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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*-difluorourea,[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 difluoroaminating 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.

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Preparation, Characterization, and Crystal Structures of the SO_3NHF^- and $SO_3NF_2^-$ Ions**

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*Dedicated to Dr. Carl Schack
on the occasion of his 70th birthday*

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[1,2] and TNFX[3] have been synthesized under strongly acidic conditions from their corresponding ketone derivatives by using an excess of difluoroamine.[4]

HNF_2 is a shock-sensitive and thermally unstable gaseous compound,[5,6] which can be generated from different precursors, for example, tetrafluorohydrazine,[7] *N*,*N*-difluorourea,[8] *N*,*N*-difluorocarbamates,[9] or trityldifluoroamine.[10] Of these precursors, only trityldifluoroamine is a stable,

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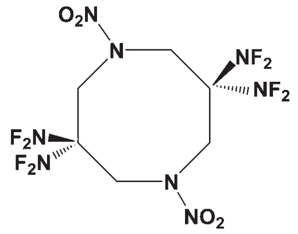
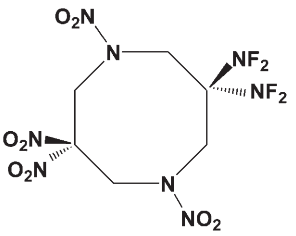


HNFX



TNFX

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_2F_4, which is not commercially available and must be prepared from difluoroamine, 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 difluoroamine source. Obvious candidates for HNF_2 sources are difluorosulfamate salts. Although the parent free acid $HOSO_2NF_2$ had been known since 1961 and has been widely used as a difluoroaminating reagent,[11,12] no reports could be found on the existence of its salts. Herein, we report the results from two independent studies.

$Na^+SO_3NF_2^-$ was isolated by fluorinating aqueous sulfamic acid at 0 °C, neutralizing the product with concentrated aqueous sodium hydroxide, filtering off the less-soluble sodium fluoride by-product, and drying the neutral solution under vacuum. This process was improved by direct fluorination of $SO_3NH_2^-$ salts with diluted elemental fluorine in aqueous solutions at 0 °C [Eq. (1)].

$$NaSO_3NH_2 + 2\,F_2 \rightarrow NaSO_3NF_2 + 2\,HF \tag{1}$$

The reaction conditions were similar to those previously used for the fluorination of urea,[8a] carbamates,[9a] and sulfamide.[13] The acidic reaction mixture was not stable above approximately 5 °C, and the difluorosulfamate [Eq. (2)] rapidly hydrolyzed upon warming to ambient temperature.

$$SO_3NF_2^- + H_2O \rightarrow SO_3OH^- + HNF_2 \tag{2}$$

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 a vacuum. This method resulted in the isolation of pure, colorless $NaSO_3NF_2$ 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 $[PNP][SO_3NF_2]\cdot CH_2Cl_2$ (PNP = bis(triphenylphosphoranylidene)ammonium) and determining its crystal structure.

The Raman and IR spectra of solid $NaSO_3NF_2$ are shown in the Supporting Information, and the observed frequencies and intensities are listed in Table 1. They were assigned by comparison with those calculated at the MP2[14] level of theory with the 6-311 + G(d) basis set. Whereas the ^{19}F NMR spectrum of naturally abundant $[^{14}N]NaSO_3NF_2$ in CD_3CN gives only a broad resonance at $\delta = 34$ ppm, the spectrum of an ^{15}N-labeled sample in the same solvent shows a sharp doublet at $\delta = 33.8$ ppm with $^1J(^{19}F\text{-}^{15}N) = 138$ Hz. The ^{15}N NMR spectrum shows a sharp triplet at $\delta = -20.4$ ppm with the same $^1J(^{15}N\text{-}^{19}F)$ coupling constant.

Table 1: Comparison of observed and unscaled calculated MP2/6-311 + G(d) vibrational frequencies (cm^{-1}) and intensities for $SO_3NF_2^-$ in point group C_s.

