the FOM of 23.7 is in an acceptable range, the triclinic cell cannot be considered as definitive. Certainly the low-symmetry crystal system and the limited number of lines have made attempts at solving the crystal structure so difficult that we are now relying on neutron and pulsed-neutron diffraction data for a solution to this problem.[15]

There is a longstanding effort under way, which involves G. D. Stucky, J. Faber, and M. H. Mueller of Argonne National Laboratory, to index and elucidate the structure by neutron diffraction by using Visser programs and other programs of deuterium substitution of dilithiomethane.[15] There is a second project under way at Brookhaven National Laboratory, involving G. D. Stucky, for a pulsed-neutron study of the structure of deuterium-substituted dilithiomethane.[16]

Acknowledgment. We are indebted to Dr. Gordon S. Smith of Lawrence Livermore Laboratory for processing our X-ray data. We thank Raymond D. Kendrick of the IBM San Jose Research Laboratory for building the probe and other electronics associated with the $^6\mathrm{Li}$–$^1\mathrm{H}$–$^{13}\mathrm{C}$ CPMAS experiments. We are grateful for support of this work from the National Science Foundation and for partial support from the Robert A. Welch Foundation.

Registry No. $\mathrm{CH_2(^7Li)_2}$, 90159-16-3; $\mathrm{CH_2(^6Li)_2}$, 91949-54-1; $\mathrm{CD_2(^7Li)_2}$, 91949-55-2; $\mathrm{CH_2Li_2}$, 21473-62-1; $\mathrm{CH_3{}^7Li}$, 19274-19-2; $\mathrm{CH_3{}^6Li}$, 19274-18-1; $\mathrm{CD_3{}^7Li}$, 19274-21-6; $\mathrm{CH_3Li}$, 917-54-4.

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(15) Neutron diffraction data are currently being utilized to derive the crystal structure to dilithiomethane-d_2: Stucky, G. D.; Faber, J.; Mueller, M. H.; Knott, H.; Steinfink, H.; Gurak, J. A.; Lagow, R. J., to be submitted for publication.

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Synthesis, Properties, and Reactions of Bis((trifluoromethyl)sulfonyl) Imide, $(\mathrm{CF_3SO_2})_2\mathrm{NH}$[1]

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Received December 13, 1983

Bis((trifluoromethyl)sulfonyl) imide, $(\mathrm{CF_3SO_2})_2\mathrm{NH}$, the parent compound of the bis((perfluoroalkyl)sulfonyl) imides, has been prepared in good yield. The strong electron-withdrawing effect of the $(\mathrm{CF_3SO_2})_2\mathrm{N}$ group is borne out by the acidity of the imide and the properties of its derivatives. The synthesis and properties of $(\mathrm{CF_3SO_2})_2\mathrm{NH}$ are described, as well as those of the derivatives $(\mathrm{CF_3SO_2})_2\mathrm{NX}$, where X = Cs, Cl, NO, $\mathrm{NO_2}$, and $\mathrm{Si(CH_3)_3}$.

Introduction

The electronegativity of the $\mathrm{CF_3SO_2}$ group and its application in organic chemistry have been well documented.[3-5] As an electron-withdrawing group on nitrogen, for example, it substantially increases the acidity of an amine, imine, or imide. Compounds such as $\mathrm{CF_3SO_2NH_2}$ and $\mathrm{CF_3SO_2N(H)C_6H_5}$ exhibit pK_a values of weak acids, and in the case of $\mathrm{CF_3SO_2NH_2}$, the lone $\mathrm{CF_3SO_2}$ group affords the dichloro and disilver derivatives reasonable stability.[6,7]

The presence of two sulfonyl groups on nitrogen drastically increases the acidity of the remaining proton, as shown by $(\mathrm{FSO_2})_2\mathrm{NH}$,[8] $(\mathrm{RSO_2})_2\mathrm{NH}$[5] (R = aryl), and certain $(\mathrm{R_fSO_2})_2\mathrm{NH}$[9] derivatives. However, the simplest member of the $(\mathrm{R_fSO_2})_2\mathrm{NH}$ series, $(\mathrm{CF_3SO_2})_2\mathrm{NH}$, had not been isolated. Our immediate interest was to compare the properties and reactivity of this imide to those of related $(\mathrm{FSO_2})_2\mathrm{NH}$. The latter has led to a variety of interesting compounds,[10] including one possessing the first example of a xenon–nitrogen bond.[11]

Experimental Section

The majority of the synthetic work was carried out by using Pyrex and stainless-steel vacuum systems equipped with glass–Teflon and stainless-steel valves. Pressures were measured by using a Wallace and Tiernan differential pressure gauge, Series 1500. Where applicable, amounts of volatile reagents were determined by *PVT* measurements, assuming ideal-gas behavior. All other reagents were measured by direct weighing. Melting points were taken on a standard capillary-tube apparatus or by a modified Stock technique.

