14. ABSTRACT

Recently, a new class of high-energy-containing materials, gem-bis(difluoramino)-substituted heterocyclic nitramines, has gained attention as high-energy oxidizers: HNFX\(^{[1,2]}\) and TNFX\(^{[3]}\) have been successfully synthesized under strongly acidic conditions from their corresponding ketone derivatives using an excess of difluoramine.\(^{[4]}\)

HNF\(_2\) is an unpredictably shock-sensitive and thermally unstable, gaseous compound\(^{[5,6]}\) which can be generated from different precursors, e.g., tetrafluorohydrazine,\(^{[7]}\) \(N,N\)-difluoroura,\(^{[8]}\) \(N,N\)-difluorocarbamates,\(^{[9]}\) or trityldifluoramine.\(^{[10]}\) Out of these precursors, only trityldifluoramine is a stable storable solid. However, it is not useful as a general reagent for the preparation of larger quantities of gem-bis(difluoramines) because its synthesis requires the use of expensive \(N_2F_4\) which is commercially unavailable and must be prepared from difluoramine, and of equivalent amounts of mercury in an organic solvent. The use of mercury presents environmental problems, and working with \(N_2F_4\) in an organic solvent can be hazardous. Therefore, it is highly desirable to develop a stable, solid, readily accessible difluoramine source. Obvious candidates for HNF\(_2\) sources were difluorosulfamate salts. Although the parent free acid, HOSO\(_2NF_2\), had been known since 1961 and has been widely used as a difluoraminating reagent,\(^{[11,12]}\) no reports could be found on the existence of its salts. In this paper, we report the results from two independent studies.

15. SUBJECT TERMS

Recently, a new class of materials having high-energy, gem-bis(difluoroamino)-substituted heterocyclic nitroamines, has gained attention for use as high-energy oxidizers: HNFX\textsuperscript{[1,2]} and TNFX\textsuperscript{[3]} have been synthesized under strongly acidic conditions from their corresponding ketone derivatives by using an excess of difluoroamine\textsuperscript{[4]}

HNF\textsubscript{2} is a shock-sensitive and thermally unstable gaseous compound\textsuperscript{[5,6]}, which can be generated from different precursors, for example, tetrafluorohydrazine\textsuperscript{[7]}, N,N-difluoroura\textsuperscript{[8]}, N,N-difluorocarbamates\textsuperscript{[9]}, or trityldifluoroamine\textsuperscript{[10]}. Of these precursors, only trityldifluoroamine is a stable,
Communications

storable solid. However, it is not useful as a general reagent for the preparation of larger quantities of gem-bis(difluoroamines) because its synthesis requires the use of expensive N,F, which is not commercially available and must be prepared from difluoromethylene, and of equivalent amounts of mercury in an organic solvent. The use of mercury presents environmental problems, and working with N,F in an organic solvent can be hazardous. Therefore, it is highly desirable to develop a stable, solid, readily accessible difluoroaminating reagent,\[11,12\] no reports could be found on such a difluoroaminating reagent,\[13\] and of equivalent amounts of NaSO3NF2 in 94% yield.

\[\text{NaSO}_3\text{NF}_2 + 2 \text{F}_2 \rightarrow \text{NaSO}_3\text{NF}_2 + 2 \text{HF}\]

(1)

The reaction conditions were similar to those previously used for the fluorination of urea,[84] carbamates,[84] and sulfamide.[33] The acidic reaction mixture was not stable above approximately 5°C, and the difluorosulfamate [Eq. (2)] rapidly hydrolyzed upon warming to ambient temperature.

\[\text{SO}_3\text{NF}_2^- + \text{H}_2\text{O} \rightarrow \text{SO}_3\text{OH}^- + \text{HF}\]

(2)

The ease of this acid-catalyzed hydrolysis can account for the lack of previous reports of isolated salts of the difluorosulfamate anion. The isolation of difluorosulfamate salts required careful control of the reaction conditions and rapid removal of the water and HF by-product at 0°C in vacuo. This method resulted in the isolation of pure, colorless NaSO3NF2 in 94% yield.

