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The Search for Tricyanomethane (Cyanoform)

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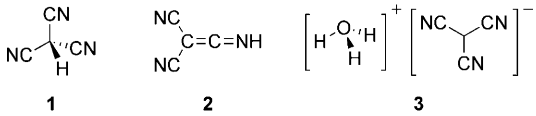
Abstract: Although listed in organic chemistry textbooks as one of the strongest carbon acids, and in spite of more than a hundred years of attempts to prepare the compound, tricyanomethane (cyanoform) has resisted isolation and characterization, either as the carbon-acid **1** or as the dicyanoketenimine tautomer **2**. Only in the vapor phase at very low pressure has the compound been identified from its microwave spectrum. Here we review and partially repeat the preparative work. With the aid of spectroscopic and diffraction methods (including powder diffraction) we have identified some of the products obtained as: hydronium tricyanomethanide (**3**), (*Z*)-3-amino-2-cyano-3-iminoacrylimide (**4**), a co-crystal of **4** with sulfuric acid (or corresponding iminium salt), and an addition product of **2** with hydrochloric acid (**5**/**6**). Quantum-mechanical calculations at the MP2/6-311++g(2d,2p) level have been made to assess the relative energies of some of the molecules involved.

Keywords: cyanoform · hydrogen bonds · hydronium tricyanomethanide · powder charge flipping · tricyanomethane

Introduction

We report here on our unsuccessful search to obtain a sample of the elusive tricyanomethane (**1**, cyanoform) or of its *aci*-tautomer dicyanoketenimine (**2**) as an isolatable product (Scheme 1). The difficulties we have encountered may not be too surprising to those who are aware that this apparently simple compound has eluded successful isolation and defied characterization for more than a century, although it is listed in textbooks of organic chemistry as one of the strongest carbon acids, with a pK_a approximately −5. Indeed, we have obtained a crystalline hydrate with properties similar to but not identical with those described earlier by others,[1–3] but it has turned out, however, to be hydronium tricyanomethanide (**3**) with planar tricyanomethanide anions identical with those observed previously in other crystalline tricyanomethanide salts.[4–8] Only in the gas phase at a pressure of less than 40 mTorr has tricyanomethane been identified by Bak and Svanhout from its microwave spectrum.[9]



Scheme 1. Molecular structures of cyanoform (**1**), dicyanoketenimine (**2**), and hydronium tricyanomethanide (**3**).

History

The tricyanomethane story begins in 1896 when Schmidtmann added dilute sulfuric acid to an aqueous solution of sodium tricyanomethanide.[1] On shaking the solution with diethyl ether, three layers formed: a colorless aqueous solution, a green aquo-ethereal layer assumed to contain cyanoform as the main product, and a colorless ethereal layer. The green color could be removed by heating the solution with charcoal but returned on exposure of the solution to the atmosphere. The aquo-ethereal solution was dried by standing over $CaCl_2$ for 24 h, followed by evaporation until "eine einheitliche, grünliche Flüssigkeit" (a uniform green

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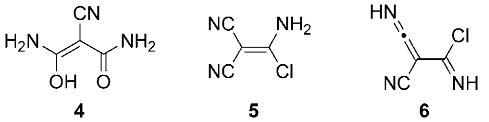
liquid) remained. Slow evaporation in vacuum then led to formation of brown-red crystals, whereas more rapid evaporation produced an orange-colored crystalline mass. Since chemical analysis of these products did not lead to interpretable results, Schmidtmann surmised that they were likely polymeric. Schmidtmann's observations were largely confirmed a few years later by Hantzsch and Osswald,[2] who noted that cyanoform acted as an extremely strong acid and put forward the proposal that it can exist as the tautomer **2** in analogy to the *aci*-form of trinitromethane. These authors also noted that an aqueous solution of cyanoform could be kept indefinitely without appreciable alteration in contrast to the products obtained by Schmidtmann.