$^{19}\mathrm{F}$ NMR spectra were normally recorded on a Varian XL-100-15 spectrometer using ~80 mol % $\mathrm{CFCl_3}$ as a solvent and internal standard. Chemical shifts are positive when found at a lower field than that of $\mathrm{CFCl_3}$. $^1\mathrm{H}$ NMR spectra were recorded on a Varian T-60 spectrometer using $\mathrm{(CH_3)_4Si}$ as an external standard.

Routine IR spectra were recorded on either a Perkin-Elmer Model 337 or 1330 spectrometer. Spectra for assignment were taken on a Perkin-Elmer Model 180 spectrometer. Gas spectra were taken with use of a 10-cm gas cell fitted with AgCl or KCl windows. Solids were taken as Nujol or Fluorolube mulls on AgCl windows.

Raman spectra were recorded on a Spex Model 14018 double monochromator employing photon-counting detection. Excitation was via the 514.5-nm line of an argon ion laser. Samples were usually run at low temperature in a glass cell similar to that of Brown et al.,[12]

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which was modified to allow direct inlet of solid samples under an inert atmosphere. Liquid nitrogen was usually the coolant, maintaining the sample near −180 °C.

EI and CI (CH_4) mass spectra were taken on a Finnigan Model 4021-C mass spectrometer at 70 eV using direct gas or solid inlet methods.

Reagents. Trifluoromethanesulfonyl fluoride, CF_3SO_2F, was prepared by electrochemical fluorination of CH_3SO_2F via the literature method.[13] Methanesulfonyl chloride was purchased from Aldrich Chemical Co. and was used as received. Hexamethyldisilazane (HMDS), $[(CH_3)_3Si]_2NH$, was purchased from PCR, Inc., and distilled once before use. Chlorine monofluoride was prepared by heating 90 mmol each of Cl_2 and F_2 in a 150-mL Monel bomb for 16 h at 260 °C. The vessel was then pumped under vacuum at −196 °C. Essentially pure ClF was obtained by cooling the cylinder to −111 °C and allowing the ClF to vaporize at this temperature. All other reagents were readily available from commercial sources and were appropriately purified as needed.

Preparation of $(CF_3SO_2)_2NH$. CH_3SO_2Cl (286 g) was added in a slow stream to solid KF (170 g) contained in a 500-mL round-bottom flask, fitted with a reflux condenser. Initially the reaction was mildly exothermic. After all the CH_3SO_2Cl was added, the mixture was stirred for 1 h at 22 °C. The CH_3SO_2F was then distilled from the flask as the fraction boiling at 123–124 °C. It was further purified by a second distillation from P_4O_{10}, giving 208 g of pure CH_3SO_2F. Electrochemical fluorination of CH_3SO_2F in anhydrous HF afforded ~180 g of CF_3SO_2F after 45 h of continuous operation at 4–5 V and a current of 7–9 A.

The following preparation of $(CF_3SO_2)_2NH$ is similar to that used for the preparation for other $(R_fSO_2)_2NH$,[9] with some modifications. In a routine preparation, CF_3SO_2F (110 g) was bubbled into 600 mL of liquid NH_3 at −78 °C, contained in a 1000-mL three-neck flask fitted with a mechanical stirrer. Reaction was immediate, forming $NH_4NHSO_2CF_3$ and NH_4F. The cold bath was removed, and the excess NH_3 was allowed to boil away inside the exhaust hood. Dioxane (600 mL) was added to make a slurry, and dry HCl was bubbled through this mixture until the pH was 2–3. The solution was then filtered, and the dioxane filtrate was rotary evaporated down to a volume of 75 mL. Addition of 200 mL of C_6H_6 resulted in crystallization of the $H_2NSO_2CF_3$, which was separated by filtration. The filtrate was further reduced by evaporation, and a second batch of crystals was obtained. The combined solids were resublimed twice, yielding 92 g of pure $H_2NSO_2CF_3$.