The dry sodium salt is stable at room temperature but decomposes when exposed to atmospheric moisture. It was stored in the dry argon atmosphere of a glove box for a period of 4 months without showing any sign of decomposition. The identity of the compound was established by the observed material balance, vibrational and multinuclear NMR spectroscopy, electronic structure calculations, and by converting it into \[\text{[PNP]}\text{[SO}_3\text{NF}_2^-]\cdot\text{CH}_2\text{Cl}_2\] (PNP = bis(triphenylphosphoranylidene)ammonium) and determining its crystal structure.

The Raman and IR spectra of solid NaSO3NF2 are shown in the Supporting Information, and the observed frequencies and intensities are listed in Table 1. They were assigned by

Table 1: Comparison of observed and unscaled calculated MP2/6-311 + G(d) vibrational frequencies (cm\(^-1\)) and intensities for SO3NF2^- in point group C\(_2\).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Approx. mode description</th>
<th>Observed(^{[a,b]})</th>
<th>Calculated(^{[d]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>a^-</td>
<td>(\nu_1)</td>
<td>1309 vs</td>
<td>1304 [0.8]</td>
</tr>
<tr>
<td></td>
<td>(\nu_2)</td>
<td>1080 s</td>
<td>1089 [10.0]</td>
</tr>
<tr>
<td></td>
<td>(\nu_3)</td>
<td>968 w</td>
<td>997 [4.0]</td>
</tr>
<tr>
<td></td>
<td>(\delta_{\text{exoc}}\text{NF}_2)</td>
<td>526</td>
<td>521 [1.6]</td>
</tr>
<tr>
<td></td>
<td>(\delta_{\text{sym}}\text{SO}_3)</td>
<td>525 vw</td>
<td>510 [21] [4.6 p]</td>
</tr>
<tr>
<td>(J(19\text{F}-15\text{N}))</td>
<td>(\nu_1)</td>
<td>1284 vs</td>
<td>1267 [0.7]</td>
</tr>
<tr>
<td>(J(19\text{F}-15\text{N}))</td>
<td>(\nu_2)</td>
<td>869w</td>
<td>868 [1.6]</td>
</tr>
<tr>
<td>(J(19\text{F}-15\text{N}))</td>
<td>(\nu_3)</td>
<td>532 w</td>
<td>532 [20]</td>
</tr>
<tr>
<td>(J(19\text{F}-15\text{N}))</td>
<td>(\nu_4)</td>
<td>390</td>
<td>325 [0.8]</td>
</tr>
<tr>
<td>(J(19\text{F}-15\text{N}))</td>
<td>(\nu_5)</td>
<td>186</td>
<td>186</td>
</tr>
<tr>
<td>(J(19\text{F}-15\text{N}))</td>
<td>(\nu_6)</td>
<td>37</td>
<td>37 [0.00]</td>
</tr>
</tbody>
</table>

[a] As Na+ salt. Relative Raman intensities given in brackets. [b] IR intensities given in km mol\(^{-1}\) (in parentheses) and Raman intensities given in cm\(^{-1}\) (in brackets). [c] Not observed, Raman spectrum recorded only between 4000 and 400 cm\(^{-1}\). [d] Not observed, Raman spectrum recorded only between 3600 and 80 cm\(^{-1}\). [e] In addition to the listed bands, IR bands at 1627 m, 1209 w, 1184 m, 365 w, and Raman bands at 1618 [0.5], 1321 [0.7], 572 [1.2] cm\(^{-1}\) were observed but were not assigned.

