J. Am. Chem. Soc. 1982, 104, 1683-1692

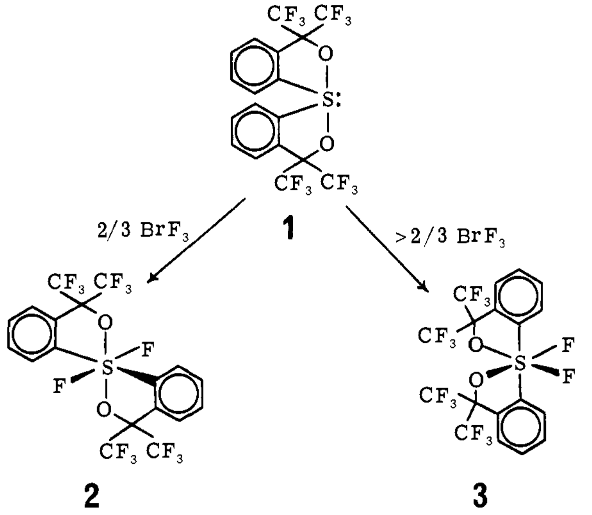
Dissociative Stereoisomerization of Persulfuranes via 10-S-5 Persulfonium Salts. Geometrical Isomers of Octahedral 12-S-6 Species[1]

Ronald S. Michalak and J. C. Martin*

Contribution from Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. *Received September 8, 1981*

Abstract: The reaction of bromine trifluoride with sulfurane **1** gives rise to the first reported isolation of geometrical isomers of 12-S-6 sulfur, the *trans*- and *cis*-difluorodialkoxydiarylpersulfuranes **2** and **3**. The cis isomer is 1.6 ± 0.1 kcal/mol more favored in free energy than the all-trans isomer in methylene chloride solution at 25 °C. Calorimetry showed trans-to-cis isomerization to be exothermic by 2.0 ± 0.5 kcal/mol. The rapid, acid-catalyzed isomerization of trans isomer **2** to give cis isomer **3** occurs by a dissociative mechanism through a pentacoordinate cationic sulfur intermediate, a 10-S-5 persulfonium ion, which was isolated as its hexafluorophosphate salt. A lower limit for the activation barrier of the unobserved nondissociative isomerization of **2** to **3** is 50 kcal/mol in quinoline solution. Polarization and other effects on the relative bond lengths and energies of the isomers are discussed. The results of complete X-ray structure determinations for **2** and **3** are described together with a PMO argument rationalizing the observed order of bond lengths.

The chemistry of persulfuranes (12-S-6 species),[2] like that of other 12-X-6 derivatives of nonmetallic elements, is not well-known. Most study has been done on sulfur hexafluoride and its mono- and disubstituted derivatives.[3] Oxidative addition of fluorine to sulfur has been accomplished by a variety of reagents, including CF_3OF,[4] ClF,[5] XeF_2,[6] AgF_2,[7] CsF,[8] and elemental fluorine.[9] The fluorinated sulfur compounds which are formed have a wide range of stabilities and reactivities. Recently Lam and Martin reported[10] the first example of a persulfurane without fluorine substituents. Our goal was to synthesize an isolable persulfurane which could undergo further substitution to give a variety of 12-S-6 and 10-S-5 species. We find that fluorination of sulfurane **1** with the inexpensive reagent BrF_3 leads, depending on reaction conditions, either to the all-trans or to a cis isomer of the difluoropersulfurane. Addition of a catalytic amount of the Lewis acid antimony pentafluoride to solutions of the trans isomer causes its isomerization to a thermodynamically more stable cis isomer. We are unaware of any previous report of permutational isomerization processes involving hexacoordinate sulfur. Fluorination of bis(perfluoroalkyl) sulfides by chlorine fluoride gives spectroscopic evidence for mixtures[11] containing cis and trans isomers of $(CF_3)_2SF_4$ and $(C_2F_5)SF_4CF_3$. While we were preparing this paper, two 12-X-6 systems, one in which X is phosphorus[12] and one in which X is tellurium,[13a] were reported to undergo geometrical isomerization. Cis and trans isomers of pseudooctahedral iodine[14] and hexacoordinate tellurium[13b] have been reported, though their interconversions have not been observed.



The synthesis of the first persulfonium ion, a cationic 10-S-5 species, fills a gap in the series of isoelectronic 10-X-5 species. More thoroughly studied members of this series include the anionic 10-Si-5 siliconates,[15] electrically neutral 10-P-5 phosphoranes,[15] and 10-S-5 sulfurane oxides[16] and sulfurane imines.[17]

Experimental Section

General Remarks. Proton and fluorine chemical shifts are reported on the δ scale, ppm downfield from tetramethylsilane and $CFCl_3$, respectively. Melting points were determined in sealed capillaries. Teflon apparatus was dried in an oven several hours before use. Elemental analyses are within 0.4% of values calculated for the listed elements, unless otherwise indicated.

---

(1) For a preliminary account of a part of these results see: (a) Michalak, R. S.; Martin, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5921. (b) Michalak, R. S.; Martin, J. C. *Ibid.* **1981**, *103*, 214. It was described in part during the Symposium on Fluorinated Heterocycles, the 180th National Meeting of the American Chemical Society, Las Vegas, Aug 1980; American Chemical Society: Washington, D.C., 1980; Fluo 39.

(2) We have proposed (Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753) a method of characterizing species in terms of the number of formal valence shell electrons (N) about an atom X and the number of ligands (L) bonded to X. This makes **2**, **3**, and **23** 12-S-6 species.

(3) (a) Roberts, H. L. "Inorganic Sulfur Chemistry"; Nickless, G., Ed.; Elsevier: New York, 1968; Chapter 12. (b) Dresdner, R. D.; Hooper, T. R. *Fluorine Chem. Rev.* **1969**, *4*. (c) Sheppard, W. A.; Sharts, C. M. "Organic Fluorine Chemistry", W. A. Benjamin: New York, 1969. (d) Opalovskii, A. A.; Lobkov, E. U. *Russ. Chem. Rev.* (*Engl. Transl.*) **1975**, *44*, 97.

