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Bis(trifluoromethyl)sulfimide, Bis(trifluoromethyl)-*N*-alkylsulfimides, and Bis(trifluoromethyl)-*N*-alkylsulfoxyimides

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Bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NH$, results when ammonia and bis(trifluoromethyl)sulfur difluoride, $(CF_3)_2SF_2$, are allowed to react in the presence of benzylamine. With primary amines, the corresponding bis(trifluoromethyl)-*N*-alkylsulfimides, $(CF_3)_2S{=}NR$ ($R = CH_3$, C_2H_5, i-C_3H_7), are formed. At reduced temperature, the sulfimide and *N*-alkylsulfimides are oxidized with *m*-chloroperbenzoic acid to the corresponding sulfoxyimide, $(CF_3)_2S(O){=}NH$, and *N*-alkylsulfoxyimides, $(CF_3)_2S(O){=}NR$.

The chemical behavior of bis(trifluoromethyl)sulfur difluoride, $(CF_3)_2SF_2$,[1] differs markedly from that of its more highly fluorinated analogues CF_3SF_3 and SF_4. A qualitative comparison of the hydrolytic stability of these compounds shows that the ease of hydrolysis decreases in the order $SF_4 > CF_3SF_3 > (CF_3)_2SF_2$. While SF_4 fumes in moist air[2,3] and CF_3SF_3 hydrolyzes in water readily at 25 °C,[4,5] $(CF_3)_2SF_2$ can be stored in the presence of a large excess of water at 25 °C for at least 1 week with no apparent hydrolysis occurring. A similar difference in reactivity occurs with anhydrous ammonia where with SF_4 reaction proceeds even at −95 °C[3] whereas with $(CF_3)_2SF_2$ no reaction takes place even upon heating.[1]

We now report that $(CF_3)_2SF_2$ will undergo metathesis reactions with primary amines to produce a series of new bis(trifluoromethyl)-*N*-alkylsulfimides, $(CF_3)_2S{=}NR$. These moderately stable compounds are oxidized readily by using *m*-chloroperbenzoic acid (MCPBA) to form the bis(trifluoromethyl)-*N*-alkylsulfoxyimides, $CF_3S(O){=}NR$.[6]

Also, we find that, in the presence of a primary amine, the reaction of ammonia and bis(trifluoromethyl)sulfur difluoride does occur readily to form the stable bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NH$.[7] Oxidation of the latter with MCPBA at low temperature gives bis(trifluoromethyl)sulfoxyimide which was reported previously.[6]

Results and Discussion

Bis(trifluoromethyl)sulfur difluoride, $(CF_3)_2SF_2$, undergoes metathetical reactions with primary amines to produce a series of new *N*-alkylsulfimides

$$(CF_3)_2SF_2 + 3RNH_2 \rightarrow (CF_3)_2S{=}NR + 2RNH_2{\cdot}HF$$
$$R = CH_3, C_2H_5, i\text{-}C_3H_7; R \neq H$$

These reactions proceed very rapidly at 25 °C. In some cases, if the rate of warming from −196 to +25 °C is too rapid, discoloration occurs and lower yields result. Based on the ease with which the above reactions occur, the fact that ammonia does not react is somewhat unexpected. However, when a primary amine is added to the NH_3–$(CF_3)_2SF_2$ mixture, reaction does occur to produce bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NH$, in reasonable yield

$$(CF_3)_2SF_2 + NH_3 \xrightarrow[R = C_6H_5CH_2]{RNH_2} (CF_3)_2S{=}NH\ (50\text{–}60\%)$$

Other primary amines can be used in this reaction, also. When methylamine is used, the $(CF_3)_2S{=}NH$ is formed in only trace quantities. Better yields are obtained when isopropylamine is utilized, but the product, bis(trifluoromethyl)-*N*-isopropylsulfimide, from the competing reaction is separated from $(CF_3)_2S{=}NH$ with considerable difficulty. Because of its low volatility, $(CF_3)_2S{=}NCH_2C_6H_5$, which is certainly formed, has not been isolated.

The new bis(trifluoromethyl)sulfimide is more stable than its hydrocarbon analogue $(CH_3)_2S{=}NH$ which was reported to be stable at −30 °C and to decompose slowly at 0 °C.[8] The inherent instability of $F_2S{=}NH$ with respect to NSF and HF probably precludes its isolation as a stable species at 25 °C, although many of its derivatives are known and are stable.[9] Bis(trifluoromethyl)sulfimide is stable at 25 °C for extended periods in Pyrex glass but decomposes slowly at 35 °C. Decomposition in glass is rapid at 60 °C. When the compound was mixed with dry air and allowed to stand at room temperature for 1 week, only trace amounts of impurities were observed.