The next noteworthy study had to wait more than half a century. In 1954, after several attempts to reproduce Schmidtmann's results, Cox and Fontaine[10] described an alternative route to tricyanomethane, namely by mixing potassium cyanide with an ethereal solution of bromomalononitrile at −15 °C. Concentration and drying of the ethereal layer produced colorless crystals with m.p. 55–56 °C, identified as cyanoform on the basis of its nitrogen content (calcd 46.14 %, found 46.0 %). These crystals were reported to be stable on exposure to air and to light for several months, in contrast to Schmidtmann's product. A few years later, however, Trofimenko was unable to reproduce this result.[3,11] On the other hand, by evaporation of an aquo-ethereal solution of "cyanoform" he obtained yellowish crystals that were sublimed to yield a white crystalline solid that he identified as dicyanoketenimine (**2**) from elemental analysis and infrared spectral data (absorption at 4.0 µ, none around 3.0 µ). A footnote to an earlier paper[12] refers to an unstable dihydrate to "be reported in a paper by Dr. R. H. Boyd." Indeed, in his 1963 paper on the ionization behavior of cyanocarbon acids, Boyd mentioned that cyanoform was found to form a dihydrate, but no details were provided.[13] By following the spectral changes occurring on addition of H_2SO_4 to solutions of potassium tricyanomethanide, Boyd estimated the pK_a of cyanoform as −5.1, thus placing it as one of the strongest known organic acids.

On the theoretical side, there appears to be general agreement that tricyanomethane **1** is more stable than the dicyanoketenimine tautomer **2**, at least in the gas phase, although the degree of stabilization is very different according to wave function based calculations and those based on electron density models. In an early study within the limitations of Hartree–Fock energy calculations (7s, 3p basis set contracted to 4s, 2p), **1** was found to be more stable than **2** by about 56 kJ mol^{-1}.[14] This value agrees surprisingly well with our own calculations at the MP2/6-311++g(2d,2p) level, which give a stabilization of 53 kJ mol^{-1}.[15] On the other hand, calculations based on density functional theory give much smaller energy differences between the two tautomers. Calculations at the B3LYP/aug-cc-pvTZ level are reported to give a stabilization of only 2.9 kJ mol^{-1} between **1** and **2**,[16] and a similarly low value also seems to be supported by very recent calculations at the ZPVE-corrected B3LYP/6-31++G** level that lead to a stabilization of 7.4 kJ mol^{-1}.[17,18] This latter value includes zero-point vibration energy corrections, but this should not affect the striking difference that seems to be present between results from the two types of calculation. While there is agreement about the superior stabilization of the tricyanomethane tautomer **1** in the gas phase, it is not clear why density functional theory should give such a different result from wave function based methods. In any case, it seems fairly clear that the superior hydrogen-bonding potentiality of the *aci*-tautomer **2** could well alter the stability preference in the condensed phases.

Results and Discussion

In our work, the acidification methods expected to produce tricyanomethane did not lead to this compound as an isolatable substance, either as **1** or **2**. Instead, we obtained addition products such as **4** and **5** (Scheme 2), resulting from the remarkable reactivity of the unobtainable target compound.[19] Moreover, the solid obtained from dilute acidic aqueous solution has turned out to be the salt, hydronium tricyanomethanide (**3**).



Scheme 2. Molecular structures of (*Z*)-3-amino-2-cyano-3-hydroxyacrylamide (**4**), 1-chloro-1-amino-2,2-dicyanoethylene (**5**), and 2-cyano-3-iminoacrylimidoyl chloride (**6**).