(4) (a) Denney, D. B.; Denney, D. Z.; Hsu, Y. F. *J. Am. Chem. Soc.* **1973**, *95*, 8191. (b) Denney, D. B.; Denney, D. Z.; Hsu, Y. F. *Ibid.* **1973**, *95*, 4064.

(5) (a) Abe, T.; Shreeve, J. M. *J. Fluorine Chem.* **1973**, *3*, 187. (b) Sauer, D. T.; Shreeve, J. M. *Z. Anorg. Allg. Chem.* **1971**, *385*, 113.

(6) (a) Zupan, M.; Zajc, B. *J. Chem. Soc., Perkin Trans. 1* **1978**, 965. (b) Marat, R. K.; Janzen, A. F. *Can. J. Chem.* **1977**, *55*, 3031.

(7) (a) Martin, L. D.; Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3595. (b) Lawless, E. W.; Harmon, L. D. *Inorg. Chem.* **1968**, *7*, 391.

(8) Kleemann, G.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 516.

(9) (a) Ruppert, I. *Chem. Ber.* **1979**, *112*, 3023. (b) Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 880.

(10) Lam, W. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 120, 127.

(11) Abe, T.; Shreeve, J. M. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 465.

(12) Font Freide, J. J. H. M.; Trippett, S. *J. Chem. Soc., Chem. Commun.* **1980**, 934.

(13) (a) Tötsch, W.; Sladky, F. *J. Chem. Soc., Chem. Commun.* **1980**, 927. (b) Lentz, D.; Pritzkow, H.; Seppelt, K. *Inorg. Chem.* **1978**, *17*, 1926.

(14) Engelbrecht, A.; Peterfy, P. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 768.

(15) Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.: Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049.

(16) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 6735.

(17) (a) Mews, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 530. (b) Kitazume, T.; Shreeve, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 3690.

0002-7863/82/1504-1683$01.25/0

Caution! Bromine trifluoride is a very powerful oxidizing agent. All operations involving BrF_3 were conducted under N_2 in dry Teflon apparatus using Freon solvents.

Solvents and Reagents. Methylene chloride and $CHCl_3$ were distilled from and stored over KOH, as were the various amines used as nucleophiles. Freon 11 ($CFCl_3$) and Freon 113 ($CF_2ClCFCl_2$) were distilled from P_2O_5.

Potassium Salt of Bis[2-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)phenyl] Sulfoxide (5). Sulfurane **1** (1.0 g, 1.9 mmol) was boiled for 7 days in 90 mL of EtOH, 10 mL of H_2O, and 10 g of KOH. After the solution was cooled, an initial filtration was necessary to remove silicates which resulted from hydroxide attack on the Pyrex flask. Removal of solvent and filtration of the precipitate gave 1.28 g (1.87 mmol, 96%) of a hygroscopic white powder, whose elemental analysis indicates the presence of four waters of crystallization: mp 242 °C dec; ^1H NMR (D_2O) δ 7.7–8.2 (m, Ar-H); ^{19}F NMR (D_2O) δ −71.0 (q, 6, CF_3), −73.9 (q, 6, CF_3). Anal. ($C_{18}H_{16}SO_7F_{12}K_2$) C, H, S.

Protonation of Dialkoxy Sulfoxide 5. After one drop of aqueous 10% HCl was added to a solution of **5** in EtOH/H_2O, the ^{19}F NMR spectrum of the solution showed exclusively, as soon as the spectrum could be obtained, the presence of sulfurane **1**.

Tetrabutylammonium Alkoxy Sulfoxide 6. To 5 mL of 40% aqueous (n-C_4H_9)$_4$NOH was added an aqueous solution of 0.74 g (1.1 mmol) of potassium dialkoxy sulfoxide **5**. A precipitate was extracted into CH_2Cl_2. Removal of solvent and recrystallization from CH_2Cl_2 gave 0.63 g (0.8 mmol, 73%) of **6**: mp 171–173 °C; ^1H NMR ($CDCl_3$) δ 1.0 (t, 14, N-$CH_2(CH_2)_2CH_3$), 1.2–2.1 (br, 16, N-$CH_2(CH_2)_2CH_3$), 7.4–8.3 (br, 8, Ar-H), δ 7.4 (s, 1, OH); ^{11}F NMR ($CDCl_3$) δ −74.0 (q, 6, CF_3), −76.1 (q, 6, CF_3). Anal. ($C_{34}H_{45}F_{12}SO_3N$) C, H, S, F.

(*trans*-*F*,*trans*-*O*,*trans*-*C*)-3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*-2,1-benzoxathiole] 1,1-Difluoride (2). (A) To sulfurane **1** (15 mg, 0.03 mmol) in 0.4 mL of CH_2Cl_2 in a Teflon-lined NMR tube was added excess CF_3OF, diluted by N_2, at −80 °C by bubbling the gas through the NMR tube for several minutes. The tube was capped and allowed to warm to room temperature. The formation of trans isomer **2** was indicated by absorptions at δ −73.7 (t, CF_3) and 104 (S–F) in the ^{19}F NMR spectrum of the solution.

