Energetic Materials

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# Synthesis and Characterization of Fluorodinitroamine, $FN(NO_2)_2$**

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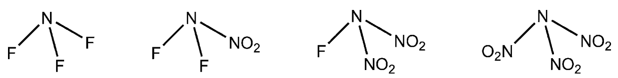
*In memory of Henry Zvi Selig*

**Abstract:** *$NF_3$ and $N(NO_2)_3$ are known compounds, whereas the mixed fluoronitroamines, $FN(NO_2)_2$ and $F_2NNO_2$, have been unknown thus far. One of these, $FN(NO_2)_2$, has now been prepared and characterized by multinuclear NMR and Raman spectroscopy. $FN(NO_2)_2$ is the first known example of an inorganic fluoronitroamine. It is a thermally unstable, highly energetic material formed by the fluorination of the dinitramide anion using $NF_4^+$ salts as the preferred fluorinating agent.*

Trifluoramine ($NF_3$) is a very stable compound and has been known for almost a century. It was first prepared in 1928 by Otto Ruff[1] by the electrolysis of $NH_4F$/HF and is well characterized.[2] By contrast, trinitroamine ($N(NO_2)_3$) is thermally unstable and decomposes above $-40\,°C$. It has not been isolated as a neat material, but instead has been identified as a minor component in a complex reaction mixture by $^{14}N$ NMR spectroscopy and by several weak low-temperature infrared absorptions (in $CH_3CN$).[3]

As the closely related $CF(NO_2)_2$ group is more stable than the $C(NO_2)_3$ group, it was interesting to synthesize and characterize mixed fluoronitroamines (Scheme 1) and to explore whether trinitroamine can also be stabilized by partial fluorine substitution. Although alkylfluoronitroamines ($RNF(NO_2)$) have been known for many years,[4] the unsubstituted fluoronitroamines, $F_nN(NO_2)_{(3-n)}$, where $n=1$ or 2, have not been known. Herein, we summarize our work on the synthesis of fluorodinitroamine carried out during the past 19 years in our laboratories at the Edwards Air Force Base and the University of Southern California.




***Scheme 1.*** Simple fluoro- and nitro-substituted amines.

In previous work, we have demonstrated the usefulness of $NF_4^+$ salts for the oxidative fluorination of anions. These reactions involve the low-temperature metathesis of $NF_4SbF_6$ with a cesium or potassium salt of an $OX^-$ anion, resulting in the formation of an intermediate thermally unstable $[NF_4^+OX^-]$ salt, followed by the thermal decomposition of $[NF_4^+OX^-]$ to $NF_3$ and the desired hypofluorite.

In this manner, high-yielding syntheses of $FOClO_3$,[5] $FONO_2$,[6] $FOSO_2F$,[7] $FOTeF_5$,[8] and $FOIOF_4$[9] have been achieved. The preferred solvent for these reactions was anhydrous HF, and $CsSbF_6$ was the by-product of choice because of its low solubility in HF. If, however, the anion was incompatible with HF, other solvents, such as $SO_2$, could also be used. For $SO_2$, the use of potassium salts was preferred because of the lower solubility of $KSbF_6$ in this solvent. The intermediate formation of the $NF_4^+OX^-$ salts was established by the isolation of $NF_4^+ClO_4^-$ [5] and $NF_4^+SO_3F^-$.[7] As the dinitramide anion ($N(NO_2)_2^-$) is well known,[10–14] it was a potential starting material for the synthesis of the yet unknown $FN(NO_2)_2$ molecule.

