

# The Existence of Tricyanomethane

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Dedicated to Professor Rolf Minkwitz on the occasion of his 75th birthday

**Abstract:** Calcium tricyanomethanide reacts with hydrogen fluoride under formation of tricyanomethane and  $\text{Ca}(\text{HF}_2)_2$ . Tricyanomethane is stable below  $-40^\circ\text{C}$  and was characterized by IR, Raman, and NMR spectroscopy. The vibrational spectra were compared to the quantum-chemical frequencies at the PBE1PBE/6-311G(3df,3dp) level of theory and confirm the predicted  $C_{3v}$  symmetry of the molecule with regular C–H (109.8 pm), C–C (146.7 pm), and C≡N (114.7 pm) bonds.

Tricyanomethane (cyanofom; **1**) is a textbook example of one of the strongest organic acids ( $\text{p}K_{\text{a}} = -5.1$  in water), but the molecule has previously only been identified by microwave spectroscopy in the gas phase at very low pressures.<sup>[1–3]</sup> The isolation of **1** was first attempted more than one century ago by Schmidtman, who used the salts of the corresponding base,  $(\text{NC})_3\text{C}^-$ , and sulfuric acid as the starting materials.<sup>[4]</sup> Since then, numerous attempts to isolate **1** have been reported, but none of them were successful. These were well described by Dunitz et al., who reinvestigated most of these attempts.<sup>[5]</sup> It has been assumed that the corresponding acid of tricyanomethanide might be the tautomeric dicyanoketenimine (**2**; Figure 1).

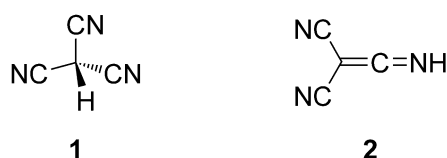


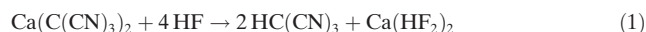
Figure 1. Tautomers of cyanofom.

Quantum-chemical calculations have shown that **1** is more stable than **2** by  $7.4 \text{ kJ mol}^{-1}$ ,<sup>[6]</sup> but the stabilities could change in the condensed phase owing to strong hydrogen bonds, and the presence of **2** would thereby explain the remarkable reactivity of cyanofom. The previously reported unsuccessful syntheses prompted us to attempt the isolation of either **1** or **2** from  $\text{Ca}(\text{C}(\text{CN})_3)_2$  in hydrogen fluoride at low temperatures.

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Under strictly anhydrous conditions,  $\text{Ca}(\text{C}(\text{CN})_3)_2$  dissolves in hydrogen fluoride at  $-50^\circ\text{C}$  under formation of a colorless homogenous solution. The NMR spectra provided a first evidence for the formation of **1** according to Eq. (1):



The  $^{13}\text{C}$  NMR spectrum displays a singlet at 106.1 ppm, typical for the cyanide group, and a doublet at 16.9 ppm, which is due to coupling with the proton ( $^1J(\text{C},\text{H}) = 147 \text{ Hz}$ ). The  $^1\text{H}$  NMR spectrum shows a singlet at 5.79 ppm for the acidic proton of **1**, and the  $^{14}\text{N}$  NMR spectrum displays only a broad signal at  $-127.1 \text{ ppm}$  for the cyanide groups. Furthermore, the  $^{19}\text{F}$  NMR spectrum confirmed the  $\text{HF}_2^-$  formation by the typical resonance at  $-150 \text{ ppm}$ .<sup>[7]</sup>

Further evidence for the formation of **1** is given by the vibrational spectra of the colorless  $\text{1/Ca}(\text{HF}_2)_2$  mixture that was obtained by removal of HF at  $-78^\circ\text{C}$ . The experimental Raman frequencies of **1**, those of deuterated  $\text{DC}(\text{CN})_3$  (**1a**), and the quantum-chemically calculated frequencies together with their assignments are summarized in Table 1. The Raman spectra are shown in Figure 2.