(B) To a Teflon flask was added 1.33 g (2.6 mmol) of sulfurane **1** and 100 mL of Freon 113. The flask was kept under a nitrogen atmosphere and cooled to −20 °C. In another Teflon flask under a nitrogen blanket was added 20 mL of Freon 113, and 0.23 g (1.7 mmol) of BrF_3 was dripped into the flask from an inverted cylinder. The weight of added BrF_3 was monitored by continuous weighing of the flask. The BrF_3/Freon solution was transferred to the flask containing the sulfurane/Freon solution through Teflon tubing by positive nitrogen pressure. The solution was allowed to warm to room temperature, and solvent was removed to give 1.14 g (2.1 mmol, 80%) of analytically pure *trans*-difluoropersulfurane **2**. Compound **2** was stored over K_2CO_3 because of its extreme acid sensitivity: mp 141–144 °C; ^1H NMR ($CDCl_3$) δ 7.80 (m, 6, Ar-H), 8.34–8.41 (m, 2, Ar-H ortho to S); ^{19}F NMR (CH_2Cl_2) δ −73.7 (t, 12, CF_3, $^5J_{F-F} = 7$ Hz), 104 (triskaidekacet, 2, S–F, $^5J_{F-F} = 7$ Hz); mass spectrum (10 eV), *m*/*e* (relative intensity) 535 (24.2, $M^{+\cdot} - F$), 485 (100, $M^{+\cdot} - CF_3$). Anal. ($C_{18}H_8O_2SF_{14}$) C, H, S, F.

(*cis*-*F*,*cis*-*O*,*trans*-*C*)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*-2,1-benzoxathiole] 1,1-Difluoride (3). Sulfurane **1** (10.1 g, 19.7 mmol) was allowed to react with 2.7 g (19.6 mmol) of BrF_3 according to the procedure discussed in method B for **2**. Solvent removal yielded 7.95 g (14.4 mmol, 73%) of *cis*-difluoropersulfurane **3**, which crystallized from solution in analytical purity. It is less sensitive to acid than its trans isomer, eliminating the need for storage over K_2CO_3: mp 160–162 °C; ^1H NMR (CD_2Cl_2) δ 7.80 (s, 6, Ar-H), 8.06–8.11 (m, 2, Ar-H ortho to S); ^{19}F NMR (CH_2Cl_2) 76.8 (m, 2, S–F), −72.8 to −73.5 (br, 6, CF_3), −73.5 to −73.9 (br, 6, CF_3); mass spectrum (10 eV) *m*/*e* (relative intensity) 554 (18, $M^{+\cdot}$), 535 (24, $M^{+\cdot} - F$), 485 (100, $M^{+\cdot} - CF_3$). Anal. ($C_{18}H_8SO_2F_{14}$) C, H, S, F.

Attempted Reaction of IF_5 with Sulfurane 1. Sulfurane **1** (0.85 g, 1.6 mmol) was allowed to react with IF_5 (0.4 g, 1.8 mmol), using the procedure discussed in method B for *trans*-difluoropersulfurane **2**. Solvent was removed by heating the Teflon flask in warm water, with a constant flow of nitrogen through the flask. A ^{19}F NMR spectrum of the remaining solid showed it to be unaltered sulfurane **1** (0.64 g, 75%).

Attempted Reaction of BrF_3 with Cyclic Bis[tetrakis(trifluoromethyl)ethylene] Orthosulfite (9). Tetraoxysulfurane **9** (2.4 g, 3.4 mmol) was allowed to react with BrF_3 (0.46 g, 3.4 mmol) using the standard procedure of method B for trans **2**. Solvent was removed by heating the Teflon flask in warm water, with a constant flow of nitrogen through the flask. Unaltered starting material (1.92, 81%) was identified by its ^{19}F NMR and mass spectra.

Reaction of BrF_3 with 3,3,3′,3′-Tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxathiole] (10). Tetramethylsulfurane **10** (0.97 g, 3.2 mmol) was allowed to react with BrF_3 (0.45 g, 3.2 mmol) using the standard procedure discussed in method B for **2**. This method was modified by using 10% $CH_2Cl_2/CFCl_3$ as the solvent instead of Freon 113, to increase the solubility of **10**. The reaction flask was cooled to −80 °C instead of −20 °C. After solvent removal a red oil remained. The ^{19}F NMR spectrum of a solution of this red oil showed no detectable absorption: ^1H NMR (0.5 mL of $CDCl_3$ and 20 μL of Me_2SO-d_6) δ 1.0–2.0 (≥4 singlets, CH_3 groups of **11**), 4.0–6.0 (br, vinyl protons of **11**), 6.7–8.0 (br, Ar-H); mass spectrum (10 eV), *m*/*e* (relative intensity) 537 (3.2, **11a**), 535 (7.4, **11a**), 533 (6.0, **11a**), 531 (3.6, **11a**), 457 (13.1, **11b**), 455 (20.0, **11b**), 453 (9.2, **11b**), 377 (97.6, **11c**), 375 (100, **11c**), 297 (99.3, **11d**).

3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*-2,1-benzoxathiole] 1-Oxide (15). (A) To 25 mL of $CHCl_3$ was added 0.51 g of *trans*-persulfurane **2**. The small amount of acid normally present in $CHCl_3$ was sufficient to cause hydrolysis of **2** to give sulfurane oxide **15** after 3 days exposure to air, and **15** was isolated as a white solid: mp 180–182 °C; ^1H NMR (CD_2Cl_2) δ 7.89 (s, 6, Ar-H), 8.72–8.76 (m, 2, Ar-H ortho to sulfur); ^{19}F NMR (CH_2Cl_2) δ −73.9 (q, 6, CF_3), −74.8 (q, 6, CF_3); mass spectrum (70 eV), *m*/*e* (relative intensity) 513 (10.1, $M^{+\cdot} - F$), 463 (100, $M^{+\cdot} - CF_3$). Anal. ($C_{18}H_8F_{12}O_3S$) C, H, S, F.

(B) To 25 mL of CH_2Cl_2 was added 20 μL of CF_3SO_3H, 10 μL of H_2O, and 0.3 g of cis isomer **3**. The solution was heated at reflux on a steam bath overnight. Solvent removal and recrystallization from CH_2Cl_2 gave 0.25 g (0.5 mmol, 95%) of a white solid. Elemental analysis and a ^{19}F NMR spectrum of the product showed it to be sulfurane oxide **15**.