Numerous experimental conditions for the synthesis of $FN(NO_2)_2$ were investigated, including the use of $KN(NO_2)_2$ or $CsN(NO_2)_2$ as starting materials, of $NF_4SbF_6$, $NF_4BF_4$, $F_2$, or $FOSO_2F$ as fluorinating agents, and of HF, $SO_2$, $CH_3CN$, $C_2H_5CN$, $CH_3NO_2$, $SO_2ClF$, $CH_2Cl_2$, $CHF_3$, or $C_3F_7H$ as solvents. $SO_2ClF$, $CH_3F$, $C_3F_7H$, and $CH_2Cl_2$ could not be used because of the low solubilities of the starting materials in these solvents at low temperature. With $CH_3NO_2$, explosions were encountered at ambient temperature. The preferred combinations were $KN(NO_2)_2$ and $NF_4SbF_6$ in either $SO_2$ at $-64\,°C$ or $CH_3CN$ at $-30\,°C$. As with $NF_4^+NO_3^-$,[6] $NF_4^+TeF_5O^-$,[8] and $NF_4^+IF_4O_2^-$,[9] the $NF_4^+N(NO_2)_2^-$ intermediate could not be isolated because of its thermal instability. The insoluble alkali metal $SbF_6^-$ salts could be filtered off at low temperature, weighed, and identified by Raman spectroscopy. However, for the isolation of $FN(NO_2)_2$, the separation of the $MSbF_6$ precipitate from the other reaction products is not required. In $SO_2$ or $CH_3CN$ solutions, the dinitramide anion is directly fluorinated by the $NF_4^+$ cation [Eq. (1), M = K].

$$NF_4^+SbF_6^- + M^+N(NO_2)_2^- \rightarrow NF_3 + FN(NO_2)_2 + MSbF_6\downarrow \qquad (1)$$

The temperature dependence of the $FN(NO_2)_2$ formation according to Eq. (1) was followed by $^{19}F$ NMR spectroscopy

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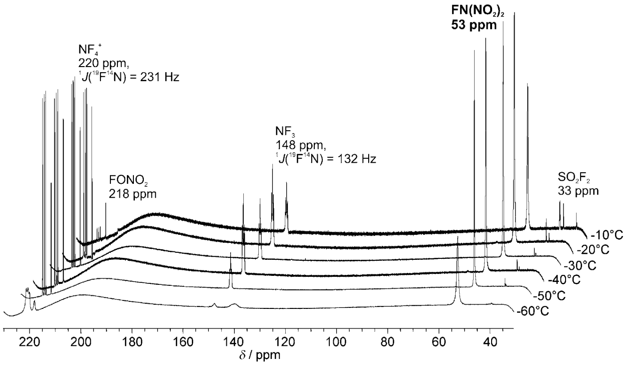


***Figure 1.*** $^{19}F$ NMR spectra of the $KN(NO_2)_2 + NF_4SbF_6$ system in $SO_2$ solution recorded as a function of temperature.

(Figure 1). As can be seen, the formation of $FN(NO_2)_2$ starts already at −60 °C and proceeds well between −50 °C and −20 °C. The increase in the intensity of the $FN(NO_2)_2$ signal is accompanied by the disappearance of the $NF_4^+$ signal and the intensity increase of the $NF_3$ signal. Above −20 °C, the concentration of $FN(NO_2)_2$ decreases as a result of decomposition.

In addition, two minor side reactions are also observed: the fluorination of $SO_2$ [Eq. (2)] and the formation of a small amount of $FONO_2$ [Eq. (3)] as a result of the presence of a small amount of $NO_3^-$, a common impurity in dinitramide salts.

$$NF_4^+SbF_6^- + SO_2 \rightarrow NF_3 + SO_2F_2 + SbF_5 \quad (2)$$

$$K^+NO_3^- + NF_4^+SbF_6^- \rightarrow NF_3 + FONO_2 + KSbF_6 \quad (3)$$

The formation of $FN(NO_2)_2$ in these solutions was also confirmed by low-temperature Raman spectroscopy. After the removal of most of the $SO_2$ or $CH_3CN$ solvents by fractional condensation through −64, −78, and −90 °C traps, the −78 and −90 °C traps contained the desired $FN(NO_2)_2$ and smaller amounts of solvent and $N_2O_4$. Complete removal of the solvent and $N_2O_4$ in this manner was not achieved.

In HF solution, the reactions are much more complicated because of the fast reaction of the dinitramide anion with HF. The results from a detailed study of this system are beyond the scope of this paper and will be reported in a separate publication.