Mode		Approx. mode description	Observed[a],[e]		Calculated[b]
			IR	Raman	
a′	ν_1	ν_{as} SO_3	1309 vs	1304 [0.8]	1286 (364) [7.2 dp]
	ν_2	ν_s SO_3	1080 s	1089 [10.0]	1051 (59) [38 p]
	ν_3	ν_s NF_2	968 w	997 [4.0] 971 [0.9]	979 (72) [4.4 p]
	ν_4	ν SN	715 m	722 [5.5]	671 (64) [17 p]
	ν_5	δ_{as} SO_3	627 s 617 s	630 [1.1]	601 (140) [0.6 dp]
	ν_6	δ_{sciss} NF_2		526 [2.6]	521 (1.6) [7.3 p]
	ν_7	δ_{sym} SO_3	525 vw		501 (25) [4.6 p]
	ν_8	δ_{rock} SO_3	[c]	337 [4.3]	298 (1.6) [8.6 p]
	ν_9	δ_{wag} NF_2	[c]	264 [1.3]	224 (0.5) [2.4 p]
a″	ν_{10}	ν_{as} SO_3	1284 vs	1267 [0.7]	1282 (362) [7.7 dp]
	ν_{11}	ν_{as} NF_2	869 m	868 [1.6]	829 (75) [2.1 dp]
	ν_{12}	δ_{as} SO_3	532 w	537 [2.0]	532 (35) [3.5 dp]
	ν_{13}	δ_{rock} SO_3	[c]	390 [2.6]	325 (0.8) [0.8 dp]
	ν_{14}	δ_{twist} NF_2	[c]	186 [1.3]	154 (0.02) [6.1 dp]
	ν_{15}	τ S-N	[c]	[d]	37 (0.00) [2.0 dp]

[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 Å^4 amu^{-1} (in brackets). [c] Not observed, IR 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, 565 w, and Raman bands at 1618 [0.5], 1321 [0.7], 572 [1.2] cm^{-1} were observed but were not assigned.

Colorless and air-stable $[PNP][SO_3NF_2]$ was obtained by neutralizing the fluorination reaction mixture, adding PNP^+Cl^-, and extracting with methylene chloride [Eq. (3)]. Single crystals of $[PNP][SO_3NF_2]\cdot CH_2Cl_2$ suitable for X-ray crystal structure determination were obtained by recrystallization from CH_2Cl_2.

$$NaSO_3NF_2 + PNP^+Cl^- \rightarrow [PNP][SO_3NF_2] + NaCl \tag{3}$$

$[PNP][SO_3NF_2]\cdot CH_2Cl_2$ crystallizes in the triclinic space group $P\bar{1}$. The X-ray structure analysis reveals the presence of two isolated $[PNP]^+$ and $[SO_3NF_2]^-$ units together with two disordered CH_2Cl_2 molecules in the unit cell (packing diagrams are given in the Supporting Information). The closest F···H and O···H contacts between neighboring cations and anions are 2.682 Å and 2.349 Å, respectively. The dimensions of the SO_3N skeleton of the $SO_3NF_2^-$ ion (Figure 1) are more similar to those of sulfamic acid[15] than to the ones reported for salts with the $SO_3NH_2^-$ ion.[16] Estimations of the double-bond character of the S–N bond are frequently made by comparison of the observed lengths with that predicted from Pauling's covalent radii (1.74 Å)[17] or with the bond length in sulfamic acid (1.772(1) Å).[15b] In the solid state, the latter has the zwitterionic structure $^+NH_3$–SO_3^-, which possesses a formal S–N single bond. The observed S–N bond length in $SO_3NF_2^-$ (1.772(4) Å) is similar to that in sulfamic acid and larger than the typical values found in the $SO_3NH_2^-$ ion (1.64 Å). The S–O bond lengths (1.428(8) Å and 1.424(3) Å)are shorter than the values reported for sulfamates (1.44–1.45 Å)[16] and sulfamic acid (1.438(1) Å, 1.436(1) Å, and 1.435(1) Å).[15b] The average O-S-O and O-S-N angles (115.9° and 101.8°, respectively) are in good agreement with those reported for sulfamic acid.