An unexpected side reaction, which results in the formation of CF_3H, occurs in the reactions of $(CF_3)_2SF_2$ with primary amines. In the case where $R = i$-C_3H_7, significant amounts of $CF_3SN(H)CH(CH_3)_2$[10] are also found. The reduction of S^{VI} to S^{IV} is accompanied by concomitant C–S bond breaking.

Table I

	Infrared spectra, cm^{-1}	Elemental anal., %			NMR^b	
		C	H	N	^{19}F	^1H
$(CF_3)_2S{=}NH$	3311 m, 1225 vs, 1177 vs, 954 s, 743 m, 600 s, 520 w, 448 w	12.77 (12.97)^a	0.66 (0.54)	7.44 (7.57)	68.4	2.45
$(CF_3)_2S{=}NCH_3$	2911 m, 1418 w, 1209 vs, 1168 s, 1128 s, 1081 s, 809 m, 440 w	18.10 (17.49)	1.50 (1.84)	7.04 (6.34)	58.0 q	2.95 h; $J_{H-F} = 2.26$
$(CF_3)_2S{=}NCH_2CH_3$	2991 m, 2952 w, 2890 w, 1386 w, 1354 m, 1213 vs, 1170 s, 1129 s, 1087 s, 774 w	22.50 (22.65)	2.35 (2.48)	6.51 (6.41)	58.7 t	CH_3 1.17 t; $J_{H-H} = 7.17$ CH_2 3.23 h of q; $J_{H-F} = 2.14$
$(CF_3)_2S{=}NCH(CH_3)_2$	2975 m, 2925 m, 1381 w, 1341 w, 1209 vs, 1168 s, 1126 s, 1087 s, 955 w	26.43 (26.49)	3.08 (2.97)	6.17 (6.17)	59.8 d	CH_3 1.14 d; $J_{H-H} = 6.23$ CH 3.28 c, u; $J_{H-F} = 0.62$
$(CF_3)_2S(O){=}NCH_2CH_3$	2981 m, 2940 w, 2889 w, 1386 s, 1335 s, 1229 vs, 1182 vs, 1121 vs, 793 m, 613 m, 579 m, 510 w	20.96 (20.81)	2.18 (2.06)	6.11 (6.29)	73.1 t	CH_3 1.09 t; $J_{H-H} = 7.21$ CH_2 3.43 q of h; $J_{H-F} = 0.77$
$(CF_3)_2S(O){=}NCH(CH_3)_2$	2977 m, 2931 w, 2878 w, 1386 s, 1337 s, 1237 vs, 1189 s, 1124 s, 760 w, 611 m, 587 m, 514 w	24.69 (24.32)	2.88 (3.14)	5.76 (5.81)	73.5 d	CH_3 1.30 d; $J_{H-H} = 6.42$ CH 3.95 c, u; $J_{H-F} = 0.93$

[a] Calculated values in parentheses. [b] ^{19}F chemical shifts relative to CCl_3F; ^1H chemical shifts relative to $Si(CH_3)_4$. *J* values in Hz; c = complex, d = doublet, h = heptet, q = quartet, t = triplet, u = unresolved.

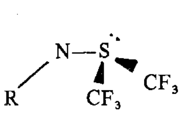
A similar mode of behavior is observed in reactions of $(CF_3)_2SF_2$ with secondary diamines.[11]

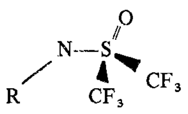
All of the sulfimides are oxidized readily with *m*-chloroperbenzoic acid (MCPBA) to sulfoxyimides, $(CF_3)_2S(O){=}NR$. The reaction is allowed to occur slowly by warming from −120 to +25 °C over a period of 3 or 4 days. Shorter reaction times result in charring and recovery of only small amounts of product. Some of the sulfoxyimides, $(CF_3)_2S(O)NH$ and $(CF_3)_2S(O)NCH_3$, were reported previously, but the synthetic method used involves oxidation of bis(trifluoromethyl) sulfoxide with ClF followed by reaction of the sulfoxydifluoride formed with ammonia or primary amine.[6] The new method is preferred since it involves a procedure with fewer steps.

In general, the mass spectra of these two series of compounds give fragmentation patterns as expected with a molecular ion present in each case. For $(CF_3)_2S{=}NH$ at normal inlet temperature (~200 °C), the fragmentation pattern appeared to be that of a dimer or other polymer. However, upon lowering of the inlet temperature to ambient temperature, the predictable pattern of the monomer, including a molecular ion, was obtained.

The nuclear magnetic resonance spectra of these compounds are first order. With the exception of $(CF_3)_2S{=}NH$, heteronuclear coupling occurs in each of the new compounds.

Based on x-ray and electron diffraction measurements of $Hg(N{=}SF_2)_2$[12] and $ClN{=}SF_2$,[13] the geometries of the new compounds must be similar, viz.