A portion of the $H_2NSO_2CF_3$ (83 g) was then dissolved in 50 mL of dry methanol. A CH_3OH solution of CH_3ONa formed from 12.8 g of Na and 150 mL of CH_3OH was then added to the $H_2NSO_2CF_3$ solution, and the methanol was removed by rotary evaporation. The resulting solid was washed with benzene, yielding 99 g of $NaNHSO_2CF_3$.

The $NaNHSO_2CF_3$ (95 g) was transferred to a 1000-mL, three-necked flask, fitted with a mechanical stirrer, a condenser, and a drying tube. After addition of 600 mL of $[(CH_3)_3Si]_2NH$, the mixture was refluxed at 145 °C for 12 h. During this time, 100 mL of dioxane was added to the flask to prevent polymerization of the HMDS. Ammonia was evolved, and the formation of $(CH_3)_3SiN(Na)SO_2CF_3$ was monitored by IR spectroscopy according to the disappearance of the N–H band of $NaNHSO_2CF_3$ and the growth of the C–H band from $(CH_3)_3SiN(Na)SO_2CF_3$. When the IR showed no $NaNHSO_2CF_3$ remaining, the $[(CH_3)_3Si]_2NH$/dioxane solvent was vacuum distilled and the remaining salt was dried under vacuum in the same flask. Due to the moisture senstivity of the compound, the yield was not determined.

Next, $(CH_3)_3SiN(Na)SO_2CF_3$ (112 g) was placed in a 500-mL stainless-steel bomb containing several steel balls and fitted with a 1000-psi pressure gauge. Dioxane (150 mL) was poured into the reactor, which was evacuated and cooled to −196 °C. CF_3SO_2F (0.51 mol) was then added by vacuum transfer, and the contents were heated to 110 °C in an oven for 3 h. Periodically, the cylinder was removed and shaken. When the pressure rose no further, the bomb was allowed to cool and the $(CH_3)_3SiF$ and CF_3SO_2F were vented in the hood. The $NaN(SO_2CF_3)_2$ was then washed out of the cylinder with dioxane, and the salt was air-dried after being filtered from a dioxane/C_6H_6 solution. Further drying on the vacuum line gave $NaN(SO_2CF_3)_2$ (100 g) as a white granular solid.

In two separate vacuum distillations, ~35- and 65-g portions of the $NaN(SO_2CF_3)_2$ isolated above were treated with 100 mL of concentrated H_2SO_4 in a 500-mL round-bottom flask. The flask was heated to no more than 90 °C at 2-μmHg pressure. The $(CF_3SO_2)_2NH$ was collected at −22 °C, along with some CF_3SO_2OH, a common contaminant. The crude $(CF_3SO_2)_2NH$ was resublimed twice at 60 °C and recrystallized from $CFCl_3$ at −50 °C to give $(CF_3SO_2)_2NH$ (95 g) in a 47% overall yield based on the starting amount of CF_3SO_2F. The product was stored in a sealed container inside the drybox. $(CF_3SO_2)_2NH$: white, crystalline solid that fumes in moist air; mp 49–50 °C; IR (gas in equilibrium with solid at 25 °C) 3395 (m), 3220 (br), 1463 (m), 1440 (m), 1300 (w), 1240 (s), 1224 (s), 1138 (s), 860 (m), 643 (vw), 614 (m), 570 (vw), 505 (w) cm^{-1}; Raman (solid, −180 °C) 3205 (w), 1464 (vw), 1458 (w), 1450 (w), 1343 (w), 1263 (s), 1142 (m), 839 (w), 778 (s), 646 (w), 591 (w), 566 (w), 537 (w), 510 (w), 392 (m), 386 (m), 346 (s), 311 (s), 276 (s), 212 (w), 195 (w), 128 (m) cm^{-1}; ^1H NMR 10.42 (acetone), 7.92 ppm ($CFCl_3$); ^{19}F NMR −75.97 (s) ppm; major *m/z* [EI] 281 (M^+), 211 ($CF_3SO_2NSO_2^+$) 147 ($CF_3SO_2N^+$) 133 ($CF_3SO_2^+$), 69 (CF_3^+); major *m/z* [CI] 282 (MH^+), 150 ($CF_3SO_3H^+$ or $CF_3SO_2NH_3^+$), 115 ($CF_2SO_2H^+$ or $CF_2SONH_2^+$). Anal. Calcd for $C_2HF_6NO_4S_2$: C, 8.54; H, 0.36; F, 40.54; N, 4.98; S, 22.8. Found: C, 8.37; H, 0.55; F, 40.02; N, 5.07; S, 22.95.