Comparison with those calculated at the MP2\(^{[14]}\) level of theory with the 6-311 + G(d) basis set. Whereas the \(^{19}\text{F}\) NMR spectrum of naturally abundant \[^{14}\text{N}\]NaSO3NF2 in CD3CN gives only a broad resonance at \(\delta = 34\) ppm, the spectrum of an \[^{15}\text{N}\]-labeled sample in the same solvent shows a sharp doublet at \(\delta = 33.8\) ppm with \(J(^{19}\text{F}-^{15}\text{N}) = 138\) Hz. The \(^{15}\text{N}\) NMR spectrum shows a sharp triplet at \(\delta = -20.4\) ppm with the same \(J(^{15}\text{N}-^{19}\text{F})\) coupling constant.

Colorless and air-stable \([\text{PNP}]\text{[SO}_3\text{NF}_2^-]\cdot\text{CH}_2\text{Cl}_2\) was obtained by neutralizing the fluorination reaction mixture, adding PNP^-Cl^-, and extracting with methylene chloride [Eq. (3)]. Single crystals of \([\text{PNP}]\text{[SO}_3\text{NF}_2^-]\cdot\text{CH}_2\text{Cl}_2\), suitable for X-ray crystal structure determination were obtained by recrystallization from CH2Cl2.

\[\text{NaSO}_3\text{NF}_2^- + \text{PNP}^-\text{Cl}^- \rightarrow [\text{PNP}]\text{[SO}_3\text{NF}_2^-] + \text{NaCl}\]

(3)
The [PPh₄][SO₃NHF] salt was obtained by metallization in the same manner as shown in Equation (3). It crystallizes in the triclinic space group P1. The X-ray structure analysis reveals the presence of two nonequivalent [PPh₄]⁺ and [SO₃NHF]⁻ units (packing diagrams are shown in the Supporting Information). One SO₃NHF⁻ ion could be refined well, but the SO₃ group of the second ion is disordered. This results in a relatively high R factor of 8.16% for the refined structure. The closest F···H and O···H contacts between neighboring cations and anions are 2.682 Å and 2.349 Å, respectively. The X-ray structure analysis of the SO₃NHF⁻ ion is depicted in Figure 2. The observed S–N bond length in SO₃NHF⁻ (1.694(5) Å) lies between those observed for SO₃NF₂⁻ (1.772(4) Å) and SO₃NH₂⁺ (1.649(5) Å). The S–O double-bond character and shortening the S–O bond results in a relatively high R factor of 8.16% for the refined structure.

Colorless and somewhat moisture sensitive NaSO₃NHF was obtained when the acidic reaction mixture was evaporated in a vacuum at 0°C. The compound was identified and characterized by its vibrational spectra and by its crystal structure as the salt [PPh₄][SO₃NHF]. The Raman and IR spectra of NaSO₃NHF are shown in Supporting Information, and the observed frequencies and intensities are listed in Table 2 and were assigned by comparison with those calculated at the MP2 level of theory with the 6-311 + G(d) basis set.

Table 2: Comparison of observed and unscaled calculated MP2/6-311 + G(d) vibrational frequencies (cm⁻¹) and intensities for SO₃NHF⁻ in point group C₂v.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Approx. mode description</th>
<th>Observed[a][b]</th>
<th>Calculated[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₁</td>
<td>ν NH</td>
<td>3100 s, br</td>
<td>3000 [1.3]</td>
</tr>
<tr>
<td>ν₂</td>
<td>δ(π) SO₃</td>
<td>1522 w</td>
<td>1510 [2.8]</td>
</tr>
</tbody>
</table>
was formed in 38% yield by using NaSO$_3$NF$_2$ in anhydrous model ketone. 1,3-Dibromo-2,2-bis(difluoroamino)propane comparison was conducted by using 1,3-dibromoacetone as a ring-carbonyl group was replaced, whereas the carbonyl case of 1-acetylpiperidin-4-one, only the oxygen atom of the difluoroamine in organic difluoroamination reactions was minimized exposure to atmospheric moisture and potential hydrolysis of the sample. Raman spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer using a Nd:YAG laser at 1064 nm with power levels of 100–200 mW and pyrex melting-point capillary tubes as sample containers. NMR spectra were recorded on Bruker AMX 500 and Varian Mercury/VX 400 NMR spectrometers at room temperature. The $^1$H and $^{19}$F NMR spectra were referenced to external samples of CFCl$_3$ and nitromethane, respectively.