For the synthesis of $FN(NO_2)_2$, reactions of $NF_4SbF_6$ with either $KN(NO_2)_2$ in $SO_2$ or $CH_3CN$ solutions or $CsN(NO_2)_2$ in HF solution were investigated [Eq. (1), M = K, Cs]. This reaction could be best controlled in $SO_2$ solution. The solvent was pumped off at −64 °C, and the volatile products, generated by the decomposition of the unstable intermediate $NF_4^+N(NO_2)_2^-$ between −60 °C and −56 °C, were pumped off from the −78 °C trap. $FN(NO_2)_2$ is formed in $SO_2$ solution in high yield (Figure 1). Several side reactions were also observed in this system. First of all, $FN(NO_2)_2$ starts to decompose at relatively low temperature, giving $N_2O$, $NO_2$/$N_2O_4$, $FNO_2$, and some *trans*-$N_2F_2$, indicative of a decomposition mechanism involving $NO_2$ and NF radicals. These products were identified by their gas-phase infrared spectra. The formation of $SO_2F_2$ was also observed by a slow attack of $SO_2$ by $NF_4^+$. Furthermore, $FNO_2$ can react with $SO_2$, resulting in the formation of solid $NO^+SO_3F^-$, which was identified by its Raman spectrum. Its formation was verified in a separate experiment [Eq. (4)].

$$FNO_2 + SO_2 \rightarrow NO^+SO_3F^- \quad (4)$$

Although the in situ yield of $FN(NO_2)_2$ from the reaction in $SO_2$ solution, determined by NMR spectroscopy, is nearly quantitative, the complete separation of $FN(NO_2)_2$ from the $SO_2$ solvent presents a major problem because of their similar volatilities and the thermal instability of $FN(NO_2)_2$. To circumvent this separation problem, the possibility of using different solvents was investigated. As in the case of the recently discovered $NCNO_2$,[15] compatibility, solubility, volatility and liquid-range problems render this a very difficult task. For example, the use of $CH_3CN$ suffers from its higher melting point of −41 °C and in some cases the formation of $CH_3COF$. Thus, when a reaction of $NF_4BF_4$ with $KN(NO_2)_2$ was carried out in this solvent at −22 °C, the $CH_3CN$ reacted with the nitramide anion and $NF_4^+$, resulting in the formation of acetyl fluoride, which was identified by its gas-phase IR spectrum.[16] When the reaction of $KN(NO_2)_2$ with $NF_4SbF_6$ was carried out in $CH_3CN$ at −30 °C, no $CH_3COF$ was observed, however complete separation of $FN(NO_2)_2$ from the solvent and $N_2O_4$ by fractional condensation was not achieved, as shown by low-temperature Raman spectroscopy. Care must be taken to predissolve the separate reagents in $CH_3CN$ when scaling up the reaction, otherwise deflagration can occur. While the desired reaction also proceeds well in propionitrile, complete separation of $FN(NO_2)_2$ from the solvent by fractional condensation was not successful.

The fluorination of $N(NO_2)_2^-$ is not restricted to the use of $NF_4^+$ salts as the fluorinating agent. For example, $F_2$ or $FOSO_2F$ were also used as fluorinating agents, but these modifications did not alleviate the separation problems.

Although the use of HF as a solvent suffers from its competing reactions with the dinitramide anion, we succeeded on one occasion to isolate an essentially pure sample of $FN(NO_2)_2$ for Raman spectroscopy from this system. When $KN(NO_2)_2$ was combined with $NF_4SbF_6$ in anhydrous HF at −78 °C, and all volatile products and the HF solvent were pumped off at −64 °C, the resulting residue was allowed to react further at −45 °C under a dynamic vacuum, and $FN(NO_2)_2$ was trapped at −95 °C. Based on its low-temperature Raman spectrum (Figure 2), the resulting product was essentially pure $FN(NO_2)_2$ containing a small amount of $N_2O_4$ as the only detectable impurity. The exact nature of this reaction is only poorly understood and was difficult to duplicate.

$FN(NO_2)_2$ is a colorless solid at low temperatures and melts at about −94 °C to a colorless liquid. Its composition was established by multinuclear NMR and Raman spectroscopy and quantum chemical calculations.

