

Formyl Azide: Properties and Solid-State Structure**

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Covalent azides are important reagents in chemistry, biology, medicine, and materials science.^[1] Owing to the explosive nature of this class of compounds, some simple azides had not been isolated as neat substances, although they have been known to exist for a long time, and it took several decades to fully disclose their structures and properties. For instance, the solid-state structure of the simplest covalent azide, HN₃, which was first synthesized by Curtius in 1890,^[2] has only very recently been reported by Klapötke et al.^[3] The same is true for the simple halogen azides ClN₃,^[4] BrN₃,^[5] and IN₃,^[6] while the molecular structure of highly explosive FN₃ is up to now only available from a gas-phase microwave study.^[7]

Preparation and characterization of relatively unstable azides, such as the parent acyl azide HC(O)N₃^[8] and alkynyl azide HCCN₃,^[9] is particularly challenging. The simplest member of the widely used acyl azides, namely formyl azide, HC(O)N₃, has been the target of many computational studies.^[8] According to calculations, it may easily decompose into HNCO through a concerted elimination of N₂ and Curtius rearrangement. This prediction was supported by a recent experimental study^[8a] in which formyl azide was generated and its thermal decomposition in solution was studied. The activation barrier was found to be (20.3 ± 1.1) kcalmol⁻¹, and the half-life in CDCl₃ at room temperature was found to be merely 20 min.

We have been interested in the synthesis, structure, and decomposition reactions of covalent azides, and a number of highly explosive azides, such as OC(N₃)₂,^[10] OP(N₃)₃, and SP(N₃)₃,^[11] have been isolated as neat substances and structurally characterized. The decomposition of these azides provides unique approaches to some fundamentally

important small molecules, such as *cyclo*-N₂CO,^[12] OPN/ONP,^[13] and SPN/SNP/*cyclo*-PSN.^[14] By analogy, formyl azide would be the ideal precursor of the elusive parent acyl nitrene intermediate (HC(O)N), which has been extensively explored by quantum-chemical calculations.^[15] As a continuation of our work on covalent azides and their decomposition intermediates, we report herein on the properties of neat formyl azide, its single-crystal structure, and also the interception of the short-lived formyl nitrene.

For the synthesis of neat HC(O)N₃, the low-temperature reaction (−30 to −15 °C) of triformamide with hexadecyltributylphosphonium azide (QN₃), which affords HC(O)N₃ with yields up to 50%,^[8a] was chosen. Both solid precursors are soluble in the high-boiling-solvent propylene carbonate, which allows the separation of the highly volatile HC(O)N₃ from the reaction mixture with an estimated yield of 40% at low temperatures. Solid HC(O)N₃ sublimes at low temperatures in vacuo, which allows its purification and transfer without noticeable decomposition (see the Supporting Information for details).

Solid HC(O)N₃ melts sharply at −50.5 °C to yield a colorless liquid that could be frozen into the solid again without incident. Thermal decomposition of gaseous HC(O)N₃ into HNCO and N₂ was monitored by IR spectroscopy. Similar to the observations in solution, the decomposition follows a first-order rate kinetics (Supporting Information, Figures S1, S2), but with a much slower rate (25.5 °C, $k = 8.80 \times 10^{-5} \text{ s}^{-1}$, $t_{1/2} = 2.2 \text{ h}$) than that observed in CDCl₃ (25 °C, $k = 5.96 \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} = 20 \text{ min}$).^[8a] However, as the decomposition of formyl azide was found to be slower in non-polar solvents such as cyclohexane, the smaller rate of this reaction in the gas phase is not surprising.

IR and Raman spectra of HC(O)N₃ are shown in Figure 1. The observed vibrational frequencies agree well with calculated anharmonic values using the CCSD(T)-F12a method (Table 1).^[8a] Assignments of the spectra are supported by a higher-resolved IR spectrum (Supporting Information, Figures S3, S4) and ^{14/15}N isotopic shifts (Supporting Information, Table S1).