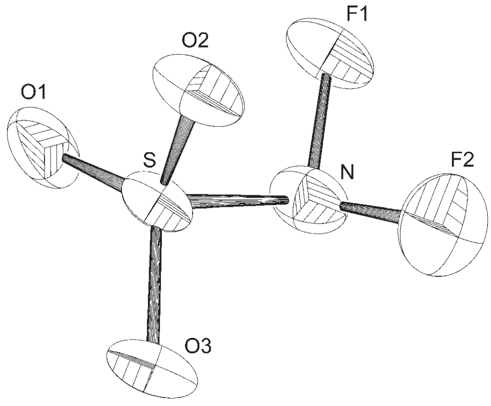


Figure 1. ORTEP drawing of the anion of $[PNP][SO_3NF_2]\cdot CH_2Cl_2$. Thermal ellipsoids are shown at the 50% probability level. Bond lengths [Å] and angles [°]: S–O1 1.428(4), S–O2 1.424(3), S–O3 1.424(3), S–N 1.772(4), F1–N 1.412(5), F2–N 1.463(6); O1-S-O2 114.7(2), O1-S-O3 116.1(2), O2-S-O3 116.8(2), O1-S-N 100.1(2), O2-S-N 106.1(2), O3-S-N 99.3(2), F1-N-F2 99.0(3), F1-N-S 104.5(3), F2-N-S 99.6(3).

The marked differences in the S–N and S–O bond lengths between $SO_3NF_2^-$ and $SO_3NH_2^-$ can be readily reconciled by the large difference between the electronegativity values of hydrogen and fluorine. The strongly electron withdrawing fluorine atoms pull some of the negative charge away from the oxygen atoms, thereby increasing the S=O double-bond character and shortening the S–O bonds. By contrast, the electron-donating hydrogen atoms increase the electron density on the nitrogen atom, which passes it on to the S=O bonds. This results in partial N=S double bond character and increased negative charge on the oxygen atoms with concomitant lengthening of the S–O bonds.

When only one equivalent of fluorine was used in the fluorination reaction of $SO_3NH_2^-$, the SO_3NHF^- ion was formed [Eq. (4)].

$$NaSO_3NH_2 + F_2 \rightarrow NaSO_3NHF + HF \qquad (4)$$

Colorless and somewhat moisture sensitive $NaSO_3NHF$ 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 $[PPh_4][SO_3NHF]$. The Raman and IR spectra of $NaSO_3NHF$ 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[11] 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 SO_3NHF^- in point group C_1.

Mode	Approx. mode description	Observed[a],[d]		Calculated[b]
		IR	Raman	(IR) [Raman]
ν_1	ν NH	3100 s, br	3000 [1.3]	3481 (2.4) [69]
ν_2	δ_{sciss} HNF	1522 w		1410 (30) [2.8]
ν_3	ν_{as} SO_3	1242 vs	1246 [1.3]	1270 (368) [7.3]
ν_4	ν_{as} SO_3	1213 vs	1225 [1.2]	1240 (401) [7.1]
ν_5	ν_s SO_3/δ_{wag} NH	1064 s	1065 [10.0]	1041 (82) [27]
ν_6	ν_s SO_3/δ_{wag} NH	1021 m	1014 [5.9]	1033 (45) [18]
ν_7	ν NF	863 m	869 [4.3]	923 (38) [14]
ν_8	ν SN	602 s	602 [5.0]	699 (161) [16]
ν_9	δ_{as} SO_3	590 s		584 (66) [4.5]
ν_{10}	δ_{as} SO_3	497 w	466 [2.6]	520 (26) [3.4]
ν_{11}	δ_{sym} SO_3	477 w	445 [3.0]	509 (26) [5.9]
ν_{12}	δ_{rock} SO_3	438 w	424 [3.7]	371 (0.1) [4.7]
ν_{13}	δ_{rock} SO_3	[c]	411 [3.0]	343 (8.1) [2.6]
ν_{14}	δ_{wag} NF	[c]		215 (1.2) [1.1]
ν_{15}	τ S-N	[c]	122 [2.0]	118 (1.9) [0.4]

[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 $Å^4 amu^{-1}$ (in brackets). [c] Not observed, IR spectrum recorded only between 4000 and 400 cm^{-1}. [d] In addition to the listed bands, IR bands at 1313 m, 1168 s, 1082 s, 918 m, 897 m, 773 m, 731 s, 617 m and Raman bands at 1168 [1.0], 1153 [1.0], 913 [1.2], 666 [1.0] cm^{-1} were observed but were not assigned.