The $^{19}F$ NMR spectrum (Figure 1) shows a single, somewhat broadened resonance at 53 ppm, which is in good agreement with those previously observed for the similar

  

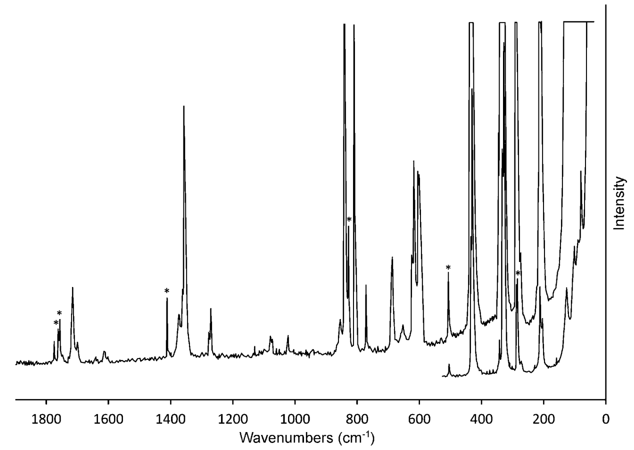


***Figure 2.*** Raman spectrum of solid $FN(NO_2)_2$ recorded at −130 °C with the 4880 Å exciting line of an Ar ion laser at two different attenuations; the bands marked by an asterisk are the result of a small amount of $N_2O_4$.

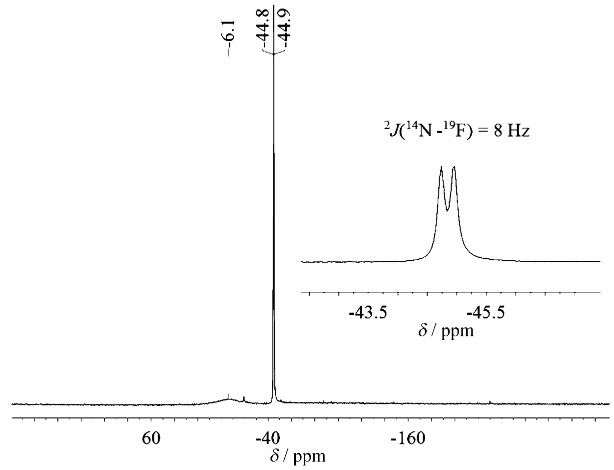


***Figure 3.*** $^{14}$N NMR spectrum of $FN(NO_2)_2$ in $SO_2$ solution recorded at −43 °C; the weak signal at −19.7 ppm is the result of a trace of $N_2O_4$.[20b]

compounds $F_2NNF_2$ (60.4 ppm),[17] FN=C(CN)($CH_3$) (60 ppm), and FN=C($CF_3$)$_2$ (48.3 ppm).[18] The $^{14}$N NMR spectrum (Figure 3) shows a broad resonance at −6.1 ppm for the amidic nitrogen atom and a sharp doublet at −44.9 ppm with a $^2J(^{14}\text{N-}^{19}\text{F})$ of 8 Hz for the nitro groups. The resonance for the amidic nitrogen (−6.1 ppm) is similar to that of −14.3 ppm found[19] for $NF_3$ in accord with the similar electronegativities of fluorine and the nitro group. The signal for the nitro groups (−44.9 ppm) is similar to that observed by us at −46.3 ppm for $HN(NO_2)_2$ in diethyl ether. The $^2J(^{14}\text{N-}^{19}\text{F})$ coupling constant of 8 Hz for the nitro groups is very similar to that of 9.8 Hz found for $FC(NO_2)_3$.[20a] The $^1J(^{14}\text{N-}^{19}\text{F})$ coupling could not be observed in the $^{14}$N NMR spectrum because of the broadness of the amidic nitrogen resonance. Attempts to observe this $^1J$ coupling constant in the $^{15}$N NMR spectrum of $FN(NO_2)_2$ with natural $^{15}$N abundance were also unsuccessful. Overall, the $^{19}$F and $^{14/15}$N NMR spectra are in accord with the proposed $FN(NO_2)_2$ structure.