Carbonyl azides can, in principle, exist as a mixture of two close-in-energy conformers by adopting *syn* or *anti* configuration of the C=O and N₃ groups with respect to the C–N_α bond. Theoretical calculations suggest the dominance of a *syn* conformation for HC(O)N₃, and the *anti* conformer has a contribution of a few percent (Supporting Information, Table S2). The latter can be distinguished from *syn* by a higher C=O stretching frequency of 46 cm⁻¹ (Supporting Information, Table S3). Indeed, a very weak shoulder appeared at 1764 cm⁻¹ beside the strong band (ν_3) at 1717 cm⁻¹ in the IR spectrum of the gaseous sample

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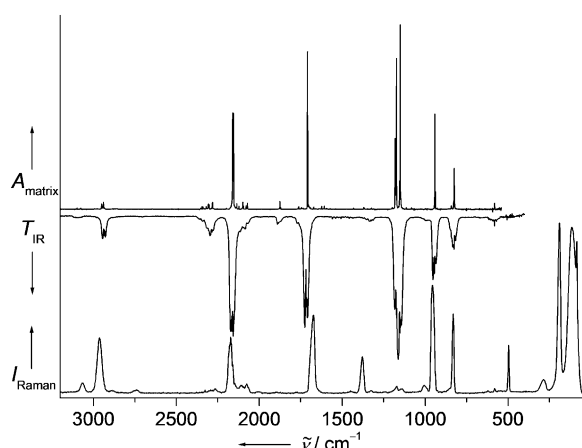


Figure 1. Upper trace: IR spectrum (absorbance A , resolution 0.25 cm^{-1}) of Ar-matrix-isolated HC(O)N_3 at 16 K. Middle trace: IR spectrum (transmittance T , resolution 2 cm^{-1}) of gaseous HC(O)N_3 at 298 K. Bottom trace: Raman spectrum (Raman intensity I , resolution 2 cm^{-1}) of solid HC(O)N_3 at 77 K.

(Supporting Information, Figure S5). When this weak feature is taken as evidence for the presence of the *anti* conformer, its relative abundance can be estimated based on calculated and observed IR intensities for these two bands to be less than 2%. In fact, in the IR spectrum of HC(O)N_3 in CCl_4 ,^[8a] an unassigned weak band (1734 cm^{-1}) also occurred beside the strong band of *syn* HC(O)N_3 (ν_3 , 1699 cm^{-1}). It is likely to be associated with the *anti* conformer, and its estimated abundance is about 10%.

The Raman spectrum of solid HC(O)N_3 is shown in Figure 1. In the C=O stretching region, only one strong band appears red-shifted by -43 cm^{-1} from the corresponding gas-phase IR band (1717 cm^{-1}). In contrast, the C-H stretch is blue-shifted by $+27\text{ cm}^{-1}$. These shifts clearly indicate the existence of so-called improper hydrogen bonds in the solid state.^[16] The IR spectrum of HC(O)N_3 isolated in an Ar matrix was also measured (Figure 1), and only one band for the C=O stretch of *syn* HC(O)N_3 was observed.

Crystallization of HC(O)N_3 was performed in a similar way to that of $\text{OC(N}_3)_2$ ^[10] by slow sublimation of a small solid sample inside a glass tube (o.d. 6 mm, length 15 cm) at -78°C . However, handling of HC(O)N_3 crystals is challenging because of the low melting point (-50.5°C) and the risk of explosion caused by pressure variations (for details, see the Supporting Information).