The $[PPh_4][SO_3NHF]$ salt was obtained by metathesis in the same manner as shown in Equation (3). It crystallizes in the triclinic space group $P\bar{1}$. The X-ray structure analysis reveals the presence of two nonequivalent $[PPh_4]^+$ and $[SO_3NHF]^-$ units (packing diagrams are shown in the Supporting Information). One SO_3NHF^- ion could be refined well, but the SO_3 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 2.566 Å and 2.373 Å, respectively. The ordered SO_3NHF^- ion is depicted in Figure 2. The observed S–N bond length in SO_3NHF^- (1.694(5) Å) lies between those observed for $SO_3NF_2^-$ (1.772(4) Å) and $SO_3NH_2^-$ (1.64 Å). This situation is in accord with the expectation that the electronic effect of an -NHF group is intermediate between those of an $-NF_2$ and an $-NH_2$ group.

The presence of one hydrogen atom and one fluorine atom attached to the same nitrogen atom was further established by proton and fluorine NMR spectroscopy. The

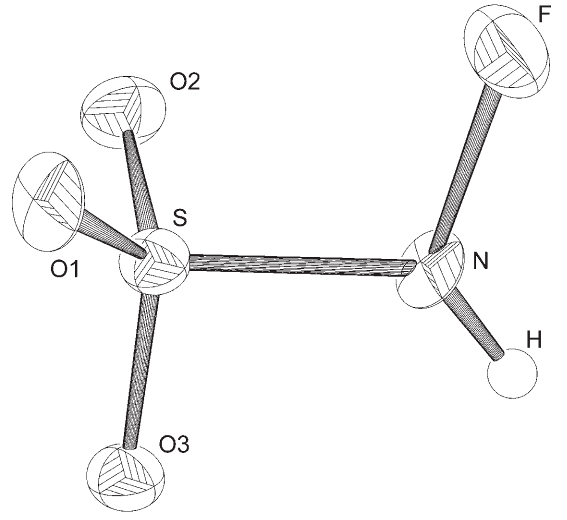


Figure 2. ORTEP drawing of the anion of [PPh_4][SO_3NHF]. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: S–O1 1.433(4), S–O2 1.457(4), S–O3 1.447(3), S–N 1.694(5), F1–N 1.474(5), O1–S-O2 114.4(2); O1-S-O3 115.3(2), O2-S-O3 114.1(2), O1-S-N 108.5(2), O2-S-N 104.3(2), O3-S-N 98.0(2), F-N-S 106.4(3).

proton and fluorine spectra showed doublets at $\delta = 8.69$ and -103.0 ppm, respectively, with the same $^2J(^1H\text{-}^{19}F)$ coupling constant (49 Hz).

The utility of $NaSO_3NF_2$ as an alternative source of difluoroamine in organic difluoroamination reactions was demonstrated by the transformation of carbonyl into *gem*-bis(difluoroamino) groups. Qualitative reactions of acetone, cyclohexanone, 3-pentanone, and 1-acetylpiperidin-4-one with the reagent in approximately 100% H_2SO_4 and 30% oleum showed formation of the expected *gem*-bis(difluoroamino)alkane by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. In the case of 1-acetylpiperidin-4-one, only the oxygen atom of the ring-carbonyl group was replaced, whereas the carbonyl oxygen atom of the acetyl group did not react. A quantitative comparison was conducted by using 1,3-dibromoacetone as a model ketone. 1,3-Dibromo-2,2-bis(difluoroamino)propane was formed in 38% yield by using $NaSO_3NF_2$ in anhydrous H_2SO_4 containing approximately 1% SO_3. This compares with a yield of 37% for conventional difluoroamination (HNF_2 in oleum) of 1,3-dibromoacetone.