Persulfonium Hexafluorophosphate (16). Into a Teflon-lined NMR tube containing 15 mg (0.3 mmol) of *trans*-difluoropersulfane **2** were condensed 0.5 mL of SO_2FCl and excess PF_5 on a vacuum line at −196 °C, and it was sealed: ^{19}F NMR (SO_2FCl) δ 89.5 (br, 1, S–F), −69 (br, PF_5–$^-PF_6$), −70.9 (br, 6, CF_3), −72.0 (br, 6, CF_3).

(B) An excess of PF_5 was condensed into a 2-mL Teflon flask containing 0.18 g (0.3 mmol) of trans **2** on a vacuum line at −196 °C. The flask was allowed to warm to −80 °C, and when the pressure slightly exceeded atmospheric pressure, the excess PF_5 was bled into a cold trap. Since the persulfonium hexafluorophosphate rapidly loses PF_5, the sample was immediately analyzed: mp 175–176 °C. Anal. ($C_{18}H_8SO_2F_{19}P$) C, H, P.

Attempted Reaction of *trans*-Difluoropersulfurane with CH_3NH_2, NH_3, $PhSO_2NH_2$, $(CH_3)_3CNH_2$, and $HN[Si(CH_3)_3]_2$. In a typical attempted reaction, 10-15 mg of *trans*-**2** was placed in a Teflon-lined NMR tube. If the nucleophile was gaseous (CH_3NH_2, NH_3), **2** was dissolved in CH_2Cl_2 and the reagent was bubbled through the NMR tube for several minutes. In the case of benzenesulfonamide, an excess of nucleophile was added and the tube was boiled for several hours. In the case of $HN[Si(CH_3)_3]_2$, the nucleophile was used as a solvent and a solution of **2** in $HN[Si(CH_3)_3]_2$ was boiled at 125 °C for several hours. The ^{19}F NMR spectrum of these solutions showed **2** to be unchanged.

Attempted Isomerization of *cis*-Difluoropersulfurane 3 to 2. A Telfon-lined NMR tube with 80 mg (0.14 mmol) of *cis*-**3**, 0.5 mL of CH_2Cl_2, and less than 0.01 g (0.05 mmol) of SbF_5 shows by ^{19}F NMR only the presence of *cis*-**3** and the persulfonium hexafluoroantimonate. The small amount of the trans isomer thought to be in equilibrium with **3** was not detected in this experiment.

Isomerization of *trans*-Difluoropersulfurane 2 to *cis*-Difluoropersulfurane 3. Persulfurane **2** (7 mg, 0.01 mmol) was treated with 0.1 mg (6×10^{-7} mol) of SbF_5 in a Teflon-lined NMR tube containing 0.4 mL of CD_2Cl_2. The relative area of the peaks for fluorine attached to hexacoordinate sulfur of (c,c,t) isomer **3** showed it to be 94 ± 1% of the equilibrium mixture. The remainder of the fluorine absorption (6 ± 1%) was for the trans isomer (**2**), which gives a $\Delta G_{25 °C}$ value of 1.6 ± 0.1 kcal/mol for the equilibrium between **2** and **3**.

Reaction of Persulfonium Hexafluorophosphate 16 with *tert*-Butylamine. To a 2-mL Teflon flask containing 212 mg (0.31 mmol) of freshly prepared **16** was added an excess of *tert*-butylamine. Mass spectrometry and ^{19}F NMR spectroscopy showed the product to be trans-isomer **2**.

Attempted Isomerization of *trans*-Difluoropersulfurane 2 in Quinoline. To an NMR tube was added 1 mL of quinoline and 20 mg of trans **2**. A small pellet of KOH was added to the tube as an acid scavenger. After boiling the solution at 238 °C for 254 h, we detected no isomerization (less than 0.4%). This sets the lower limit for the activation barrier, ΔG^*, for isomerization of **2** to **3** at 50 kcal/mol.

Calorimetry. The calorimeter used was an adaptation of a design by Arnett[18] and Beak,[19] which was built by Dr. Michael R. Ross. It will be described in a future publication.[20] The calibration was checked by

---

[18] Arnett, E. M.; Bentrude, W. G.; Burke, J. J.; Duggleby, P. M. *J. Am. Chem. Soc.* **1965**, *87*, 1541.

[19] Beak, P.; Bonham, J.; Lee, J. T., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 1569.

measuring the heat of solution of 100-mg samples of KCl in water. From six independent determinations the average value was 4.12 ± 0.1 kcal/mol (literature, 4.14 kcal/mol[21]). Heats of solution for the trans and cis isomers were measured by dissolving 150-mg samples of each isomer in 100 mL of toluene containing a pellet of KOH to prevent acidic hydrolysis. The heats of solution for the cis and trans isomers were 4.27 ± 0.2 and 4.90 ± 0.1 kcal/mol, respectively. The heats of hydrolysis for the isomers were measured by dissolving 150-mg samples of each isomer in 100 mL of 30% CF_3CO_2H/toluene to which 1% water had been added. The values for the heats of hydrolysis for the cis and trans isomers were −5.55 ± 0.1 and −8.18 ± 0.3 kcal/mol, respectively. Uncertainties are standard deviations.

Crystal Growth. Crystallization was induced for **2** and **3** by the slow evaporation of saturated solutions of **2** or **3** in CH_2Cl_2 to which a pellet of KOH had been added to prevent acid-catalyzed hydrolysis.