Formyl azide crystallizes in a monoclinic space group (Pc) with four molecules in the unit cell,^[17] and there are two crystallographically nonequivalent molecules (I and II, Figure 2) with essentially identical (within standard deviation) molecular parameters (Supporting Information, Table S4). They form coplanar pairs linked by $\text{C-H (II)}\cdots\text{O=C (I)}$ bonds of 2.46 \AA , while these pairs are further linked to infinite zigzag chains through slightly shorter (2.43 \AA) $\text{C-H (I)}\cdots\text{O=C (II)}$ interactions (Supporting Information, Figure S6). The shorter $\text{H}\cdots\text{O}$ contact (2.43 \AA) corresponds to a heavy-atom $\text{C-H}\cdots\text{O}$ distance of $3.241(2)\text{ \AA}$ along with an angle of $143.3(1)^\circ$, whereas the longer $\text{H}\cdots\text{O}$ contact of 2.46 \AA correlates to a $\text{C-H}\cdots\text{O}$ distance of $3.321(2)\text{ \AA}$ and an angle of $150.6(1)^\circ$. Similar

Table 1: Experimental and calculated vibrational frequencies [cm^{-1}] of HC(O)N_3 .

| CCl_4 ^[b] 298 K | Experiment ^[a] | | | Raman Solid 77 K | Calculated ^[e] CCSD(T) | Assignment ^[f] |
|--|---------------------------|------------------------------|----------------------------------|------------------------|--------------------------------------|---|
| | IR Gas phase 298 K | $\Delta(P,R)$ ^[c] | Ar matrix ^[d] 16 K | | | |
| | 3423 vvw | | 3402 vvw | | 3416 (4) | $2\nu_3$ (A') |
| | 3301 vvw | | | | 3302 (1) | $\nu_2 + \nu_5$ (A') |
| | 3093 vvw | | 3098.5 vw | 3067 m | 3095 (3) | $\nu_3 + \nu_4$ (A') |
| 2932 w | 2937 w | 17 | 2939.9 w | 2964 s | 2938 (52) | ν_1 , C-H stretch (A') |
| | 2288 w | | 2282.3 w | 2267 vw | 2288 (29) | $2\nu_5$ (A') |
| 2152 s | 2164 vs | 16 | 2159.7 vs | 2172 s | 2172 (192) | ν_2 , out-of-phase N–N stretches (A') |
| | 2085 w, sh | | 2079.2 w | | 2087 (15) | $\nu_5 + \nu_6$ (A') |
| | 1883 w | | 1875.4 w | | 1887 (8) | $2\nu_6$ (A') |
| 1699 s | 1717 s | 17 | 1708.1 s | 1674 s | 1718 (258) | ν_3 , C=O stretch (A') |
| | | | 1370.1 vvw | 1374 ms | 1360 (<1) | ν_4 , in-plane HCO bend (A') |
| | 1323 vw | | 1322 vvw | | 1332 (4) | $\nu_5 + \nu_9$ (A') |
| 1169 s | 1174 s, sh | 20 | 1173.1 s | 1171 w | 1175 (163) | $2\nu_{11}$ (A') |
| 1146 s | 1151 vs | 17 | 1149.1 vs | 1142 vw | 1151 (357) | ν_5 , in-phase N–N stretches (A') |
| | | | | 1006 vw | 993 (<1) | ν_{10} , C-H out-of-plane bend (A'') |
| 942 m | 945 ms | 17 | 941.3 s | 956 vs | 947 (101) | ν_6 , C-N stretch (A') |
| | 847 w, sh | | 842 vw | | 844 (9) | $\nu_{11} + \nu_{12}$ (A') |
| 827 w | 820 m | 16 | 824.6 m | 831 s | 829 (42) | ν_7 , in-plane OCN bend (A') |
| | 582 vw | | 581.4 w | 581 vw | 584 (8) | ν_{11} , out-of-plane N_3 bend (A'') |
| | | | | 496 m | 491 (<1) | ν_8 , in-plane N_3 bend (A') |
| | | | | 286 w | 251 (14) | ν_{12} , torsion (A'') |
| | | | | 190 s | 171 (<1) | ν_9 , in-plane CNN bend (A') |

[a] Observed band positions and relative intensities: vs = very strong, s = strong, ms = medium strong, w = weak, vw = very weak, vvw = very very weak. [b] In CCl_4 solution; see Ref. [8a]. [c] P , R separation in cm^{-1} . [d] Most intense matrix site. [e] Calculated anharmonic frequencies and IR intensities (km mol^{-1} , in parenthesis) using the CCSD(T)-F12a method. [f] Tentative assignments for the vibration modes of the *syn* conformer according to calculated displacement vectors.