The structures of the various solid materials obtained in this work were determined by X-ray analysis. Compounds **3** and **4** were analyzed by single-crystal X-ray measurements. The atomic arrangements of the polycrystalline solids **4**-H_2SO_4 co-crystal (or corresponding salt) and **5** (or tautomer **6**) were determined from their X-ray powder diffraction patterns by the application of new procedures based on charge-flipping methods.[20] Basically, charge-flipping methods start from the assignment of random phases to the measured structure factor amplitudes, leading to an electron density map with positive and negative regions. The signs of all electron densities that fall below some small positive threshold are reversed (flipped). In essence, negative electron density, which is not physically meaningful, is made positive. This new density distribution serves as the basis for a structure factor calculation that provides a new set of phases for the measured amplitudes, leading to a new electron density map. The process is repeated until only positive electron density peaks are obtained and calculated amplitudes match measured ones. For polycrystalline materials, there is the problem of overlapping of reflections in the measured diffraction pattern. This is addressed by applying a second type of density modification based on histogram matching (a computer technique developed for image processing) and using the ratios of the structure factor amplitudes derived from this map to repartition the reflection intensities within each overlap group.[21] The two structures reported here (see below) are among the first organic structures to be solved by using the powder charge-flipping algorithm.

In our repetition of the experiments reported by Schmidtmann,[1] Hantsch,[2] and Trofimenko,[3] we obtained by rapid evaporation of the "middle aquo-ethereal layer" the pale yellow crystalline solid hydronium tricyanomethanide (**3**). Exposed to air, this material gradually became more and more deeply colored, ending as a deep purple mass, presumably polymeric.

In contrast to the disordered structure (tumbling ?) of the cation observed in the *Pnma* polymorph of hydronium perchlorate,[22a] the hydronium cation in this structure is ordered (Figure 1) with much shorter hydrogen bond lengths (O−H···N 2.604 Å, and 2.617 Å ×2), suggesting that the hydrogen bonds here are stronger than in the disordered perchlorate salt. These distances are also shorter than those in the ordered $P2_1/n$ polymorph of hydronium perchlorate.[22b] Indeed, they are among the shortest O−H···N distances found to date. The dimensions of the tricyanomethanide anion found here (C−C 1.401–1.402 Å; C−N 1.148–1.150 Å) are more reliable than those found in the earlier crystal structure analyses.[6–8] Note that the hydrogen bonds are all directed towards the N atoms of the tricyanomethanide anion and not towards the central C atom with its formal negative charge.

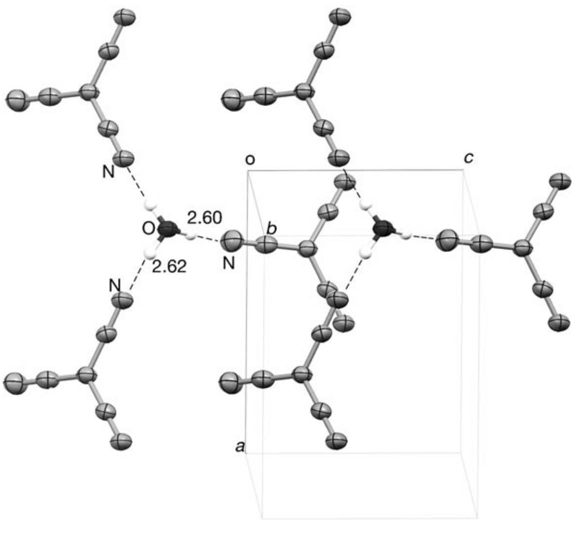


Figure 1. Crystal structure at 223 K of hydronium tricyanomethanide (**3**) showing hydrogen bond pattern with O···N distances in Å. Molecular dimensions: C−C 1.401 1.402 Å; C−N 1.148, 1.150 Å (s.u. 0.002 Å). Vibration ellipsoids are drawn at the 50 % probability level.

Protonation of the tricyanomethanide anion was also attempted by adding the sodium salt in small portions to concentrated sulfuric acid. After adding this mixture to diethyl ether and filtering off the sodium sulfate precipitate, a crystalline white solid separated from the ethereal solution after storage at −20 °C for several days. Single-crystal X-ray analysis showed the compound to be (*Z*)-3-amino-2-cyano-3-hydroxyacrylamide (**4**), the dihydrate of cyanoform (Figure 2). Although the molecule has no crystallographic site symmetry, it shows nearly perfect *C*2*v* (*mm2*) symmetry with chemically equivalent bond lengths equal within 0.01 Å. Each molecule forms five hydrogen bonds, four intermolecular to build a strongly layered crystal structure (N−H···O 2.940, 2.924 Å; N−H···N 3.053, 3.078 Å), and the fifth intramolecular, connecting the two oxygen atoms, with an O···O distance of 2.418 Å. This belongs to the category of very short, symmetrical hydrogen bonds—the topic of a recent computational study[23]—and is a further indication of the maintenance of the effective *C*2*v* molecular symmetry.