Crystal Data of 2: $C_{18}H_8F_{14}SO_2$, mol wt 554.3; triclinic; $a = 7.442$ (1) Å, $b = 10.764$ (2) Å, $c = 14.022$ (2) Å, $\alpha = 106.00$ (1)°, $\beta = 103.27$ (1)°, $\gamma = 105.00$ (1)°, $V = 986.7$ Å^3, $Z = 2$, $\rho_{calcd} = 1.87$ g cm^{-3}, μ (Mo Kα) = 3.3 cm^{-1}, $F(000) = 548$, no systematic absences; however, the structure determination showed the correct space group to be $P\bar{1}$. The cell dimensions were obtained by a least-squares fit to the automatically centered settings for 15 reflections on a Syntex P2$_1$ diffractometer equipped with a graphite monochromator (λ(Mo Kα) = 0.71069 Å).

Solution and Refinement of the Structure of 2. A crystal with dimensions ca. 0.85 × 0.60 × 0.30 mm was used for data collection in the θ–2θ scan mode. The variable scan option was used (2.0–15.0°/mm) with the total background time/scan time set at 0.5. Three standards from different parts of the reciprocal space were monitored every 57 reflections. Examination of these reflections showed no evidence for crystal deterioration. The $\pm h,-k,\pm l$ octants were collected out to $2\theta = 60°$. Out of the possible 5793 unique reflections collected, 4041 were considered observed at the $3\sigma(I)$ criterion level. The data were corrected for Lorentz and polarization effects but not for absorption.

The parity group distribution showed that $(k + l = \text{odd})/(k + l = \text{even}) \simeq {}^1/_3$, implying a pseudo A centering. The solution was found by assuming that there were two half-molecules at the inversion centers 0,0,0 and 0, $^1/_2$, $^1/_2$. A study of the origin removed, sharpened Patterson map yielded three or four S vectors about each origin consistent with the model assumed. The rest of the structure including the hydrogen atoms were revealed in subsequent difference Fourier maps.

Refinements on the positional and anisotropic thermal parameters of the nonhydrogen atoms and positional and isotropic thermal parameters of the hydrogen atom proceeded smoothly except for the position of H7, which persisted in moving to a distance of ~1.3 Å from C7 and becoming negative in B_{iso}. There was no evidence based on NMR data for any disorder as that site by an oxygen. The position of H7 was then fixed as those given by the difference map. Final full-matrix least squares refinements converged to agreement factors $R_1 = 0.047$, $R_2 = 0.056$, and $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m is the number of observations and n is the number of variables, was 2.94. The final difference map showed no peak greater than 35% of a hydrogen atom. The top six peaks were within 1 Å of the sulfur atoms. The positional parameters are shown in Table I; the thermal parameters, observed and calculated structure factors, and a complete list of bond lengths and angles are available in supplementary material.

Crystal Data of 3. $C_{18}H_8F_{14}SO_2$; monoclinic; $a = 18.800$ (5) Å, $b = 7.641$ (2) Å, $c = 16.599$ (4) Å, $\beta = 124.29$ (2)°, $V = 1970$ Å^3; $F(000) = 1096$ e; μ(Mo Kα) = 2.98 cm^{-1}. Systematic absences for hkl, $h + k = 2n + 1$, and for $h0l$, $l = 2n + 1$ established the space group as Cc or $C2/c$; successful refinement in the centrosymmetric space group confirmed $C2/c$ as the correct choice. The calculated density for $Z = 4$ was 1.869 g cm^{-3} which was in good agreement with the experimental density of 1.85 g cm^{-3} measured by flotation in a mixture of methylene chloride/methylene bromide; this imposes 2-fold symmetry on the molecule. A Syntex P2$_1$ diffractometer equipped with a graphite monochromator, λ(Mo Kα_1) = 0.70926 Å, was used to obtain the data set and cell parameters for a transparent crystal of dimensions 0.35 × 0.43 × 0.45 mm. The quadrant $\pm hkl$ for $h + k = 2n$ was collected in the 2θ–θ scan mode for $3 \leq 2\theta \leq 55°$ with a variable scan rate between 2 and 58.6°/min. Each peak was scanned from 1.0° = 2θ below the calculated Kα_1 peak position to 1.1° above the calculated Kα_2 and the background to scan time ratio was 0.5. Out of a total of 2272 unique reflections, 1265 were considered observed at the $3\sigma(I)$ criterion level. The data was corrected for Lorentz and polarization effects and empirically for absorption and extinction; the isotropic extinction coefficient refined to a value of 5.8 × 10^{-8}.[22]

Table I. Final Coordinates of Trans-Isomer **2**[a]