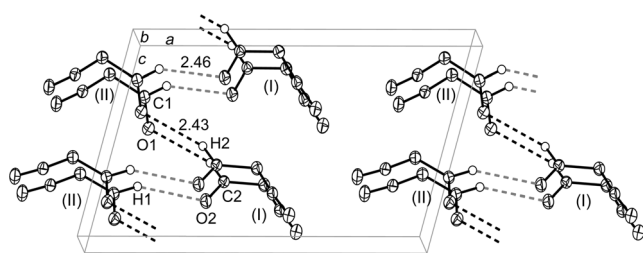


Figure 2. Packing of HC(O)N₃ molecules (I and II) in the unit cell. Short intermolecular H...O distances are indicated by dashed lines and their distances in [Å].

C–H...O hydrogen bonds were also found in solid formaldehyde (3.246(1) and 3.321(2) Å).^[18] The presence of these hydrogen bonds is also supported by aforementioned spectroscopic results.

The HC(O)N₃ molecule in the solid state adopts an almost planar *syn* conformation (Figure 3), and the dihedral angles OCN_αN_β and CN_αN_βN_γ are 1.3 and 178.8°, respectively. Its molecular structure is comparable to those of related covalent

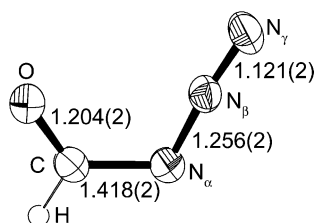


Figure 3. Solid-state structures of HC(O)N₃ (molecule I). Ellipsoids are set at 50% probability. Bond lengths are given in [Å]; angles are given in the Supporting Information, Table S4.

azides OC(N₃)₂^[10] and HN₃^[3] in the solid state. The C–O (1.204(2) Å) and the C–N (1.418(2) Å) bond lengths in HC(O)N₃ are (within the standard deviations) similar to those in OC(N₃)₂ (C–O 1.200(6) Å, C–N 1.412(7) and 1.407(8) Å), while the OCN angle (125.21(16)°) is slightly smaller than that of OC(N₃)₂ (127.2(5)°), which is probably due to the lower spatial requirement of the hydrogen atom compared to that of a second N₃ group. The N_α–N_β bond lengths are also similar in the carbonyl azides HC(O)N₃ (1.256(2) Å) and OC(N₃)₂ (1.265(7) and 1.274(7) Å), but longer than that of HN₃ (1.233(5) Å), while the N_β–N_γ bond lengths in HC(O)N₃ (1.121(2) Å), HN₃ (1.121(5) Å) and OC(N₃)₂ (1.111(6) and 1.111(7) Å) show much less variations. On the other side, the N_αN_βN_γ angle in HC(O)N₃ (174.49(17)°) is slightly larger than those in HN₃ (172.8(2)°) and OC(N₃)₂ (172.1(5)°, 172.6(6)°).

According to recent *ab initio* calculations, formyl nitrene is one of the rare nitrenes that has a singlet ground state with a rather small singlet–triplet gap ($\Delta E_{S-T} = -0.13$ kcal mol^{−1}, CCSD(T)/cc-pVQZ);^[15a] however, such a small ΔE_{S-T} implies that the ground state multiplicity of formyl nitrene can hardly be assured using theoretical calculations. This precarious situation encouraged us to study the photolysis of HC(O)N₃ isolated in solid noble gas matrices. Formyl azide exhibits