Experimental Section

Materials and Apparatus (USC): All reactions were carried out in teflon-FEP ampules closed by stainless steel valves or pyrex glass vessels closed by grease-free Kontes glass-teflon valves. Volatile materials were handled in stainless steel/teflon-FEP[18] or pyrex glass vacuum lines. Nonvolatile solids were handled in the dry argon atmosphere of a glove box. Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Midac, M Series, FT-IR spectrometer using KBr pellets. The pellets were prepared inside the glove box using an Econo mini-press (Barnes Engineering Co.) and transferred in a closed container to the spectrometer before placing them quickly into the sample compartment, which was purged with dry nitrogen to minimize exposure to atmospheric moisture and potential hydrolysis of the sample. Raman spectra were recorded on a Bruker Equinox 55 FT-RA 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 unlocked on Bruker AMX 500 and Varian Mercury/VX 400 NMR spectrometers at room temperature. The ^{19}F and ^{15}N NMR spectra were referenced to external samples of $CFCl_3$ and nitromethane, respectively.

The starting materials H_2NSO_3H, H_2SO_4, [$P(C_6H_5)_4$]Cl, [PNP]Cl, NaOH (all Aldrich), [$^{15}N_2$]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. $NaSO_3NH_2$ was obtained by neutralization of HSO_3NH_2 with NaOH. [^{15}N]HSO_3NH_2 was prepared from [$^{15}N_2$]urea and H_2SO_4 according to a modified literature method.[19]

$NaSO_3NHF$ (USC): A solution of $NaSO_3NH_2$ (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 calcd for 3.19 mmol $NaSO_3NHF = 0.437$ g).

[PPh_4][SO_3NHF] (USC): A solution of $NaSO_3NH_2$ (0.695 g, 5.00 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 (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_4Cl (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_2Cl_2. The combined organic phases were dried over $MgSO_4$ and pumped to dryness at ambient temperature, leaving behind a colorless solid (2.039 g; weight calcd for 5.00 mmol $PPh_4SO_3NHF = 2.267$ g). Crystals were grown from a solution in CH_2Cl_2 by slow evaporation of the solvent with a stream of dry nitrogen.

$NaSO_3NF_2$ (USC): A solution of $NaSO_3NH_2$ (0.236 g, 1.98 mmol) in water (7 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 (10% v/v in nitrogen) was introduced at a rate of 110 $mL\,min^{-1}$. After 45 min, the fluorination was discontinued, and the reaction mixture pumped to dryness at 0°C, leaving behind a colorless solid (0.288 g; weight calcd for 1.98 mmol $NaSO_3NF_2 =$ 0.307 g).

$NaSO_3NF_2$ (TPL): Sulfamic acid (16.42 g, 0.169 mol) was dissolved in H_2O (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 $CFCl_3$ in [D_6]acetone) 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. On the basis of its ^{19}F NMR spectrum, the filtrate appeared to be a 96:4 mixture of $NaSO_3NF_2$ and NaF. The viscous filtrate was quickly dried at room temperature in a vacuum desiccator over excess P_2O_5. After 24 h, ^{19}F NMR spectroscopy of the dried solid showed the same $SO_3NF_2^-/F^-$ ratio as the initial filtrate.

[A][SO_3NF_2] (A = PNP, PPh_4, $AsPh_4$) (USC): A solution of $NaSO_3NH_2$ (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_2Cl_2. The combined organic phases were dried over $MgSO_4$ and pumped to dryness at ambient temperature, leaving behind colorless solids ([PPh_4][SO_3NF_2]: 1.283 g, calcd weight for 3.00 mmol = 1.414 g; [$AsPh_4$][SO_3NF_2]: 1.466 g, calcd weight for 3.00 mmol = 1.543 g; [PNP][SO_3NF_2]: 2.071 g, calcd weight for 3.00 mmol = 2.011 g). Crystals were grown from a solution in CH_2Cl_2 by slow evaporation of the solvent with a stream of dry nitrogen.