The starting materials H$_2$SO$_3$H, H$_2$SO$_4$, [P(C$_6$H$_5$)$_4$]Cl, [PNP]Cl, NaOH (all Aldrich), [$^{15}$N]urea (MSD Isotopes), and fluorine (Air Products and Chemicals Inc.) were used without further purification. Solvents were dried by standard methods and freshly distilled prior to use. NaSO$_3$NH$_2$ was obtained by neutralization of HSO$_3$NH$_2$ with NaOH. [$^{15}$NH]HSO$_3$NH$_2$ was prepared from [$^{15}$N]urea and H$_2$SO$_4$ according to a modified literature method.

NaSO$_3$NF$_2$ (USC): A solution of NaSO$_3$NH$_2$ (0.380 g, 3.19 mmol) in water (4 mL) was placed into a teflon-FEP ampule equipped with a teflon-coated magnetic stirring bar and a teflon gas-inlet tube. After cooling to 0°C, fluorine (3.19 mmol; 10% v/v in nitrogen) was introduced at a rate of 110 mL/min$^{-1}$. The reaction mixture was pumped to dryness at 0°C, leaving behind a colorless solid (0.391 g; weight calculated for 3.19 mmol NaSO$_3$NF$_2$ = 0.437 g).

NaSO$_3$NF$_2$ (USC): A solution of NaSO$_3$NH$_2$ (0.695 g, 5.00 mmol) in water (10 mL) was placed into a teflon-FEP ampule equipped with a magnetic stirrer and a teflon gas-inlet tube. After cooling to 0°C, fluorine (5.00 mmol; 10% v/v in nitrogen) was introduced at a rate of 110 mL/min$^{-1}$. The reaction mixture was neutralized by adding cold solid NaHCO$_3$ and filtered through a cold porcelain frit. A cold solution of PPh$_4$Cl (5.00 mmol) in water (50 mL) was added to the clear filtrate. The resulting milky solution was extracted three times with 50 mL of cold CH$_2$Cl$_2$. The combined organic phases were dried over MgSO$_4$ and pumped to dryness at 0°C. After 45 min, the fluorination was discontinued, and the reaction mixture was neutralized with concentrated aqueous NaOH. The NaF precipitate was removed by filtration. The basis of its $^{19}$F NMR spectrum, the filtrate appeared to be a 96:4 mixture of NaSO$_3$NF$_2$ and NaF. The viscous filtrate was quickly dried at room temperature in a vacuum desiccator over excess P$_2$O$_5$. After 24 h, $^{19}$F NMR spectroscopy of the dried solid showed the same SO$_3$NF$_2$/F$^−$ ratio as the initial filtrate.

Sulfamic acid (16.42 g, 0.169 mol) was dissolved in H$_2$O (30 mL), and NaOH (8.1 g, 0.20 mol) was added. Fluorine (10% v/v in nitrogen) was bubbled through the solution at 0°C. The progress of the fluorination of sulfamate was monitored by $^{19}$F NMR spectroscopy of reaction aliquots to observe the conversion of monofluorosulfamate ($\delta = -102.1$ ppm vs. external CFC$_3$, in D$_2$O/jactone) into difluorosulfamate ($\delta = 36.6$ ppm). After 1.5 h, the fluorination was complete, and the cloudy mixture was neutralized with concentrated aqueous NaOH. The NaF precipitate was removed by filtration. The basis of its $^{19}$F NMR spectrum, the filtrate appeared to be a 96:4 mixture of NaSO$_3$NF$_2$ and NaF. The viscous filtrate was quickly dried at room temperature in a vacuum desiccator over excess P$_2$O$_5$. After 24 h, $^{19}$F NMR spectroscopy of the dried solid showed the same SO$_3$NF$_2$/F$^−$ ratio as the initial filtrate.