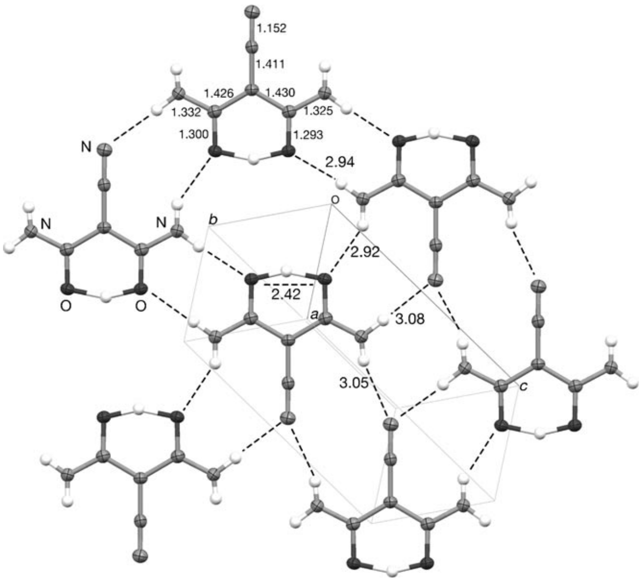


Figure 2. A molecular layer in the crystal structure of (*Z*)-3-amino-2-cyano-3-hydroxyacrylamide (**4**) at 223 K, with O and N atoms labeled. Molecular dimensions in Å and hydrogen bonds are indicated. Vibration ellipsoids are drawn at the 50 % probability level.

When the procedure for obtaining compound **4** was repeated, it sometimes led to a different polycrystalline product as a **4**-H_2SO_4 co-crystal or a $[\mathbf{4}–\text{H}]^+[\text{HSO4}]^-$ salt. The structure (Figure 3) was solved from the powder pattern obtained at the Swiss Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble. Although the heavy atom arrangement could be clearly established, an unequivocal distinction between the O and N atoms of the amide groups on the basis of their electron densities was not possible. However, the detailed analysis showed a slight preference for the conformer shown in Figure 3 rather than the more symmetrical conformer observed in the crystal structure of **4**. Also, the short intramolecular O···O distance of 2.418 Å in **4** has no equivalent here, the corresponding distance being 2.63 Å. The hydrogen bond pattern can be inferred from the arrangement of short intermolecular distances and angles, but our lack of knowledge about the H positions means that we have to

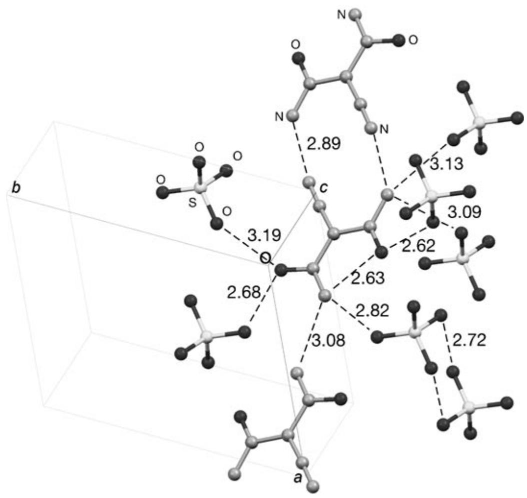


Figure 3. Section through the crystal structure of the 1:1 co-crystal (or salt) containing molecule **4** and sulfuric acid at room temperature. In the conformation shown (see text), O and N atoms are labeled. Possible hydrogen bonds (distances in Å) are indicated by dashed lines.