Preparation of $CsN(SO_2CF_3)_2$. In a typical reaction using a 20-mL FEP reactor, $(CF_3SO_2)_2NH$ (7.00 g) was added to an equimolar amount of CsF (3.78 g) in the drybox. The reactor was cooled to −196 °C, and CH_3CN was added by vacuum transfer, to a volume of 6 mL. When the mixture was warmed to 0 °C, a rapid reaction ensued, forming a clear solution. CH_3CN and HF (identified by the formation of SiF_4 in the presence of glass) were pumped away at 22 °C, leaving a wet solid. This solid was dissolved in 10 mL of absolute ethanol followed by 200 mL of dry $CFCl_3$, resulting in the immediate formation of white crystals. The salt was filtered, air-dried, and then vacuum-dried at 80 °C for 1 h to yield 8.39 g (81.6%) of $CsN(SO_2CF_3)_2$: mp 115 °C; IR (KBr Pellet) 1345 (s), 1328 (m), 1196 (s), 1130 (s), 1053 (m), 792 (w), 762 (vw), 739 (m), 650 (w), 597 (m), 574 (m), 512 (w), 410 (vw) cm^{-1}; Raman (solid, 22 °C) 1331 (m), 1244 (m), 1222 (w, sh), 1150 (m), 798 (vw), 747 (s), 664 (w), 576 (vw), 560 (w), 415 (w), 353 (m), 335 (s), 309 (m), 291 (s), 222 (w), 177 (w), 138 (m), 119 (vw) cm^{-1}; ^{19}F NMR (CH_3CN) −79.3 (s) ppm. Attempts to obtain a mass spectrum by direct solid inlet were unsuccessful.

Preparation of $(CF_3SO_2)_2NCl$. Into a 30-mL FEP reactor at −196 °C containing $(CF_3SO_2)_2NH$ (23.6 mmol) was added ClF (37 mmol) by vacuum transfer. The reactor was placed in a $CFCl_3$ bath at −111 °C and left to warm to 0 °C over 12 h. At that point, there were two distinct layers: a lower yellow-green layer of impure $(CF_3SO_2)NCl$ and an upper clear layer of HF. Purification was achieved by first pumping away any volatile materials at −111 °C and then transferring the entire contents onto a large excess of NaF at −196 °C. The mixture was shaken at 22 °C, and the container was then pumped under vacuum through a −78 °C bath, where essentially pure $(CF_3SO_2)_2NCl$ (6.82 g, 92%) collected. *Caution! On several occasions, reactions on a larger scale (40 mmol) resulted in explosions of considerable force. Due care must be exercised in carrying out this reaction on any scale.* $(CF_3SO_2)_2NCl$: clear, viscous liquid with an acrid odor; mp (glass formed at −196 °C) −96 to −93 °C; vp (22 °C) 8 torr; IR (6 torr) 1461 (s), 1445 (m), 1330 (w), 1234 (vs), 1200 (w), 1124 (s), 1112 (sh), 1015 (w), 915 (w), 840 (s), 766 (w), 644 (w), 593 (s), 567 (w), 499 (m) cm^{-1}; Raman (liquid, −50 °C) 1464 (5, dp), 1440 (6, dp), 1296 (1, p), 1252 (47, p), 1226 sh (4, dp), 1125 (15, p), 920 (3, dp), 776 (100, p), 651 (27, p), 578 (19, p), 567 (5, dp), 560 (5, dp), 536 (13, p), 500 (1, dp), 431 (37, p), 382 (18, dp), 350 (80, p), 326 (31, p), 299 (26, dp), 269 (93, p), 222 (13, dp), 207 sh (2, dp?), 184 (5, p?), 117 (30, p), 86 (18, dp?) cm^{-1}; ^{19}F NMR −71.9 (s) ppm; major *m/z* [CI] 316 (MH^+), 281 ($MH - Cl^+$), 133 ($CF_3SO_2^+$), 69 (CF_3^+).