[$\text{A}$][SO$_3$NF$_2$]: (A = PNP, PPh$_3$, AsPh$_3$) (USC): A solution of NaSO$_3$NH$_2$ (0.357 g, 3.00 mmol) in water (10 mL) was placed into a teflon-FEP ampule equipped with a magnetic stirring bar and a teflon gas-inlet tube. After cooling to 0°C, fluorine (10% v/v in nitrogen) was introduced at a rate of 110 mL/min$^{-1}$. After 60 min, the fluorination was discontinued, and the reaction mixture was neutralized by adding cold solid NaHCO$_3$. The reaction mixture was filtered through a cold porcelain frit, and a cold aqueous solution of 3.00 mmol A$^−$Cl$^-$ was added to the clear filtrate. The resulting milky solution was extracted three times with 10 mL of cold CH$_2$Cl$_2$. The combined organic phases were dried over MgSO$_4$ and pumped to...
dryness at ambient temperature, leaving behind colorless solids ([PPh₃][SO₃NF₂]: 1.283 g, calc'd weight for 3.00 mmol = 1.414 g; [AsPh₃][SO₃NF₂]: 1.466 g, calc'd weight for 3.00 mmol = 1.543 g; [PNP][SO₃NF₂]: 2.071 g, calc'd weight for 3.00 mmol = 2.011 g). Crystals were grown from a solution in CH₂Cl₂ by slow evaporation of the solvent with a stream of dry nitrogen.

Transition states ("X") were determined if they were minima (positive definite hessian) or saddle points. Transition states for the reaction were found to be energy minimum along the reaction coordinate. Theoretical Methods: The molecular structures and harmonic frequencies were calculated by using second-order many-electron perturbation theory.[20] Vibrational frequencies were calculated by using second-order many-electron perturbation theory.[20]

1.3-Dibromo-2,2-bis(difluoromethyl)propane (TPL): 1.3-Dibromoacetonitrile (24.72 g, 0.114 mol) was added to a mixture of sodium difluorosulfamate (61 g, 2.071 g, calc'd weight for 3.00 mmol = 2.011 g) and a solution of 1-acetyl-4,4-bis(difluoroamines) in CH₂Cl₂ by slow evaporation of the solvent with a stream of dry nitrogen.

X-ray structure determination: The collection, reduction, and indexing of X-ray data was performed using TEXSAN.[20] Crystal data for C₆H₄F₂N₂O₂S·PF₆: M = 755.55, triclinic, space group PI, a = 11.8650(12), b = 11.9167(12), c = 14.5180(15) Å, α = 66.755(2), β = 68.964(2), γ = 71.034(2)°, V = 1719.7(3) Å³, F(000) = 780, ρcalc (Z = 2) = 1.459 g cm⁻³, μ = 0.395 mm⁻¹. Crystals were grown from a solution in CH₂Cl₂ by slow evaporation of the solvent with a stream of dry nitrogen.

Theoretical Methods: The molecular structures and harmonic vibrational frequencies were calculated by using second-order many-electron perturbation theory,[20] denoted as MP2, but also known as MBPT(2) and 6-311G basis set. Hessians (energy second derivatives) were calculated for the final equilibrium structures to determine if they were minima (positive definite hessian) or saddle points. Transition states for the reaction were found to be energy minimum along the reaction coordinate.

Crystal data for C₆H₄F₂N₂O₂S·PF₆: M = 755.55, triclinic, space group PI, a = 11.8650(12), b = 11.9167(12), c = 14.5180(15) Å, α = 66.755(2), β = 68.964(2), γ = 71.034(2)°, V = 1719.7(3) Å³, F(000) = 780, ρcalc (Z = 2) = 1.459 g cm⁻³, μ = 0.395 mm⁻¹. Crystals were grown from a solution in CH₂Cl₂ by slow evaporation of the solvent with a stream of dry nitrogen.

Received: March 15, 2006
Published online: July 6, 2006

Keywords: difluoroamines - fluorine - structure elucidation - sulfamates