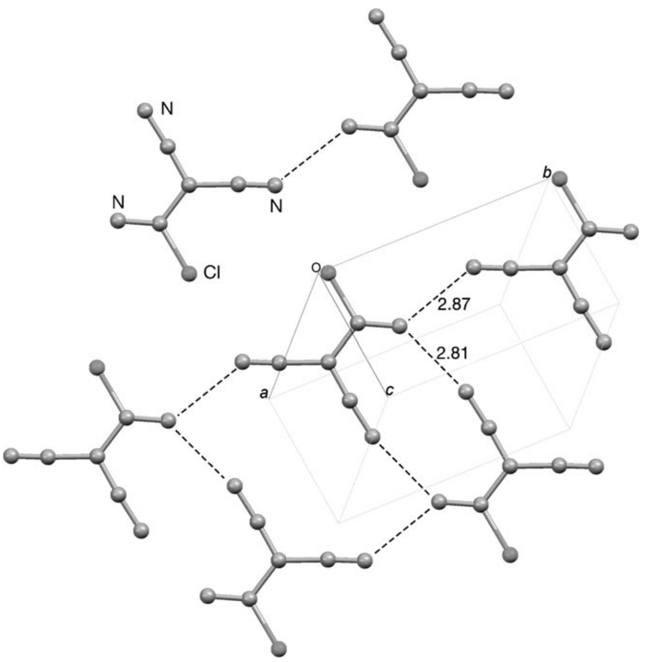


Figure 4. Hydrogen-bonded layer in the room temperature crystal structure of product **5/6** with N and Cl atoms labeled. Hydrogen bonds (distances in Å) are indicated by dashed lines.

leave open the question of the ionization state of the sulfuric acid moiety. On the one hand, it is known from conductivity measurements that nitriles behave as bases in concentrated sulfuric acid (see below). On the other hand, the observed interatomic distances and angles provide no indication that the organic moiety is protonated. We leave it open as to whether the product is better described as a co-crystal or as the hydrosulfate salt of protonated **4**.

To exclude the presence of water in the preparation of cyanoform, we used gaseous HCl to acidify the suspension of sodium tricyanomethanide in anhydrous THF. After filtration, an off-white solid was obtained from the filtrate. By X-ray powder diffraction methods, the polycrystalline product was found to be 1-chloro-1-amino-2,2-dicyanoethylene (**5**) or its tautomer 2-cyano-3-iminoacrylimidoyl chloride (**6**). A diagram of the strongly layered crystal structure is shown in Figure 4. The heavy atom skeleton is essentially planar and corresponds to that of the compound prepared by Allenstein and identified by elemental analysis and infrared spectroscopy as the HCl addition product of cyanoform.[24] While interatomic distances derived from our structure are not of high accuracy, they appear to slightly favor tautomer **5** over **6**. Although the positions of the hydrogen atoms cannot be determined directly from our analysis, the hydrogen bond pattern can be inferred from the intermolecular distances and angles.

It may appear surprising that the hydration reaction to give **4** occurs in the virtual absence of water. Removal of water from H_2SO_4 would involve formation of sulfur trioxide SO_3 and subsequently pyrosulfuric acid $H_2S_2O_7$. However, we have checked that, according to calculations at the MP2/6-311++G(2d,2p) level, the gas-phase reaction [Eq. (1)] is strongly exothermic by 111.7 kJ mol^{-1} and even more exothermic starting from the less stable ketenimine tautomer. So there is no problem about the thermodynamic aspect of the hydration reaction.

$$C_4HN_3 \text{ (cyanoform)} + 2\,H_2SO_4 \rightarrow C_4H_5N_3O_2 \text{ (}\mathbf{4}\text{)} + 2\,SO_3 \quad (1)$$

The earliest specific recognition we have found that nitriles are converted to amides by concentrated sulfuric acid dates from 1958 when Liler and Kosanovic found that the electric conductivity of solutions of acetonitrile in sulfuric acid decrease with time, finally reaching a limiting value.[25] They assumed that the hydration of the nitrile is represented by Equation (2):

$$RCN + 2H_2SO_4 \rightarrow RCONH_2 + H_2S_2O_7 \quad (2)$$

with subsequent ionization of the products, or Equation (3).