Preparation of $(CF_3SO_2)_2NNO_2$. $(CF_3SO_2)_2NCl$ (1.65 g, 5.2 mmol) and a 5:1 molar excess of N_2O_4 were successively condensed into a 20-mL FEP reactor at −196 °C. The mixture was allowed to warm directly to 22 °C and let stand for 4 h. There were no condensable gases at −111 °C, indicating that no N_2, O_2, or Cl_2 was given off. Only $ClNO_2$ and excess N_2O_4 were removed at 22 °C, leaving a white crystalline solid $(CF_3SO_2)_2NNO_2$ (1.67 g, 98%): dec pt 107 °C; IR (solid on KCl) 1754 (m), 1737 (m), 1355 (w), 1297 (s), 1179 (s),

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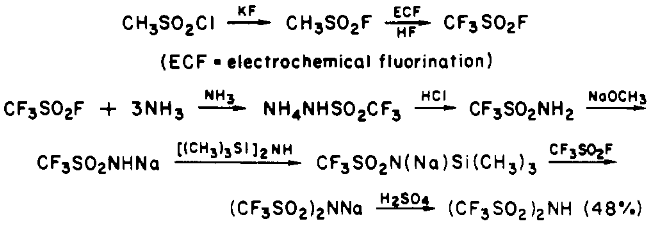
Scheme I



1109 (s), 1039 (s), 788 (m), 762 (w), 734 (m), 638 (m), 590 (m), 578 (m), 504 (w) cm^{-1}; Raman (solid, −180 °C) 1408 (vs), 1322 (w), 1315 (w), 1252 (s), 1136 (s), 1123 (m), 804 (w), 771 (w) 748 (vs), 633 (w), 593 (w), 564 (w), 554 (w), 537 (w), 417 (m), 403 (m), 348 (m), 324 (s), 301 (m), 288 (s), 185 (w), 163 (w), 132 (s) cm^{-1}; ^{19}F NMR ($CFCl_3$) −77.43 (s) ppm.

Preparation of $(CF_3SO_2)_2NNO$. Nitric oxide (8.8 mmol) was condensed onto $(CF_3SO_2)_2NCl$ (1.38 g, 4.37 mmole in a 20-mL FEP reactor at −196 °C. Reaction was started at −155 °C, at which point the NO was blue-black on top of the frozen $(CF_3SO_2)_2NCl$. As the reaction warmed, the color became less intense. After 14 h at −20 °C, the reaction was essentially complete, and only a white solid remained. NOCl and excess NO were pumped away at −10 °C, giving $(CF_3SO_2)_2NNO$ (1.35 g, 100%): mp 118 °C; IR (Nujol) 2287 (w), 1318 (vs), 1189 (vs), 1115 (vs), 1048 (s), 793 (m), 767 (w), 739 (m), 639 (s), 584 (s), 572 (s), 511 (s) cm^{-1}; Raman (solid, 22 °C) 2295 (vs), 1358 (vw), 1310 (w), 1238 (w), 1210 (vw), 1149 (w), 1131 (w), 1060 (vw), 805 (vw), 742 (s), 653 (vw), 610 (vw), 552 (vw), 433 (vw), 410 (w), 351 (w), 331 (m), 310 (w), 295 (w), 280 (w), 228 (m, br), 128 (vw) cm^{-1}; ^{19}F NMR ($CFCl_3$) −79.2 (s) ppm.

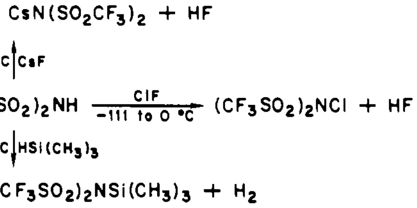
Preparation of $(CF_3SO_2)_2NSi(CH_3)_3$. In an FEP reactor, $(CF_3SO_2)_2NH$ (0.85 g) was allowed to react with a 3:1 molar excess of $(CH_3)_3SiH$. When the mixture was allowed to warm from −196 °C, an initial rapid reaction occurred near 22 °C. After 4 h and occasional agitation, the homogeneous mixture was cooled slowly to −196 °C. A quantitative amount of hydrogen was recovered, and the excess silane was pumped away at 10 °C, giving $(CF_3SO_2)_2NSi(CH_3)_3$ (0.98 g, 92%) as a low-volatile colorless liquid: ^{19}F NMR ($CFCl_3$) −77.47 (s) ppm; ^{1}H NMR 0.57 (s) ppm; major *m*/*e* [CI] 163 ($[(CH_3)_3Si]_2OH^+$), 147 ($CF_3SO_2N^+$), 77 (?), 73 ($Si(CH_3)_3^+$) with weak ions at 282 ($(CF_3SO_2)_2NH_2^+$) and 354 (M^+).

