N_6O_3$	$C_2H_6N_8O_3$	$CH_4N_6O_4$
IS [J][a]	5	<1	<1	<1	6	40	≤3
FS [N][b]	48	0.5	0.4	<0.1	20	324	≤40
ESD [J][c]	0.1	n.d.	0.065	<0.01	0.16	0.27	n.d.
ρ [g/cm][d]	1.814	1.708	1.891	1.986	1.683	1.604	1.803
N+O [%][e]	87.0	90.0	78.4	69.8	89.2	84.2	90.2
Ω [%][f]	−11.6	6.1	0	0	−10.8	−33.7	0
T_{dec} [°C][g]	156	83	81	120	79	115	93
$\Delta_f H^0$ [kJ/mol; kJ/g][h]	−88.5; −0.65	147.5; 1.13	−350.6; −2.05	−63.4; −0.375	85.6; 0.578	63.6; 0.334	141.8; 0.864
EXPLO5 V6.05.02							
$-\Delta_{ex}U^0$ [kJ/kg][i]	–	5066	–	4227	4924	3853	6233
P_{CJ} [kbar][j]	–	270	–	223	293	222	367
V_{det} [m/s][k]	–	8333	–	7441	8620	7879	9460

[a] Impact sensitivity. [b] Friction sensitivity. [c] Electrostatic discharge. [d] From X-ray diffraction analysis recalculated to 298 K. [e] Combined nitrogen and oxygen content. [f] Oxygen balance with respect to CO_2 formation. [g] Decomposition temperature (onset values; β = 5 °C min^{-1}). [h] Calculated enthalpy of formation. [i] Calculated energy of formation. [j] Detonation pressure. [k] Detonation velocity.

showed a positive result in an initiation test on 200 mg of PETN. A mechanism for the decomposition of **2** was proposed and verified by two trapping experiments. The mechanism does not follow the Curtius rearrangement as is usual for carbonyl azides, but instead, elimination of hydrazoic acid to form an intermediate nitroisocyanate occurs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c12507.

Crystallographic data for **1**−**8** (CIF)

Experimental section, crystal refinements, and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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