	positional parameters[b]		
atom	x	y	z
S	0.0000 (0)	0.5000 (0)	0.5000 (0)
S′	0.0000 (0)	0.0000 (0)	0.0000 (0)
F1	0.2128 (2)	0.4792 (1)	0.5028 (1)
O1	0.0026 (2)	0.5586 (2)	0.3998 (1)
C2	0.0898 (4)	0.7004 (3)	0.4261 (2)
C3	0.1666 (3)	0.7672 (3)	0.5445 (2)
C4	0.1284 (3)	0.6743 (2)	0.5940 (2)
C5	0.1848 (4)	0.7155 (3)	0.7027 (2)
C6	0.2837 (4)	0.8552 (3)	0.7598 (2)
C7	0.3231 (4)	0.9484 (3)	0.7109 (2)
C8	0.2638 (4)	0.9056 (3)	0.6020 (2)
C9	0.2578 (5)	0.7201 (3)	0.3780 (2)
C10	−0.0707 (5)	0.7511 (3)	0.3756 (2)
F2	0.3914 (3)	0.6728 (2)	0.4194 (2)
F3	0.3490 (4)	0.8506 (2)	0.3954 (2)
F4	0.1947 (3)	0.6540 (2)	0.2763 (1)
F5	−0.1587 (3)	0.6790 (2)	0.2756 (1)
F6	0.0034 (4)	0.8819 (2)	0.3854 (2)
F7	−0.2052 (3)	0.7446 (2)	0.4218 (2)
F1′	0.1852 (2)	−0.0535 (1)	−0.0105 (1)
O1′	0.0944 (2)	0.1310 (2)	−0.0384 (1)
C2′	0.2214 (3)	0.2558 (2)	0.0403 (2)
C3′	0.2435 (3)	0.2372 (2)	0.1447 (2)
C4′	0.1383 (3)	0.1071 (2)	0.1360 (2)
C5′	0.1414 (4)	0.0694 (3)	0.2227 (2)
C6′	0.2517 (4)	0.1684 (3)	0.3205 (2)
C7′	0.3555 (4)	0.3004 (3)	0.3307 (2)
C8′	0.3543 (4)	0.3369 (3)	0.2437 (2)
C9′	0.4178 (4)	0.2872 (3)	0.0164 (2)
C10′	0.1274 (5)	0.3652 (3)	0.0310 (2)
F2′	0.4903 (2)	0.1875 (2)	0.0183 (1)
F3′	0.5532 (3)	0.4030 (2)	0.0867 (2)
F4′	0.3962 (3)	0.2971 (2)	−0.0773 (1)
F5′	−0.0305 (3)	0.3449 (2)	0.0613 (2)
F6′	0.2493 (3)	0.4908 (2)	0.0908 (2)
F7′	0.0727 (3)	0.3633 (2)	−0.0660 (2)
H5	0.150 (3)	0.646 (2)	0.735 (2)
H6	0.321 (3)	0.886 (3)	0.831 (2)
H7	0.375 (0)	1.042 (0)	0.750 (0)
H8	0.275 (4)	0.965 (3)	0.561 (2)
H5′	0.074 (4)	−0.015 (3)	0.221 (2)
H6′	0.258 (4)	0.150 (3)	0.382 (2)
H7′	0.422 (4)	0.360 (3)	0.390 (2)
H8′	0.425 (4)	0.432 (3)	0.246 (2)

[a] Estimated standard deviations in parentheses. [b] Positional parameters are given as fractions of the unit cell edges.

Solution and Refinement of the Structure of 3. Direct methods in the noncentrosymmetric space group Cc gave the difluoropersulfurane without difficulty.[23] Subsequent refinement in the centrosymmetric space group $C2/c$ significantly improved the structural model. In the final cycle of least squares all nonhydrogen atoms were varied with anisotropic thermal coefficients, all hydrogen atoms were varied with isotropic thermal parameters; all variables were well behaved with reasonable estimated standard deviations, and the largest change/error was 0.05. The function minimized was $\sum w||F_o| - |F_c||^2$, where F_o and F_c are the observed and calculated structure factors, respectively. Refinements converged to conventional agreement factors of $R_1 = 0.037$ and $R_2 = 0.038$ ($R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^2$). The final difference Fourier was featureless with a range of peaks from +0.20 to −0.20 e Å^{-3}. No systematic errors were apparent in the data. The positional parameters are shown in Table II. The thermal parameters, observed and calculated structure factors, and a complete list of bond lengths and angles are available in supplemental material.

Semiempirical Molecular Orbital Calculations. The MINDO/3,[24] CNDO,[25] and extended Hückel[26] calculations were performed on a

---

(20) Ross, M. R.; Martin, J. C.; manuscript in preparation.

(21) "Handbook of Chemistry and Physics" 56th ed.; CRC Press: Cleveland, Ohio, 1975.

(22) (a) Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139. (b) Zachariasen, W. H. *Acta Crystallogr., Sect. A* **1968**, *A24*, 212.

(23) Sheldrick, G. M. "SHELX 76", a program for crystal structure determination; University of Cambridge: England, 1976.

(24) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

(25) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

Table II. Final Coordinates of Isomer 3[a]

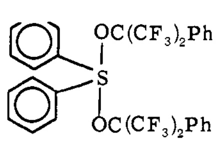
	positional parameters[b]		
atom	*x*	*y*	*z*
S	0.0000	0.2981 (1)	0.2500
F1	0.0490 (1)	0.7535 (2)	0.2130 (1)
F2	0.1813 (1)	0.7680 (3)	0.2657 (2)
F3	0.1431 (1)	0.7776 (2)	0.3656 (1)
F4	0.2814 (1)	0.4948 (3)	0.3559 (2)
F5	0.2486 (1)	0.4994 (3)	0.4597 (1)
F6	0.2294 (1)	0.2694 (3)	0.3784 (2)
F7	0.0696 (1)	0.1430 (2)	0.3106 (1)
O	0.0773 (1)	0.4515 (2)	0.3212 (1)
C2	0.1320 (2)	0.5025 (4)	0.2927 (2)
C3	0.0998 (2)	0.4161 (4)	0.1959 (2)
C4	0.1312 (2)	0.4372 (5)	0.1382 (3)
C5	0.0916 (3)	0.3470 (6)	0.0505 (3)
C6	0.0230 (3)	0.2396 (5)	0.0215 (3)
C7	−0.0092 (3)	0.2172 (4)	0.0773 (2)
C8	0.0306 (2)	0.3077 (4)	0.1648 (2)
C9	0.1264 (2)	0.7026 (4)	0.2843 (2)
C10	0.2240 (2)	0.4414 (5)	0.3729 (3)
H4	0.179 (2)	0.508 (4)	0.161 (2)
H5	0.113 (2)	0.357 (4)	0.008 (2)
H6	−0.007 (2)	0.179 (4)	−0.042 (2)
H7	−0.055 (2)	0.141 (4)	0.058 (2)

[a] Estimated standard deviations in parentheses. [b] Positional parameters are given as fractions of the unit cell edges.

VAX-11780 computer. The geometry for persulfurane **24** was determined from the bond lengths and angles obtained in the X-ray crystallographic study of **2**. Figure 5 was plotted from a program written for the VAX-11780 computer.