a broad UV absorption at $\lambda_{\text{max}} = 233$ nm.^[8a] Photolysis of the azide isolated in an Ar matrix at 16 K using UV irradiation of either 193 or 255 nm solely furnished HNCO (Supporting Information, Figure S7). The failure to detect HC(O)N in the photolysis products might be consistent with the preference of a concerted decomposition mechanism for HC(O)N₃.^[8a] However, the possible formation of the singlet nitrene with subsequent Curtius rearrangement under the photolysis conditions cannot be ruled out. Thus a conventional nitrene trapping experiment with CO was performed by irradiating ($\lambda = 255$ nm) HC(O)N₃ in a CO-doped Ar matrix (azide/CO/Ar = 1:50:500). Along with the IR bands of HNCO, another set of new bands at 2248, 1733, 1425, and 963 cm^{−1} was obtained (Supporting Information, Figure S8). Their ^{14/15}N and ^{12/13}C isotopic shifts have been determined in experiments using a ¹⁵N-labeled sample (Supporting Information, Figure S9) and a ¹³CO-doped Ar matrix, respectively (Supporting Information, Table S5). The collected IR data of the photoproduct strongly suggest the formation of formyl isocyanate, HC(O)NCO. Surprisingly, calculated IR frequencies and their relative intensities show better agreement for the higher-energy *anti* conformer (Supporting Information, Tables S5–S7). The relative amounts of HNCO and HC(O)NCO produced by photolysis of HC(O)N₃ in the CO-doped Ar matrix was roughly estimated from the observed and calculated intensities of the IR bands for these two species (Supporting Information, Table S8), and it appears that both were formed in nearly equal amounts.

Taking into account the preference of a concerted decomposition pathway for HC(O)N₃, the formation of HC(O)NCO from photolysis of the azide in the presence of CO is intriguing. According to the calculations,^[8a] the transition state for the concerted decomposition is 6.5 kcal mol^{−1} lower in energy than that for the formation of the nitrene. This small energy difference implies that both processes could occur when a large excess of energy is applied to the azide, such as UV light irradiation ($\lambda = 193$ or 255 nm). This reasoning may explain the formation of both HNCO and HC(O)NCO by UV photolysis of CO matrix-isolated azide. The stereoselective formation of the higher-energy *anti* HC(O)NCO can be explained by considering the molecular structure of the singlet nitrene HC(O)N intermediate. A planar cyclic structure with a significantly smaller OCN angle (88.0°) in the singlet than that in the triplet (121.0°) was calculated for HC(O)N (B3LYP/6-311++G(3df, 3pd)). Similar results were also found for other singlet nitrenes, and attributed to an intramolecular O→N interaction.^[15a,19] Thus, nucleophilic attack of CO to the nitrene center is expected to occur from the opposite side of this supposed N–O interaction, that is, the *anti* position with respect to the carbonyl oxygen.

The intervention of formyl nitrene during the photodecomposition of HC(O)N₃ is also supported by the formation of traces of either *N*-(1,1-dimethylpropyl)formamide or *N*-cyclopentylformamide during its photolysis in 2-methylbutane or cyclopentane solutions. These formamides can be regarded as trapping products of HC(O)N by insertion into C–H bonds of the solvents (Supporting Information, Figures S10–S12).

In summary, the unstable parent acyl azide HC(O)N_3 has been isolated as a neat substance and structurally characterized. While solely the lower-energy *syn* conformer was observed in cryogenic Ar matrices and in the solid state, traces of the *anti* conformer ($< 2\%$) were detected in the gas phase. In the solid state, the molecules are linked by two different types of intermolecular $\text{C}\cdots\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds. UV photodecomposition of HC(O)N_3 in a CO-doped Ar matrix yields, along with HNCO, the parent acyl isocyanate HC(O)NCO in an *anti* conformation. The stereoselective formation of *anti* HC(O)NCO with CO was rationalized by capturing elusive singlet HC(O)N and by considering a planar cyclic structure for this nitrene that is due to intramolecular $\text{O}\rightarrow\text{N}$ interaction.

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