$$RCNH^+ + HSO_4^- + H_2SO_4 \rightarrow RCONH_3^+ + HS_2O_7^- \quad (3)$$

In the course of this reaction the concentration of the highly conducting HSO_4^- ions is reduced, so the conductivity decreases. Indeed, Hantzsch[26] had found in 1909 from cryoscopic studies that acetonitrile acts as a base in 100% sulfuric acid, as confirmed half a century later by NMR studies.[27] Of course, we do not know whether the water involved in the hydration of **2** in concentrated sulfuric acid derives from the small amount of water present or from the acid itself. The reaction with ^{18}O-labeled sulfuric acid would settle the matter.

A rather spectacular example of the use of this reaction, hydration of a nitrile by concentrated sulfuric acid in the absence of water, was provided in the Eschenmoser synthesis of Vitamin B12, when it was necessary at one of the later stages to convert a peripheral nitrile group to an amide group in the presence of six ester functionalities.[28]

Although quantum-mechanical calculations agree that tricyanomethane (**1**) is substantially more stable (in the gas phase) than its keteneimine tautomer **2**, it seems likely that **1** is virtually unobtainable in condensed phases. The keteneimine **2** is surely the kinetically preferred product obtained by protonation of the planar tricyanomethanide anion since its formation does not involve drastic rehybridization of the central carbon. If the keteneimine tautomer were unreactive enough to exist in solution over a long enough time, it would convert to the more stable tautomer, but it rapidly reacts further to form more stable products such as **4** or **5**. In the solid state, all these products rapidly polymerize at ambient or elevated temperatures. Thus, it may be misleading to classify tricyanomethane (cyanoform) as a very strong acid with pK_a around −5. The strong acid is the keteneimine tautomer, an N-acid, not the C-acid, which may be many powers of ten weaker.

There is a certain analogy with the difference in acid dissociation constants between the C-acid nitroethane ($K_a = 3.5\times10^{-9}$) and its *aci*-tautomer ($K_a = 4\times10^{-5}$). There, the *aci*-tautomer is obtained directly by acidification of a salt solution, and transformation to the more stable C-acid occurs slowly enough that the two dissociation constants can be measured separately.[29] The C-acid is much weaker than the *aci* O-acid.

Since the pK_a of hydronium ion is known to be −1.7, the existence of the solid tricyanomethide salt confirms that its conjugate acid must be very strong indeed. As mentioned earlier, a pK_a of approximately −5 was estimated by Boyd on the basis of spectral changes accompanying the addition of concentrated sulfuric acid to solutions of potassium tricyanomethanide.[13] The question remains: is the strong acid tricyanomethane **1** or the dicyanoketeneimine tautomer **2**, and we have given reasons for believing that it is the latter.

Conclusion

Our lack of success in our attempts to obtain a sample of cyanoform as an isolatable product allows us to offer some words of advice to others who might wish to seek the same goal. Acidification of tricyanomethanide salts, the most obvious path, seems unlikely to lead to the desired product, since protonation of the planar anion will invariably lead to dicyanoketenimine, the kinetically preferred but less stable product, which then reacts further to other more stable products with coplanar geometry at the central carbon atom. Despite our failure to reproduce the Cox–Fontaine experiment[10] leading to the desired product, schemes proceeding from molecules with tetrahedral geometry at the central carbon atom appear to be more promising. Experiments involving the action of super acids on tricyanomethanide salts are under way.[30]