Results

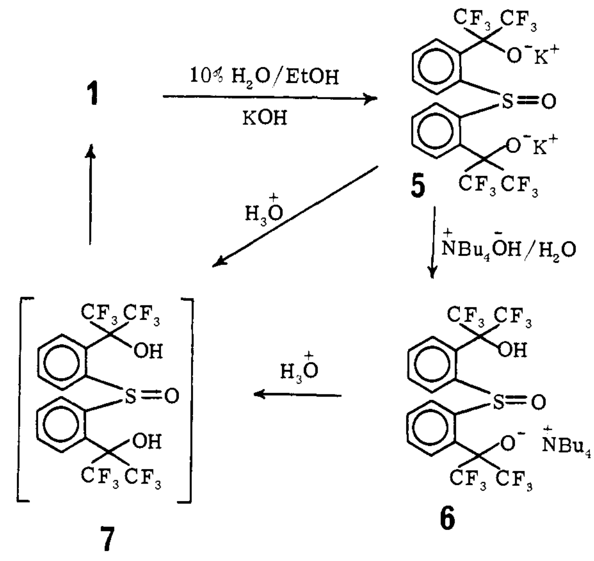
The synthesis of the extraordinarily stable sulfurane **1** has been reported.[15] Previous attempts to hydrolyze a close analogue of **1** were unsuccessful.[27] The hydrolysis of **4** is, in contrast, rapid even upon exposure to atmospheric moisture[28] in relatively dry air.



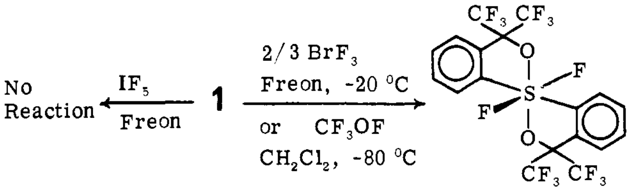
4

Upon extended treatment with a boiling solution of potassium hydroxide in aqueous ethanol, **1** undergoes hydrolysis to give dialkoxy sulfoxide **5**. The reaction can be followed by ^{19}F NMR, which shows a disappearance of the two quartets assigned to the nonequivalent CF$_3$ groups of **1** (at −73.5 and −76.7 ppm) with simultaneous appearance of the two broad absorptions assigned to the nonequivalent CF$_3$ groups of **5** (at −73.9 and −75.8 ppm). The hygroscopic character of **5** made it difficult to obtain satisfactory elemental analyses and the hydrolysis product of **1** was identified as its more tractable tetrabutylammonium salt derivative, **6**. The peak for the hydrogen of the hydroxyl group of **6** occurs at δ 7.45, and elemental analysis of **6** indicates the presence of no potassium. Upon addition of acid to solutions of **5** or **6**, the intermediate diol sulfoxide is not seen. Cyclization to **1** is so rapid that only the quartets for the CF$_3$ groups of **1** appear in the ^{19}F NMR spectra as soon as the spectrum can be obtained after addition of acid. Addition of less than an equivalent amount of acid resulted in rapid formation of a stoichiometric amount of **1**. The failure to observe the intermediate, **7**, is in agreement with the results of an effort to synthesize **7** by oxidation of the sulfide,[29] which gave only **1**. This was also interpreted in terms of a rapid cyclization of **7** to give **1**.

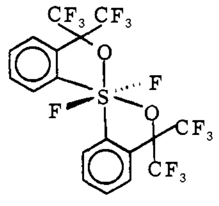
Scheme I



The fluorination of **1** using 0.667 mol of bromine trifluoride/mol of **1** proceeds smoothly at −20 °C to give the difluoropersulfurane isomer which has a trans arrangement about the central sulfur atom for the two carbon, the two fluorine, and the oxygen atoms. This all-trans isomer is given the designation (t,t,t). This geometry was initially postulated on the basis of its ^{19}F NMR spectrum, which shows a triplet at δ −73.7 ($^5J_{F-F}$ = 7 Hz) for all of the CF$_3$ groups of **2** and a multiplet for the fluorines on sulfur at δ 104 ($^5J_{F'-F}$ = 7 Hz). Only seven of the thirteen lines theoretically expected to results from virtual coupling of the S–F fluorines to the twelve CF$_3$ fluorines were visible in the spectrum of **2**. In view of the low solubility of **2** in organic solvents and the fact that the six outermost lines of a triskaidekacet would be less than 4% of the intensity of the center line, it is not surprising they were not seen. The only other static structure compatible with the NMR evidence is **8**, which was ruled out by the results of an X-ray crystallographic structure determination reported here. Using an order of priority for the substituents about the sulfur atom based on atomic number, we may designate **8** as the trans-F,cis-O,cis-C or the (t,c,c) isomer. Another fluorinating agent, trifluoromethyl hypofluorite also gave **2** upon reaction with sulfurane **1**, but the milder fluorinating agent iodine pentafluoride was unreactive toward **1** even upon heating a solution of iodine pentafluoride and **1** in Freon 113 at 45 °C for several minutes.



2 (t,t,t)



8 (t,c,c)

---

(26) Pensak, D. A.; McKinney, R. J. *Inorg. Chem.* **1979**, *18*, 3407.

(27) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 578.

(28) Martin, J. C.; Arhart, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 2341.

(29) Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1974**, *96*, 3155.