Photolysis of $ClN(SO_2CF_3)_2$. $ClN(SO_2CF_3)_2$ (1.20 g, 3.78 mmol) was added by vacuum transfer to a 12-mm o.d. Pyrex tube. The portion of the tube containing the liquid sample was irradiated at 22 °C for 0.75 h with a medium-pressure, 250-W Hg lamp. The volatile products were separated via −78 and −196 °C traps. The −196 °C trap contained pure CF_3Cl (3.80 mmol) identified by IR spectroscopy. A white solid residue remained in the reactor; the empirical formula was, by difference, $CF_3S_2O_4N$. This material could be readily sublimed and was found to be nearly identical with the previously reported $(CF_3SO_2NSO_2)_2$:[14] mp 54–55 °C; IR (gas in equilibrium with solid, 25 °C) 1458 (s), 1430 (w), 1240 (s), 1208 (m), 1133 (m), 907 (s), 865 (w), 661 (m), 601 (w), 519 (w), 475 (w) cm^{-1}; Raman (solid, 22 °C) 1468 (w), 1458 (w), 1442 (w), 1279 (vs), 1218 (s), 1133 (w), 1058 (vw), 1042 (vw), 783 (s), 667 (vs), 606 (m), 575 (w), 562 (vw), 396 (m), 348 (m), 333 (vs), 291 (vs), 272 (m), 216 (m), 146 (w), 130 (m) cm^{-1}; ^{19}F NMR ($CFCl_3/CH_2Cl_2$) −74.2 (s) ppm. The CI mass spectrum of the vapor in equilibrium with the solid at 22 °C was complex, but peaks above 200 amu at *m*/*z* 423 (MH^+), 359 ($MH^+ - SO_2$) and 212 ($(M/2)H^+$) support the presence of the dimer of $CF_3SO_2NSO_2$ and perhaps the monomer.

Results and Discussion

Synthesis and Properties of $(CF_3SO_2)_2NH$. The synthesis of $(CF_3SO_2)_2NH$ was accomplished in moderate overall yield as shown in Scheme I. The method was based in part on that used by Meussdorffer and Niederprum to prepare other $R_fSO_2N(H)SO_2R_f'$ derivatives, where $R_f = CF_3$, C_4F_9, and C_8F_{17} and $R_f' = C_4F_9$ and C_8F_{17}.[9] Surprisingly, these authors did not report $(CF_3SO_2)_2NH$. The moderate yield is due to the last two reactions in Scheme I, since $CF_3SO_2N(Na)Si(CH_3)_3$ is formed in over 80% yield based on starting CF_3SO_2F.

Scheme II



Crystalline $(CF_3SO_2)_2NH$ fumes in air and dissolves exothermically in H_2O. Aqueous solutions of the compound appear to be stable, and the compound exhibits a typical strong-acid titration curve when titrated with aqueous NaOH. The pK_a of the imide in water was 1.7, which compares closely with that of 1.3 for $(FSO_2)_2NH$.[8] As an additional comparison, the pK_a of a commercial sample of $(PhSO_2)_2NH$ in water was determined to be 1.4. These values probably indicate that all bis(sulfonyl)amines are relative strong acids in H_2O.

In an effort to gain a more meaningful comparison of the acid strengths of $(CF_3SO_2)_2NH$ vs. $(FSO_2)_2NH$, the ^{1}H NMR method of Rode, Engelbrecht, and Schantl was applied.[15] This method consists of measuring δ(OH) of a solution of an acid in glacial acetic acid and comparing it to δ(OH) of the pure solvent. A linear correlation between p*K* values for the overall dissocation of strong acids in glacial acetic acid and the specific chemical shifts of acid protons in these dilute solutions was demonstrated for a series of strong acids. The p*K* values for $(CF_3SO_2)_2NH$ and $(FSO_2)_2NH$ were determined in this way to be 7.8 and 8.7, respectively, as compared to p*K* values for CF_3CO_2H (11.4), HNO_3 (10.1), $HOTeF_5$ (8.8), H_2SO_4 (7.0), $HOSO_2F$ (6.1), HI (5.8), $HOIOF_4$ (5.0), $HClO_4$ (4.9), and CF_3SO_3H (4.2) determined in the same way. If the values determined for $(CF_3SO_2)_2NH$ and $(FSO_2)_2NH$ are valid, these compounds are remarkably strong acids.