Experimental Section

Materials and general methods: Reagents and solvents were purchased at reagent grade from Acros, Aldrich, and Fluka, and used as received; sodium tricyanomethanide was provided by Lonza AG. THF was freshly distilled from sodium benzophenone ketyl under nitrogen atmosphere. Anhydrous gaseous HCl was purchased from PanGas AG. ^{1}H NMR and ^{13}C NMR spectra were measured at 25 °C with a Varian Gemini 300, Varian Mercury 300, Bruker DRX 400, or Bruker AV 400 spectrometer. Chemical shifts are reported in ppm relative to the signal of Me_4Si. Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference. IR spectra were recorded on a Perkin–Elmer BX FT-IR spectrophotometer. HR-EI spectra were measured with a Waters Micromass AutoSpec-Ultima spectrometer. The most important signals are reported in m/z units with M^+ as the molecular ion. Elemental analysis was performed with a LECO CHN/900 instrument.

Hydronium tricyanomethanide (3): Sodium tricyanomethanide (0.5 g) was dissolved in a dilute sulfuric acid solution (ca. 8 drops 98 % H_2SO_4 in 5 mL de-ionized water) in a test tube (diameter = 1.5 cm). Diethyl ether (5 mL) was added to the top of the aqueous solution, resulting in two distinct layers. After thorough mixing, an additional greenish yellow layer appeared between the upper ether layer and the lower aqueous layer. A sample of the middle layer was pipetted onto a glass plate, and the solvents were removed by evaporation at approximately −30 °C with the aid of N_2 flow to give hydronium tricyanomethanide as a slightly yellow crystalline solid. ^{1}H NMR (300 MHz) spectrum of the middle ethereal layer shows two broad peaks: $\delta = 6.43$, 6.37 ppm in $CDCl_3$ or $\delta = 5.83$, 5.74 ppm in [D$_6$]acetone.

(Z)-3-Amino-2-cyano-3-hydroxyacrylamide (4) or a 1:1 co-crystal (or salt) of 4-H_2SO_4: Sodium tricyanomethanide (5 g) was cautiously and slowly dissolved in concentrated sulfuric acid (the mixing is exothermic). The resulting yellow solution was poured into a flask with diethyl ether (ca. 600 mL) with stirring at −78 °C. A thick white slurry formed and was filtered (the white precipitation should be Na_2SO_4). The filtrate was kept overnight at −20 °C. The white crust formed was rinsed with cold diethyl ether. Single crystal X-ray analysis revealed the compound to be (*Z*)-3-amino-2-cyano-3-hydroxyacrylamide **4**. When the procedure was repeated, sometimes a 1:1 co-crystal (or salt) of **4** and H_2SO_4 was obtained.

1-Chloro-1-amino-2,2-dicyanoethylene (5) or 2-cyano-3-iminoacrylimidoyl chloride (6): A suspension of sodium tricyanomethanide (1.5 g) in anhydrous THF (100 mL) was stirred vigorously at 0 °C in a two-necked round bottom flask. A flow of gaseous HCl was introduced via glass tubing into this suspension from one neck, and the excess HCl was released from the other outlet to keep the system under atmosphere pressure. After 10 min of HCl introduction, the flow was stopped and the suspension was stirred for 1 h. This cycle was repeated three times. The mixture was filtered, and the solvent and HCl in the filtrate were evaporated. The resulting off-white solid was further washed with a small amount of cold diethyl ether. M.p. > 150 °C (decomposed); ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta = 8.75$ ppm; ^{13}C NMR (100 MHz, [D$_8$]THF): $\delta = 54.6$, 113.5, 114.3, 162.1 ppm; IR (ATR): $\tilde{\nu} = 3298$, 3139, 2228, 2213, 1623, 1543, 1361 cm^{-1}; HRMS (EI) calcd for $C_4H_2N_3{}^{35}Cl$ 126.9893; found 92.0206 [100 %, $(M-Cl)^+$], 126.9893 [23.4 %, $M^+(^{35}Cl)$], 128.9858 [7.62 %, $M^+(^{37}Cl)$]; elemental analysis calcd (%) for $C_4H_2N_3Cl$: C 37.67, H 1.58, N 32.95; found: C 37.39, H 1.69, N 32.25.