2,2-Bis(difluoroamino)propane and 1-acetyl-4,4-bis(difluoroamino)piperidine (USC): $NaSO_3NF_2$ (2.5 equiv.) was added in increments at 4 °C to a vigorously stirred mixture of $CDCl_3$ (1.5 mL), 30 % oleum (1.5 mL), and the ketone starting material (1.0 mmol). Immediate gas evolution was observed. After 15 min, the upper organic phase was analyzed by ^{19}F, ^{1}H, and ^{13}C NMR spectroscopy, showing the formation of the desired *gem*-bis(difluoroamines).

1,3-Dibromo-2,2-bis(difluoroamino)propane (TPL): 1,3-Dibromoacetone (24.72 g, 0.114 mol) was added to a mixture of sodium difluorosulfamate (61 g, ≤ 0.39 mol) in sulfuric acid (310 mL) containing approximately 1 % SO_3 (made from 30 % oleum plus concd H_2SO_4) plus 100 mL dichloromethane. The reaction mixture was stirred for 4 days at 0 °C, quenched in water, neutralized, and extracted with dichloromethane. Removal of the solvent produced 13.2 g of solute, the major constituent of which was 1,3-dibromo-2,2-bis(difluoroamino)propane (38 % crude yield). Three short-path distillations (room temperature at 1–3 Torr) produced material that was > 95 % pure (elemental analysis and ^{1}H NMR) with residual 1,3-dibromoacetone as the main impurity. ^{1}H NMR spectroscopy (200 MHz, $CDCl_3$, TMS): $\delta = 3.98$ ppm (quint., 1.25 Hz). $^{13}C\{^{1}H\}$ NMR spectroscopy ($CDCl_3$): $\delta = 23.75$ (quint., 5.5 Hz), 99 ppm (m). ^{19}F NMR spectroscopy ($CDCl_3$): $\delta = 29.9$ ppm (s). ^{1}H NMR spectroscopy (C_6D_6): $\delta = 3.24$ ppm (quint., 1.27 Hz). ^{13}C NMR spectroscopy (C_6D_6): $\delta = 23.69$ (quint., 5.7 Hz), 95.37 ppm (quint., 6.4 Hz). ^{19}F NMR spectroscopy (C_6D_6): $\delta = 30.26$ ppm (s). Elemental analysis calcd for (0.953)$C_3H_4F_4N_2Br_2$ + (0.047)$C_3H_4Br_2O$: C 12.08, H 1.35, N 8.78, F 23.83; found: C 12.12, H 1.30, N 8.93, F 23.53 %.

Theoretical Methods: The molecular structures and harmonic vibrational frequencies were calculated by using second-order many-body perturbation theory[14] (denoted as MP2, but also known as MBPT(2)) and a 6-311+G(d) basis set. Hessians (energy second derivatives) were calculated for the final equilibrium structures to determine if they were minima (positive definite hessian) or *n*th-order transition states ("*n*" negative eigenvalues). All calculations were performed by using the electronic structure code GAMESS.[20]

X-ray structure determination: The collection, reduction, and processing of X-ray data was described previously.[21] Crystal data for $C_{37}H_{32}Cl_2F_2N_2O_3P_2S$: $M_r = 755.55$, triclinic, space group $P\bar{1}$, $a = 11.8650(12)$, $b = 11.9167(12)$, $c = 14.5180(15)$ Å, $\alpha = 66.755(2)$, $\beta = 68.964(2)$, $\gamma = 71.034(2)°$, $V = 1719.7(3)$ Å^3, $F(000) = 780$, $\rho_{calcd.}$ $(Z = 2) = 1.459\ g\,cm^{-3}$, $\mu = 0.395\ mm^{-1}$, approximate crystal dimensions $0.29 \times 0.21 \times 0.05\ mm^3$, θ range = 1.58 to 27.49°, index ranges $-15 \leq h \leq 12$, $-15 \leq k \leq 12$, $-18 \leq l \leq 18$, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $T = 133(2)$ K, 10657 measured reflections, of which 7433 ($R_{int} = 0.0487$) were unique, data to parameters ratio = 16.9:1, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0731$, $wR2 = 0.1949$, R indices (all data): $R1 = 0.1087$, $wR2 = 0.2102$, GOF on $F^2 = 1.012$.

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CCDC-274108 and -274109 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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