Experimental Section

Materials. $(CF_3)_2SF_2$ was prepared according to the literature method.[1] ClF (Ozark-Mahoning Co.), NH_3 (Linde), and CH_3NH_2 (Linde) were used as received without further purification. $CH_3CH_2NH_2$ (Eastman) was distilled prior to use. A water solution of $(CH_3)_2CHNH_2$ (Aldrich) was distilled to obtain anhydrous $(CH_3)_2CHNH_2$. The *m*-chloroperbenzoic acid (Aldrich) was used directly as received but was stored under refrigeration.

General Procedures. Most gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise Bourdon tube gauge. All starting materials and products were measured quantitatively by *PVT* techniques. Products were purified by fractional condensation (trap-to-trap distillation). Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer with a 10-cm cell equipped with KBr windows. ^{19}F NMR spectra were obtained on a Varian HA-100 spectrometer by using CCl_3F as an internal standard. ^1H NMR spectra were obtained on either a Varian EM 360 or a Varian HA-100 spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at an ionization potential of 17 eV. Elemental analyses were performed with the aid of a Perkin-Elmer 240 elemental analyzer. Infrared, NMR, and elemental analysis data are given in Table I. Although the *N*-alkylsulfimides are stable for several hours at 25 °C, decomposition occurred on heating and precluded determination of boiling point and thermodynamic data. For gas chromatographic separations, the columns were constructed of 0.25-in. copper tubing packed with 20% Kel-F oil (3M Co.) or FS-1265 on Chromosorb P.

Preparation of Bis(trifluoromethyl)-*N*-methylsulfimide, $(CF_3)_2S{=}NCH_3$. Bis(trifluoromethyl)sulfur difluoride (1.0 mmol) was condensed onto monomethylamine (3.0 mmol) in a Pyrex glass vessel equipped with a Kontes Teflon stopcock. The reaction mixture was allowed to warm from −196 to +25 °C over a period of several hours. Bis(trifluoromethyl)-*N*-methylsulfimide was recovered in about 57% yield. Small amounts of unreacted $(CF_3)_2SF_2$ and CF_3NH_2 were recovered. Fluoroform (0.4 mmol) was also identified in the reaction mixture. $(CF_3)_2S{=}NCH_3$ was purified by fractional condensation and gas chromatography.

Preparation of Bis(trifluoromethyl)-*N*-ethylsulfimide, $(CF_3)_2S{=}NCH_2CH_3$. In the usual procedure, 1.0 mmol of $(CF_3)_2SF_2$ was condensed onto 3.0 mmol of monoethylamine. The reaction mixture was allowed to warm from −196 to +25 °C over a period of several hours. The yield of $(CF_3)_2S{=}NCH_2CH_3$ was about 67%. Small amounts of the starting materials and 0.6 mmol of CF_3H were recovered. The new compound was purified by fractional condensation and gas chromatography.

Preparation of Bis(trifluoromethyl)-*N*-isopropylsulfimide, $(CF_3)_2S{=}NCH(CH_3)_2$. When $(CF_3)_2SF_2$ (1.0 mmol) was condensed onto 3.0 mmol of monoisopropylamine, the yield of $(CF_3)_2S{=}NCH(CH_3)_2$ was about 45%. The same reaction conditions were used as in the previous preparation. Also found in the reaction mixture were 0.3 mmol of CF_3H and 0.25 mmol of $CF_3SNHCH(CH_3)_2$.[11] Purification was accomplished by fractional condensation followed by gas chromatography.

Preparation of Bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NH$. In a typical reaction, 1.0 mmol of $(CF_3)_2SF_2$ was condensed onto 1.0 mmol of benzylamine. To this mixture 4 mmol of ammonia was added at −196 °C. The mixture was allowed to warm slowly to 25 °C over a period of several hours in a cold Dewar. Maximum yields for this reaction approach 60% based on $(CF_3)_2SF_2$ consumed. The new compound was purified by fractional condensation and gas chromatography.

Preparation of Bis(trifluoromethyl)-*N*-alkylsulfoxyimides, $(CF_3)_2S(O){=}NR$. An excess of *m*-chloroperbenzoic acid (MCPBA) was placed in the bottom of a Pyrex glass reaction vessel equipped with a Teflon stopcock and 3.0 mmol of the appropriate sulfimide was condensed into the vessel at −196 °C. The reaction vessel was placed in an ethanol slush bath (−120 °C) and allowed to warm very slowly to room temperature over a period of 3 or 4 days. The volatile products were removed and purification was accomplished by fractional condensation and gas chromatography.

