

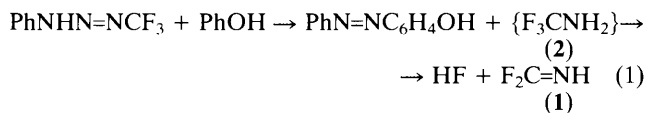
Difluoromethanimine, $F_2C=NH$, a Novel Unstable Molecule

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Difluoromethanimine, $F_2C=NH$, which is stable only below ~ 260 K has been synthesized by the reaction of F_3CNH_2 with triethylamine and characterized by ^{19}F n.m.r. and i.r. spectroscopy, from which all vibrational fundamentals and rotational constants were determined.

Of the difluoromethanimines, $F_2C=NX$, only the *N*-halogeno derivatives, $X = F, Cl, \text{ and } Br$, have been fully characterized.¹ Makarov *et al.* reported the synthesis of $F_2C=NH$ by cleavage of 1-trifluoromethyl-3-phenyltriazene with phenol, equation (1). FCN and HF were formed by pyrolysis of (1) over NaF at 690–720 K.² Later, it was claimed³ that (1) was also obtained when reaction (1) was carried out over NaF at 323–333 K and 150–160 mmHg. However, (1) was not characterized beyond an elemental analysis (see below) and its boiling point (288 K, with decomposition). The reported syntheses could not be confirmed,⁴ and furthermore, (1) was not obtained by pyrolysis of F_2HCN_3 .⁴ Likewise, FCN rather than (1) was found as decomposition product of the moderately stable amine F_3CNH_2 (2).⁵

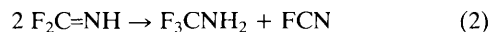


In order to clarify the contradictory observations concerning the existence of (1) and to characterize this interesting molecule unambiguously, we have repeated reaction (1) according to ref. 2. In agreement with ref. 5, only pure (2) was obtained which, when decomposed in the gas phase, did not yield any (1). If reaction (1) was carried out according to ref. 3, not (1) but a mixture of (2) and FCN was isolated, whose

elemental analysis, as reported,³ was eventually close to that of (1).

If, however, (2) was dissolved at 195 K in neat NEt_3 and this solution warmed to 253–263 K *in vacuo*, gaseous material was evolved which was identified as (1). Optimization of the synthesis furnished pure (1) in good yield.† Similarly, $F_2C=ND$ was obtained from F_3CND_2 . After its properties had been determined, we discovered that (1) may also be prepared by hydrolysis of F_3CNCO with wet NEt_3 .

The imine (1) is a colourless gas, m.p. 183–184 K, which is stable for hours at ambient temperature in the gas phase at pressures below 5 mmHg, while rapid disproportionation according to reaction (2) occurs at higher pressures. Rapid H/D exchange of (1) with protic species has been observed in the gas phase. Since at ambient temperature the equilibrium (2) lies to the right, (1) cannot be formed in the gas phase by decomposition of (2). In our opinion the conditions previously reported^{2,3} for the synthesis of (1) suggest that only (2) and FCN rather than (1) had been obtained.



† *Typical procedure:* F_3CNH_2 (0.02 mol) was dissolved in NEt_3 (0.08 mol) at 195 K and the mixture distilled *in vacuo* employing a low-temperature slit-tube column (Fischer). With a vessel temperature of 263 K and the still-head held at 233 K, the pressure was adjusted to 20 mmHg. Pure (1) was pumped from the still-head *via* a needle valve and condensed and stored in a liquid N_2 trap (67% yield).

Compound (**1**) was identified and characterized by ^{19}F n.m.r. and gas-phase i.r. spectroscopy. In i.r. and Raman spectra of the solid, several fundamentals of the monomer are doubled, the two components exhibiting mutual exclusion which may suggest that a centrosymmetric oligomer is formed in the solid state. The ^{19}F n.m.r. spectrum of (**1**) in CFCl_3 [in which (**1**) is stable at 195 K but rapidly decomposes >273 K] reveals two signals (δF_{cis} -32.6 p.p.m. and δF_{trans} -59.2 p.p.m.) with a pattern typical of an ABX spin system, $^2J(\text{FF})$ 54.6 Hz, $^3J(\text{FH})_{\text{trans}}$ 52.7 Hz, $^3J(\text{FH})_{\text{cis}}$ 3.3 Hz. The nine vibrational fundamentals of $\text{F}_2\text{C}=\text{NH}/\text{F}_2\text{C}=\text{ND}$ in the gas phase were observed in the i.r. spectrum: $\nu(\text{NH/D})$ 3402.3/2519.3, $\nu(\text{CN})$ 1785.2/1780.0, $\nu_{\text{as}}(\text{CF}_2)$ 1307/1280, $\delta(\text{CNH/D})$ 1031.2/836.0, $\nu_{\text{s}}(\text{CF}_2)$ 947.2/954.0, $\delta(\text{CF}_2)$ 618/609, $\rho(\text{CF}_2)$ 542.0/491.8, $\tau(\text{NH/D})$ 831.7/613.9, and $\gamma(\text{CF}_2)$ 695.2/705.1 cm^{-1} . Analogy of the spectra with those of F_2CO and other $\text{F}_2\text{C}=\text{NX}$ compounds is noted, and the assignment was confirmed by both a normal co-ordinate analysis and the band contours. The latter are typical of a (very slightly asymmetric) oblate top, as is to be expected from the planar geometry predicted by *ab initio* calculations, $A = 0.37442$, $B = 0.36667$, and $C = 0.18525$ cm^{-1} .⁶ With a resolution of 0.12 cm^{-1} , we have resolved rotational fine structure for several i.r. bands, and we were able to determine therefrom the quantities $1/2(A + B) = 0.37696$ and $1/2(A + B - 2C) = 0.18843$ cm^{-1} (from which $C = 0.18853$ cm^{-1}) by means of polynomial analyses of the parallel band at 832 and the perpendicular band at 1031 cm^{-1} , respectively. The observed rotational-vibrational struc-

ture is an important piece of evidence for the identity, constitution, and geometry of monomeric $\text{F}_2\text{C}=\text{NH}$.

In conclusion, we believe that this is the first genuine report of a successful detection, isolation, and characterization of monomeric (**1**), and that the material previously claimed^{2,3} to be (**1**) was a mixture of the more stable amine (**2**) with its decomposition product FCN. Though (**1**) may well be an intermediate in this decomposition, it is not likely to attain a significant abundance under the reported conditions.

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