The Raman spectrum of solid $FN(NO_2)_2$ is shown in Figure 2, and the observed frequencies and their assignments are listed in Table 1. The agreement between observed and calculated vibrational spectra is very good, particularly when keeping in mind that the observed spectrum is for the solid, where solid-state effects can influence some of the frequencies and cause additional splittings of some of the bands. The only observed impurities in the spectrum were small amounts of the decomposition product $N_2O_4$. Thus, the Raman spectrum clearly establishes the identity of this compound as $FN(NO_2)_2$.

In the absence of a crystal structure, the good agreement between the observed and calculated vibrational spectrum lends strong support to the minimum energy structure predicted by our calculations for free gaseous $FN(NO_2)_2$ (Figure 4). The structure is derived from a pseudo-tetrahedron with the four ligand positions being occupied by two nitro groups, one fluorine atom and a sterically active free valence electron pair. The only symmetry element is a sym-

***Table 1:*** Observed and calculated Raman spectra of $FN(NO_2)_2$.

| Vibrational assignments in $C_s$ symmetry, approximate mode description | Observed frequencies [relative Raman intensities][a] | Calculated frequencies [relative Raman intensities][a,b] |
|---|---|---|
| A′ $\nu_1$ $\nu_{as}$ $NO_2$ ip[c] | 1743 [1] | 1715 [16] |
| $\nu_2$ $\nu_{sym}$ $NO_2$ ip | 1351 [3], 1335 [2], 1332 [14] | 1329 [100] |
| $\nu_3$ ν NF | 1064 [1], 1054 [0.5] | 1064 [8] |
| $\nu_4$ $\delta_{sciss}$ $NO_2$ ip | 842 [2], 825 [31] | 831 [63] |
| $\nu_5$ $\nu_{sym}$ $N_3$ | 794 [22] | 798 [14] |
| $\nu_6$ $\delta_{rock}$ NF | 615 [4], 606 [9] | 607 [15] |
| $\nu_7$ $\delta_{sciss}$ $N_3$ | 430 sh, 425 [88] | 428 [86] |
| $\nu_8$ $\delta_{rock}$ $NO_2$ + $\delta_{rock}$ NF ip | 329 [70] | 318 [24] |
| $\nu_9$ $\delta_{wag}$ $NO_2$ ip | 207 [26], 200 [15] | 198 [16] |
| $\nu_{10}$ τ $NO_2$ ip | 77 [30] | 59 [9] |
| A″ $\nu_{11}$ $\nu_{as}$ $NO_2$ oop[c] | 1682 sh, 1680 [4], 1668 [0.5] | 1693 [44] |
| $\nu_{12}$ $\nu_{sym}$ $NO_2$ oop | 1254 [1], 1249 [3] | 1244 [7] |
| $\nu_{13}$ $\delta_{sciss}$ $NO_2$ oop | 758 [3] | 743 [0] |
| $\nu_{14}$ $\nu_{asym}$ $N_3$ | 680 sh, 675 [5] | 692 [3] |
| $\nu_{15}$ $\delta_{wag}$ NF | 593 [9], 589 [9] | 604 [17] |
| $\nu_{16}$ $\delta_{rock}$ $NO_2$ + $\delta_{rock}$ NF oop | 337 [10] | 328 [3] |
| $\nu_{17}$ $\nu_{sym}$ $NO_2$ oop | 324 [100] | 306 [50] |
| $\nu_{18}$ τ $NO_2$ oop | not observed | (33) [5] |
| lattice vibrations | 165 [20], 99 [20], 87 [8] | |

[a] Frequencies in $cm^{-1}$; uncorrected intensities based on peak heights in percent based on the most intense band being 100. [b] Calculated at the COSMO-mPW2PLYP/Def2-TZVPP level using individual anharmonicity corrections for each mode obtained by comparing harmonic and anharmonic B3LYP/aug-cc-pVTZ frequency calculations; Raman intensities were calculated at the B3LYP/aug-cc-pVTZ level of theory. [c] ip and oop stand for in-phase and out-of-phase, respectively.