Single-crystal X-ray analysis: X-ray data collection was carried out on a Bruker KappaCCD diffractometer equipped with a graphite monochromator ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) and an Oxford Cryostream low-temperature device. Cell dimensions were obtained by least-squares refinement of all measured reflections (HKL, Scalepack[31a]), $\theta_{max} = 27.5°$.

All structures were solved by direct methods (SIR97[31b]). All non-hydrogen atoms were refined anisotropically, H atoms isotropically by full-matrix least-squares with SHELXL-97[31c] using experimental weights ($1/[\sigma^2(I_o)+(I_o+I_c)^2/900]$).

X-ray crystal structure of compound **3**: Single crystals were obtained by rapid evaporation of solvents from the aquo-ethereal solution of **3** with the aid of N_2 flow at approximately −30 °C: $C_4H_3N_3O$, $M_r=109.09$, $a=8.879(<1)$, $b=9.740(<1)$, $c=6.618(<1)$ Å, $V=572.3(<1)$ Å^3, $\rho_{calcd}=1.27\ \mathrm{g\,cm^{-3}}$, $\mu=0.097\ \mathrm{mm^{-1}}$, space group *Ima2*, $Z=4$, $Z'=0.50$, $R=0.033$, $T=173$ K.[31d]

X-ray crystal structure of compound **4**: Single crystals were found in the diethyl ether solution at approximately −20 °C during the time of precipitation: $C_4H_5N_3O_2$, $M_r=127.10$, $a=4.945(<1)$, $b=5.294(<1)$, $c=10.481(<1)$ Å, $\alpha=90.80(<1)°$, $\beta=90.56(<1)°$, $\gamma=98.88(<1)°$, $V=271.0(<1)$ Å^3, $\rho_{calcd}=1.56\ \mathrm{g\,cm^{-3}}$, $\mu=0.128\ \mathrm{mm^{-1}}$, space group $P\bar{1}$, $Z=2$, $Z'=1$, $R=0.040$, $T=173$ K.[31d]

X-ray powder diffraction analysis: Crystallographic information for compounds **5/6** and **4**-H_2SO_4 are given below. Three indexing programs based on different algorithms (ITO,[32a] TREOR[32b] and DICVOL[32c]) were used to verify that the patterns could be indexed only with triclinic unit cells. Then reflection intensities were extracted from the powder diffraction patterns using the program EXTRAC[33a] in the XRS-82[33b] suite of programs. These intensities were used as input to the powder charge-flipping (*pCF*) algorithm[21] in the program Superflip.[34] For both compounds studied here, the model obtained from the Superflip electron density map was used as a starting point for Rietveld refinement using XRS-82.[33b] Isotropic displacement parameters for all atoms were kept fixed at 0.025 Å^2 and neutral scattering factors were used for all atoms. Hydrogen atoms were not included in the models of either compound. Data were measured at room temperature. More details regarding the structure determinations and structure refinements are described in the Supporting Information.

X-ray crystal structure of compound **5/6**: Polycrystalline powder sample were obtained after evaporation of the reaction mixture of HCl and $NaC(CN)_3$: $C_4H_2N_3Cl$, $M_r=127.53$, $a=7.465(2)$ Å, $b=7.522(1)$ Å, $c=5.4362(4)$ Å, $\alpha=86.13(7)°$, $\beta=103.94(4)°$, $\gamma=109.65(4)°$, space group $P\bar{1}$, $R_F=0.075$, $R_{wp}=0.127$, $T=298$ K.[31d]

X-ray crystal structure of compound **4**-H_2SO_4: Polycrystalline powder sample were obtained after evaporation of the reaction mixture of H_2SO_4 and $NaC(CN)_3$: $C_4H_7N_3O_6S$, $M_r=225.18$, $a=8.459(6)$, $b=9.858(7)$, $c=5.3192(8)$ Å, $\alpha=95.9(2)°$, $\beta=94.8(1)°$, $\gamma=110.5(1)°$, space group $P\bar{1}$, $R_F=0.060$, $R_{wp}=0.148$, $T=298$ K.[31d]

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