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Registry No. $(CF_3)_2S{=}NH$, 60646-40-4; $(CF_3)_2S{=}NCH_3$, 60646-41-5; $(CF_3)_2S{=}NCH_2CH_3$, 60646-42-6; $(CF_3)_2S{=}NCH(CH_3)_2$, 60646-43-7; $(CF_3)_2S(O){=}NCH_2CH_3$, 60646-44-8; $(CF_3)_2S(O){=}NCH(CH_3)_2$, 60646-45-9; $(CF_3)_2SF_2$, 30341-38-9; CH_3NH_2, 74-89-5; $CH_3CH_2NH_2$, 75-04-7; $(CH_3)_2CHNH_2$, 75-31-0; NH_3, 7664-41-7.

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Conformational Analysis. 121. Elemental Sulfur

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A force field has been developed to permit molecular mechanics calculations on various molecular structures of elemental sulfur. The conformational characteristics of sulfur rings containing 5–12, 14, 16, 18, or 20 sulfur atoms have been examined. Comparison with experimental data is made in all cases where such data exist, and predictions are made for other cases. Ab initio molecular orbital calculations using an STO-3G basis set were carried out for *cyclo*-hexasulfur and are consistent with the molecular mechanics calculations in indicating that the chair and the twist forms are two stable conformations, with the chair about 15 kcal/mol more stable, while the boat (C_{2v}) is a twist–twist rotational transition state.

Elemental sulfur[3,4] can exist in a polymeric form and as a variety of rings containing different numbers of sulfur atoms, many of which have been isolated. The molecular structures of only a few of these different allotropes have so far been studied. The most straightforward way of determining the structures and conformations of these sulfur allotropes would be by electron diffraction and x-ray diffraction. The ring structures of S_6, S_8, S_{12}, S_{18}, and S_{20}, have been studied[5–9] by the x-ray method, but the accuracy for most compounds is generally not too high. Only a preliminary structure of S_7 has been reported. The structures of S_9, S_{10}, and S_{11} have not yet been studied experimentally. The x-ray method is the only experimental technique so far having been used. No sulfur allotrope appears to have yet had its structure studied experimentally in the gas phase.

On the other hand, a variety of theoretical methods are also readily applicable to the conformational study of these compounds. The molecular mechanics or force field method[10] has been successful in calculating the structures and energies of a variety of types of related compounds including thiaalkanes,[11] sulfoxides,[12] disulfides,[13,14] and polysulfides.[13] In the present work, the molecular mechanics method has been applied to the conformational study of elemental sulfur.

The Molecular Mechanics Method

The method previously developed for the calculation of the structures and energies of disulfides[13] was used as a starting point, and these force field calculations were extended to a study of elemental sulfur. *cyclo*-Hexasulfur was the only sulfur allotrope examined in our preliminary study.[13] In the present study, *cyclo*-hexasulfur,[5] *cyclo*-octasulfur (α_{15}),[6] *cyclo*-dodecasulfur,[7] *cyclo*-octadecasulfur (α),[8] *cyclo*-icosasulfur,[8b,9] and fibrous sulfur[15] were used as model compounds from which to obtain the necessary force field parameters. Three parameters, the natural bond length of the S–S bond, the natural bond angle for the S–S–S angle, and the S–S–S–S torsional function, were modified from the earlier more approximate values to meet the more demanding experimental observations on compounds included in this study. The S–S–S natural bond angle and the S–S natural bond length are now assigned values of respectively 106.5° and 2.050 Å, while previously 104.0° and 2.024 Å were used.

Our previous assignment for the natural bond length of the S–S bond was based on both the experimental electron diffraction data[16a] and microwave data[16b] for dimethyl disulfide. However, experimental S–S single bond lengths span quite a range (for example, 1.90 Å in FSSF,[17a] 2.03 Å in CH_3SSCH_3,[16] 2.07 Å in $Cl_3CSSCCl_3$,[17b] and 2.10 Å in 1,2-dithiolane-4-carboxylic acid[17c]) and are very sensitive to substituents. The bond length given is clearly better for elemental sulfur. The wide range of S–S single bond lengths is presumably due to secondary environmental effects caused by the lone-pair electrons on the sulfur atoms[18] although experimental error may be a problem in some cases. Dependence of the S–S bond length and the stretching vibration on the dihedral angle was postulated[19] in 1973 and was also made probable by the CNDO/2 calculations[20] for the case of CH_3SSCH_3. But this has been disputed[21] since clearly other effects, e.g., the conformation of the substituents,[22] can also play a part. This problem seems complex and cannot be regarded as convincingly solved. The CNDO/2 results with the spd parameterization in particular gives very questionable results.[14]

Due to the limited scope in this study (to elemental sulfur only) the substituent effect on the S–S bond length will not be further considered here, except that to say we assumed a longer natural bond length relative to the one used for disulfides. It should also be emphasized here that the choice of natural bond length is not critical in our current confor-