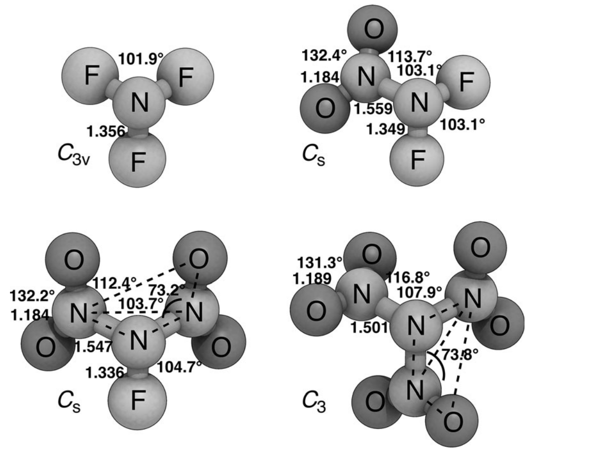


***Figure 4.*** Minimum energy structures of $NF_3$, $F_2N(NO_2)$, $FN(NO_2)_2$, and $N(NO_2)_3$ predicted at the M06-2X/aug-cc-pVTZ level (bond lengths in Å and bond angles in deg) viewed along the sterically active free valence electron pair on the central nitrogen atom.

metry plane bisecting the fluorine ligand, the free valence electron pair, and the central nitrogen atom. As can be seen from the N-N-N and F-N-N bond angles of 103.7° and 104.7°, respectively, the sterically active lone pair is arguably more voluminous than the remaining ligands, compressing their bond angles from the ideal tetrahedral angle of 109.5° by about 5°. This view is supported by a quantum chemical topological study of the lone pair domain by the HELP method[21] (see the Supporting Information). Because of the planarity of the $N(NO_2)$ group, the N-N-O bond angles are 113.9°. The predicted N−F bond length of 1.34 Å is similar but slightly shorter than that of 1.37 Å experimentally found for $NF_3$,[22] and the N−O bond lengths are as expected for a normal $NO_2$ group. The N−N bonds of 1.55 Å are predicted to be considerably longer than those of 1.35–1.44 Å typically found in organic nitramines,[23] in accord with the decreased stability of $FN(NO_2)_2$. Therefore, the predicted structure is in agreement with the observed decomposition mode, that is, the strong N−F and N−O bonds and weak N−N bonds result in an easy loss of $NO_2$ groups producing $N_2O_4$, and in the formation of NF radicals producing *trans*-$N_2F_2$.

For a meaningful comparison of the trends within the $NF_3$, $F_2N(NO_2)$, $FN(NO_2)_2$, and $N(NO_2)_3$ series, it was necessary to calculate the structures of all the members at the same level of theory, as only the structure of $NF_3$ is experimentally known.[22] The results are shown in Figure 4. A comparison of the observed structure of $NF_3$, *r*N-F = 1.37 Å, ∡F-N-F = 102.1°,[22] with that predicted by us, *r*N-F = 1.36 Å, ∡F-N-F = 101.9°, indicates that our predicted structures are good approximations to the actual structures. As can be seen from Figure 4, substitution of a fluorine ligand in $NF_3$ by a nitro group slightly shortens the N−F bonds. The N−N bonds in $N(NO_2)_3$ become increasingly longer and weaker with increasing fluorine substitution. Thus, the calculated N−N bond dissociation enthalpies for $N(NO_2)_3$, $FN(NO_2)_2$, and $F_2N(NO_2)$ are 28.2, 22.1, and 14.2 kcal mol$^{-1}$, respectively, and $F_2N(NO_2)$ is predicted to be the least stable compound within this series. As expected, the tetrahedral angle is the smallest for $NF_3$ and increases with an increasing number of the more bulky nitro groups.