For the assignment of the vibrational modes of **1**,  $C_{3v}$  symmetry was assumed in agreement with the quantum-chemical calculations. Therefore, the molecule should exhibit 18 fundamental vibrations ( $\Gamma_{\text{vib}}(C_{3v}) = 5A_1 + A_2 + 6E$ ); whereas the  $A_1$  and  $E$  modes should be Raman and IR active, the  $A_2$  mode is inactive in both spectroscopic methods. The presence of  $\text{Ca}(\text{HF}_2)_2$  does not cause any difficulties, as only one vibration of the  $\text{HF}_2^-$  anion (at ca.  $600 \text{ cm}^{-1}$ ) is active

Table 1: Observed and calculated Raman frequencies [ $\text{cm}^{-1}$ ] for  $\text{HC}(\text{CN})_3$  (**1**) and  $\text{DC}(\text{CN})_3$  (**1a**) at  $-196^\circ\text{C}$ .

| $\text{HC}(\text{CN})_3$ ( <b>1</b> ) |                      | $\text{DC}(\text{CN})_3$ ( <b>1a</b> ) |                      | Assignment<br>X = H, D                    |
|---------------------------------------|----------------------|--|----------------------|---|
| Raman                                 | calcd <sup>[a]</sup> | Raman                                  | calcd <sup>[a]</sup> |   |
| 2885 (38)                             | 2922 (57)            | 2126 (66)                              | 2145 (30)            | $\nu(\text{CX})$ ( $A_1$ )                |
| 2287 (100)                            | 2316 (100)           | 2286 (100)                             | 2316 (100)           | $\nu_s(\text{CN})$ ( $A_1$ )              |
| 2259 (7)                              | 2310 (40)            | 2319 (13)                              | 2310 (42)            | $\nu_{\text{as}}(\text{CN})$ ( $E$ )      |
| 1253 (5)                              | 1232 (4)             | 849 (15)                               | 831 (0.1)            | $\delta(\text{CCX})$ ( $E$ )              |
| 1022 (7)                              | 1002 (2)             | 1116 (6)                               | 1098 (2)             | $\nu_{\text{as}}(\text{CC})$ ( $E$ )      |
| 825 (24)                              | 813 (4)              | 806 (27)                               | 794 (5)              | $\nu_s(\text{CC})$ ( $A_1$ )              |
| 575 (7)                               | 559 (2)              | 570 (15)                               | 559 (2)              | $\delta(\text{CCC})$ ( $E$ )              |
| 567 (16)                              | 556 (3)              | 561 (7)                                | 556 (3)              | $\delta(\text{CCN})$ ( $A_1$ )            |
| 347 (45)                              | 345 (2)              | 339 (67)                               | 336 (2)              | $\delta(\text{CCN})$ ( $E$ )              |
|                                       | 160 (1)              |  | 159 (1)              | $\delta(\text{C}(\text{CN})_3)$ ( $A_1$ ) |
|                                       | 126 (4)              |  | 126 (4)              | $\delta(\text{C}(\text{CN})_3)$ ( $E$ )   |

[a] Calculated at the PBE1PBE/6-311G(3df,3dp) level of theory. Frequencies were scaled by an empirical factor of 0.96. The relative Raman activities are given in %.

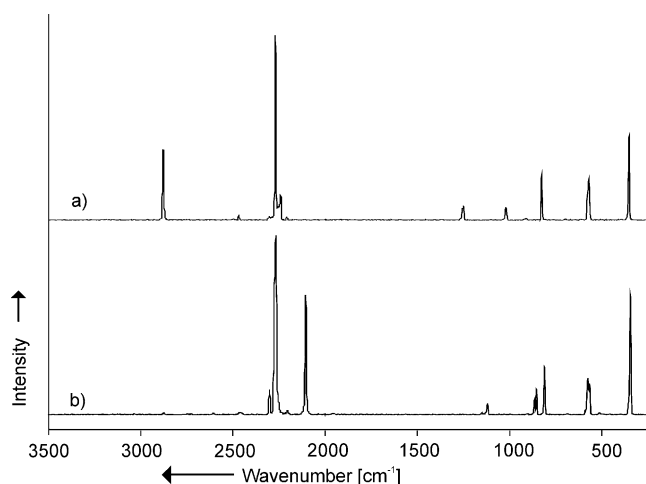


Figure 2. Raman spectra of a)  $\text{HC}(\text{CN})_3$  (**1**) and b)  $\text{DC}(\text{CN})_3$  (**1a**).