The characterization of $(CF_3SO_2)_2NH$ by vibrational and NMR spectroscopy is straightforward. The ^{19}F NMR exhibits a singlet in the region characteristic of covalent CF_3SO_2 derivatives. Values for a variety of CF_3SO_2O and CF_3SO_2N compounds fall in the range of −71 to −80 ppm ($CFCl_3$) and tend toward higher field as the charge on the CF_3SO_2 group increases, i.e. $CF_3SO_2OCF_3$[16] (−76.2), CF_3SO_2OCl[17] (−73.5), CF_3SO_2OH[16] (−78.5), $(CF_3SO_2)_2NCF_3$[18] (−72.7), $(CF_3SO_2)_2NCl$ (−71.9), and $(CF_3SO_2)_2NH$ (−76.0).

The Raman spectrum of $(CF_3SO_2)_2NH$ is, as expected, rather similar to those of other CF_3SO_2X derivatives (X = F, OH, and OCl) in the 750–1500 cm^{-1} region.[17] A comparison of the spectra of the pseudoisoelectronic pair $(CF_3SO_2)_2O(l)$ and $(CF_3SO_2)_2NH(s)$ shows a very strong overall similarity in the Raman (50–1500 cm^{-1}), as do the low-pressure gas-phase IR spectra (400–1500 cm^{-1}).[18]

Derivatives of $(CF_3SO_2)_2NH$. The strong acidity of $(CF_3SO_2)_2NH$ allows the preparation of many derivatives to be carried out in a straightforward manner. Scheme II shows three derivatives that were synthesized because of their potential utility as reagents for further synthetic reactions.

The cesium salt is rather covalent judging from its low melting point of 115 °C. However, the Raman spectrum of the solid clearly supports the presence of the $(CF_3SO_2)_2N^-$

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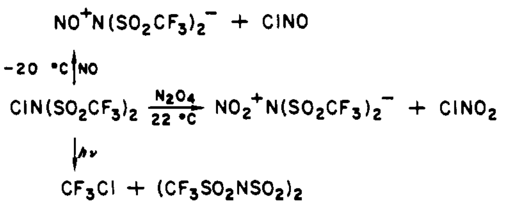
Scheme III



anion, as shown by an expected decrease in the antisymmetric $\nu(SO_2)$ to 1331 cm^{-1} from 1460, 1440 cm^{-1} in $(CF_3SO_2)_2NH$ and the similarity in other aspects to the spectrum of the isoelectronic $(CF_3SO_2)_2O$.[18] These observations agree well with those for the related compounds $CsN(SO_2F)_2$, $HN(SO_2F)_2$, and $S_2O_5F_2$.[11,19]

The trimethylsilyl derivative represents a potentially useful ligand-transfer reagent of considerable scope. As previously reported, the compound was used to prepare the novel compound $Xe[N(SO_2CF_3)_2]_2$ by reaction with XeF_2,[20] and the high reactivity of the compound with H_2O also suggests a variety of other reactions. However, an attempt to react this material with CF_3SO_2F to form $(CF_3SO_2)_3N$ was unsuccessful. At temperatures of 180–200 °C, some $(CH_3)_3SiF$ was produced, but extensive degradation of the starting materials was evident and no evidence was found for the desired tris((trifluoromethyl)sulfonyl)amine.

The *N*-chlorobis((trifluoromethyl)sulfonyl)amine, $ClN(SO_2CF_3)_2$, was very useful for further synthetic reactions as shown in Scheme III.

The presence of the NO^+ and NO_2^+ cations in $ONN(SO_2CF_3)_2$ and $O_2NN(SO_2CF_3)_2$ are readily apparent from the vibrational spectra with $\nu_1(NO^+)$ at 2295 cm^{-1} and $\nu_1(NO_2^+)$ at 1408 cm^{-1}. These values are essentially identical with those of the related fluorosulfates, $ONOSO_2F$ and O_2NOSO_2F.[21] The remainder of the spectra are fully in accord with an ionic formulation.