In conclusion, $FN(NO_2)_2$, one of the two thus far unknown mixed fluoronitroamines, has been prepared and characterized by multinuclear NMR and Raman spectroscopy. It is a thermally unstable compound that readily decomposes to $N_2O_4$, *trans*-$N_2F_2$, $N_2O$, and $FNO_2$. It is shown that in contrast to the closely related trinitromethyl compounds, fluorine substitution weakens the relatively labile N−N bonds in $N(NO_2)_3$, and that the yet unknown $F_2N(NO_2)$ molecule will be even less stable than $FN(NO_2)_2$, but might be accessible by low-temperature fluorination of the known $FN(NO_2)^-$ anion.[24]

## Experimental Section

Caution! Anhydrous HF can cause severe burns and contact with the skin must be avoided. Many of the materials described in this work are energetic and should be handled on a small scale while taking appropriate safety measures, such as wearing face shields, leather gloves and protective clothing, and working in a well-ventilated environment.

All volatile materials were handled in either a stainless-steel/Teflon-FEP[25] or Pyrex-glass vacuum line with greaseless Teflon stopcocks. Solids were handled in the dry Ar atmosphere of a glove box. HF was dried by storage over $BiF_5$ or $TaF_5$.[26] Acetonitrile was dried by storage over $P_4O_{10}$ and Linde 3 Å molecular sieves and distilled prior to use. A reported method was used for the preparation of $NF_4SbF_6$,[27] and the sample of $KN(NO_2)_2$ was kindly donated by EURENCO Bofors.

NMR spectra were recorded on a Bruker AMX 500 ($^{14}N$, $\nu_0 =$ 36.13 MHz) and on a Varian-400 spectrometer. Spectra were externally referenced to neat $CH_3NO_2$ ($\delta_0 = 0.00$ ppm). Raman spectra were recorded in 3 mm Pyrex tubes on a Cary Model 83 using the 4880 Å excitation line of an Ar ion laser.

Preparation of $FN(NO_2)_2$: In a typical experiment, $NF_4SbF_6$ (2.00 mmol) and $KN(NO_2)_2$ (2.00 mmol) were loaded in the drybox into a passivated $^1/_4$″ o.d. Teflon-FEP ampule closed by a stainless steel valve. The solvent ($SO_2$ or $CH_3CN$, 2–5 mL) was added at −196 °C on the vacuum line and the mixture was warmed to the melting point of the solvent at which point $NF_3$ evolution began. The volatile products were separated by repeated fractional condensations through a series of −64, −80, −95, and −196 °C traps in a dynamic vacuum. The bulk of the desired $FN(NO_2)_2$ product was found in the −78 and −95 °C traps. The purity of the isolated materials was estimated by Raman and NMR measurements.

Computational Details: Structure optimizations of $NF_3$, $F_2N(NO_2)$, $FN(NO_2)_2$, and $N(NO_2)_3$ in the gas phase were calculated using the hybrid meta exchange-correlation density functional M06-2X, the aug-cc-pVTZ basis set, and Gaussian 09, rev A02.[28] M06-2X[29] is a reliable general-purpose density functional theory (DFT) functional for main-group chemistry, with a mean absolute deviation of 2.2 kcal mol$^{-1}$, as demonstrated by several benchmarks.[30] The CBS-QB3[31] composite method was employed for calculating adiabatic bond dissociation energies. CBS-QB3 is based on CCSD(T) energies extrapolated to the basis set limit using MP2 and MP4 calculations together with empirical corrections, and is expected to be highly reliable for thermochemistry.[31,32] Its mean absolute deviation in the G2 test set is reported to be 0.87 kcal mol$^{-1}$.[33] Harmonic frequencies were calculated at the mPW2PLYP/Def2-TZVPP level[33] of theory using the ORCA 3.0 code, with implicit consideration of $CH_3CN$ solution, as treated by the COSMO method. Raman intensities were calculated at the B3LYP/aug-cc-pVTZ level of theory, using the standard implementation of the polarizable continuum model (PCM) of Gaussian09'. HELP analyses[21] were performed using DGRID 4.6,[34] see the Supporting Information for further details.

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**Keywords:** dinitramide anion · energetic materials · fluoronitroamines · quantum chemical calculations

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