in the Raman spectrum and displays a very low line intensity.<sup>[8]</sup> The C–H, C≡N, and C–C stretching vibrations of **1** are seen in their typical regions and confirm the structure of **1**, whereas the absence of C=C and N=N stretching modes (both usually of high Raman intensity) excludes the formation of **2**.<sup>[8]</sup> The isotopic H/D shift from 2885 to 2145  $\text{cm}^{-1}$  corroborates the CH stretching vibration. Overall, the experimental and calculated frequencies in Table 1 agree fairly well, especially considering that the calculated frequencies do not take interactions between molecules into account. The calculated gas-phase structure of **1** at the PBE1PBE/6-311G(3df,3dp) level of theory is comparable to that previously determined at the MP2/6-311++G(2d,2p) level.<sup>[9–12]</sup> The calculations predict regular C–H (109.8 pm), C–C (146.7 pm), and C≡N (114.7 pm) bonds with the expected linear C–C≡N arrangement and a C–C–C angle of 111.4°.<sup>[13]</sup>

The separation of **1** from the by-product  $\text{Ca}(\text{HF}_2)_2$  was found to be difficult and has not yet been achieved because **1** is only stable below  $-40^\circ\text{C}$  and very moisture-sensitive. Furthermore, both **1** and  $\text{Ca}(\text{HF}_2)_2$  are soluble in hydrogen fluoride. Attempts to extract **1** with diethyl ether at low temperatures led to red solutions, which are reminiscent of the decomposition products already observed during the unsuccessful attempts to prepare **1** as reported in literature.<sup>[5]</sup> The vapor pressure of **1** below  $-40^\circ\text{C}$  is not sufficient for a high-vacuum sublimation. Even though the purification of **1** remains to be a significant challenge, its existence in the condensed phase has been confirmed. Considering the numerous previously reported attempts to prepare **1**, we attribute the success of our strategy mainly to the low reaction temperature and the choice of hydrogen fluoride as a suitable acid and solvent.

## Experimental Section

$\text{Ca}(\text{C}(\text{CN})_3)_2$  (220 mg, 1 mmol), which was prepared according to a literature method,<sup>[14]</sup> was placed into a reactor (FEP tube), and then

an excess of anhydrous hydrogen fluoride (3.00 g) was condensed by cooling to  $-196^\circ\text{C}$ . The reactor was warmed up to  $-50^\circ\text{C}$  for approximately 10 min until the  $\text{Ca}(\text{C}(\text{CN})_3)_2$  had completely dissolved. The colorless solution was then cooled to  $-78^\circ\text{C}$  (dry ice), and the excess hydrogen fluoride was removed in dynamic vacuum over night. The remaining colorless microcrystalline product (300 mg) was a 2:1 mixture of  $\text{HC}(\text{CN})_3$  and  $\text{Ca}(\text{HF}_2)_2$ . It decomposed above  $-40^\circ\text{C}$  with a color change from colorless to yellow to red. The deuterated  $\text{DC}(\text{CN})_3$  was prepared analogously with DF instead of HF.  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]$ acetone,  $-45^\circ\text{C}$ , TMS):  $\delta = 5.79$  ppm (s).  $^{13}\text{C}$  NMR (100.6 MHz,  $[\text{D}_6]$ acetone,  $-45^\circ\text{C}$ , TMS):  $\delta = 16.9$  (d,  $^1J(\text{C},\text{H}) = 147$  Hz, CH), 106.1 ppm (s, CN).  $^{14}\text{N}$  NMR (28.9 MHz,  $[\text{D}_6]$ acetone,  $-45^\circ\text{C}$ , nitromethane):  $\delta = -127.1$  ppm. IR (neat,  $-120^\circ\text{C}$ ):  $\tilde{\nu} = 2915$  (s), 2886 (m), 2310 (vw), 2212 (vw), 1349 (w), 1248 (vw), 1025 (s), 1006 (m), 918 (w), 829 (s), 569  $\text{cm}^{-1}$  (vs).

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