The photolysis of $ClN(SO_2CF_3)_2$ was initially carried out to prepare the hydrazine analogue $[(CF_3SO_2)_2N]_2$, a known reaction for the related $(FSO_2)_2NCl$.[10] However, the observed reaction further demonstrates the instability of $CF_3SO_2X\cdot$ radicals. For example, CF_3SO_2OCl and $(CF_3SO_2O)_2$ both decompose in a manner consistent with loss of CF_3 from an intermediate $CF_3SO_2\cdot$ radical:[16,17,22]

$$CF_3SO_2OCl \rightarrow CF_3SO_3\cdot + Cl\cdot \rightarrow CF_3Cl + SO_3$$

$$(CF_3SO_2O)_2 \rightarrow 2CF_3SO_3\cdot \rightarrow CF_3SO_2OCF_3 + SO_3$$

Thus the photolysis of $ClN(SO_2CF_3)$ and the previously observed decomposition of $Xe[N(SO_2CF_3)_2]_2$[20] are exactly analogous:

$$ClN(SO_2CF_3)_2 \rightarrow Cl\cdot + \cdot N(SO_2CF_3)_2 \rightarrow CF_3Cl + {}^1/_2(CF_3SO_2NSO_2)_2$$

$$Xe[N(SO_2CF_3)_2]_2 \rightarrow \cdot XeN(SO_2CF_3)_2 + \cdot N(SO_2CF_3)_2 \rightarrow Xe + CF_3N(SO_2CF_3)_2 + {}^1/_2(CF_3SO_2NSO_2)$$

Furthermore, this mode of decomposition for R_fSO_2X radicals appears to be general, as shown by related reactions involving $C_4F_9SO_2$ derivatives:[18,23]

$$C_4F_9SO_2OCl \rightarrow C_4F_9SO_3\cdot + Cl\cdot \rightarrow C_4F_9Cl + SO_3$$

$$(C_4F_9SO_2)_2NH + ClF \rightarrow \text{“}(C_4F_9SO_2)_2NCl\text{”} + HF \rightarrow (C_4F_9SO_2)_2N\cdot + Cl\cdot \rightarrow {}^1/_2(C_4F_9SO_2NSO_2)_2 + C_4F_9Cl$$

Summary

The synthesis of the novel $(CF_3SO_2)_2NH$ has been successfully carried out from a series of reactions involving CF_3SO_2F, prepared by electrochemical fluorination of CH_3SO_2F. The imide is probably the most acidic NH compound known, and the unique properties of the very electronegative $(CF_3SO_2)_2N$ group have been demonstrated by the formation of selected derivatives. Finally, the general instability of CF_3SO_2X radicals toward the loss of CF_3 has been substantiated.

Acknowledgment. The support of this research by the National Science Foundation is greatly appreciated. The 3M Co. is acknowledged for the gift of CF_3SO_2F in the early stages of this research. D.D.D. thanks the Alexander von Humboldt Stiftung for a fellowship during part of this research.

Registry No. $(CF_3SO_2)_2NH$, 82113-65-3; $CsN(SO_2CF_3)_2$, 91742-16-4; $(CF_3SO_2)_2NCl$, 91742-17-5; $(CF_3SO_2)_2NNO_2$, 91742-18-6; $(CF_3SO_2)_2NNO$, 91742-19-7; $(CF_3SO_2)_2NSi(CH_3)_3$, 82113-66-4; $CFCl_3$, 75-69-4; $(CF_3SO_2NSO_2)_2$, 68751-12-2; CH_3SO_2F, 558-25-8; CF_3SO_2F, 335-05-7; $H_2NSO_2CF_3$, 421-85-2; $NaNHSO_2CF_3$, 35534-15-7; $(CH_3)_3SiN(Na)SO_2CF_3$, 91742-20-0; $NaN(SO_2CF_3)_2$, 91742-21-1; CH_3SO_2Cl, 124-63-0; KF, 7789-23-3; NH_3, 7664-41-7; $[(CH_3)_3Si]_2NH$, 999-97-3; CsF, 13400-13-0; ClF, 7790-89-8; N_2O_4, 10544-72-6; NO, 10102-43-9; $(CH_3)_3SiH$, 993-07-7.

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(22) A reviewer pointed out that an internal S_Ni type mechanism might be equally attractive. Since small amounts of C_2F_6 are observed in certain decompositions of CF_3SO_2O- derivatives, we prefer the radical path. However, it is certainly true that the proposed radical path has not been proven.

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