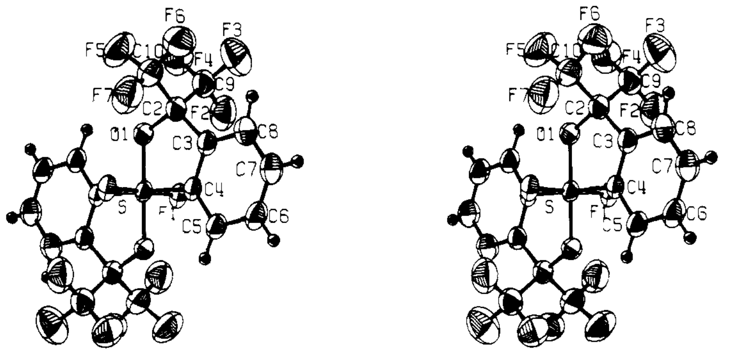
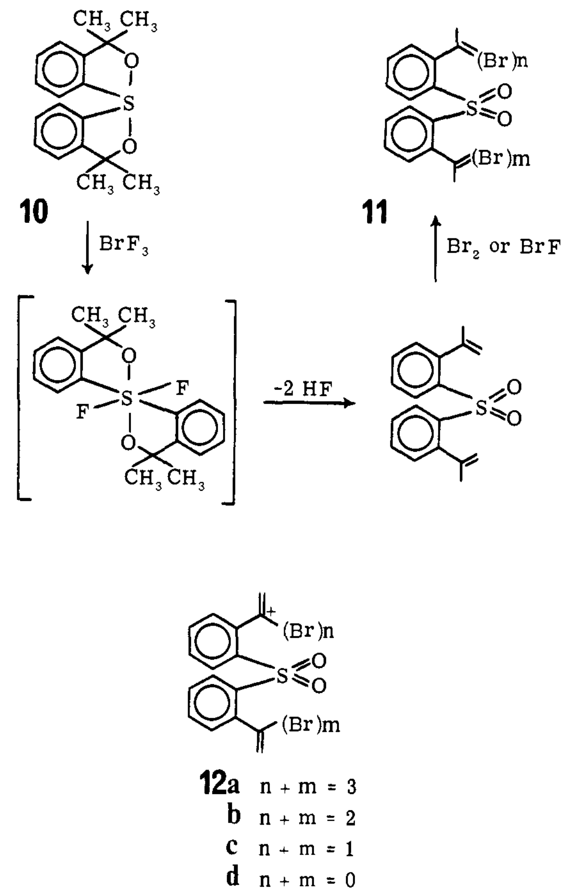
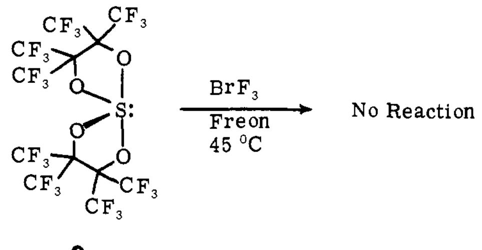


Figure 1. Stereoscopic view of the single molecule of isomer **2**.

Scheme II



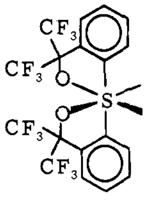
Attempts to prepare certain other difluoropersulfuranes were unsuccessful. Sulfurane 9[30] was inert to fluorination by bromine trifluoride even upon heating a Freon solution of **9** and bromine trifluoride at 45 °C for several minutes. This is a reflection of the decreased electron density on sulfur as substituents about the sulfur atom become more electronegative.



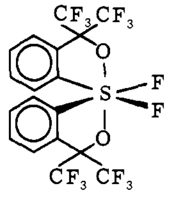
9

The tetramethyl analogue of **1**, sulfurane **10**, gave brominated sulfones upon reaction with bromine trifluoride. This could occur by formation of the difluoropersulfurane, followed by cleavage of the S–F and C–O bonds and substitution by bromine or bromine fluoride to form olefinic sulfones of general structure **11**. The mass spectrum of the product of the reaction of bromine trifluoride with **10** shows molecular ion peaks for **12a**, **12b**, and **12c**. All of these ions could result from parent compounds which lose a bromine atom upon electron impact.

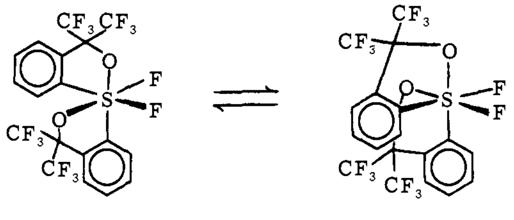
When more than 0.67 mol of bromine trifluoride/mol of sulfurane **1** is used to prepare the difluoropersulfurane, the product of the reaction is an isomer of **2** which has an identical elemental analysis and shows a molecular ion in its mass spectrum at *m/e* 554, as well as absorptions for $M^{3}\cdot$ – F at *m/e* 535 and for $m^{3}+\cdot$ – CF_3 at 485; however, the product has a melting point 20 °C higher than **2** (at 160–162 °C). The ^{19}F NMR spectra of the product shows an unresolved multiplet at δ 76.8 (2, S–F) and two unresolved multiplets for the nonequivalent CF_3 groups at δ –73.2 and –73.7. Structures which are compatible with this NMR data are isomer **3** (c,c,t) and **13** (c,t,c) and structures **14** (c,c,c), which would have to be rapidly interconverting on the NMR time scale to give the two observed CF_3 multiplets.



3 (c,c,t)



13 (c,t,c)



14 (c,c,c)

The structures of **2** and **3** were confirmed by X-ray crystallographic structure determinations. Figures 1 and 2 show the stereoviews of a single molecule and the packing in the unit cell of **2**. Figures 3 and 4 show comparable views for **3**. Selected bond lengths and bond angles are given in Table III. Complete listings of structure factor amplitudes, bond lengths and angles, thermal parameters, and atomic coordinates are available in supplementary material. The geometry about the central sulfur atom in **2** is essentially octahedral, and all of the bond angles between cis bonds to sulfur are 90° ± 1°. Each five-membered ring and the phenyl rings fused to it are essentially planar in **2**—the largest deviation from the best planes is 0.007 (3) Å. The geometry about the sulfur atom of **3** is a slightly distorted octahedron. The largest deviation

---

(30) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 2895.
(31) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 186.

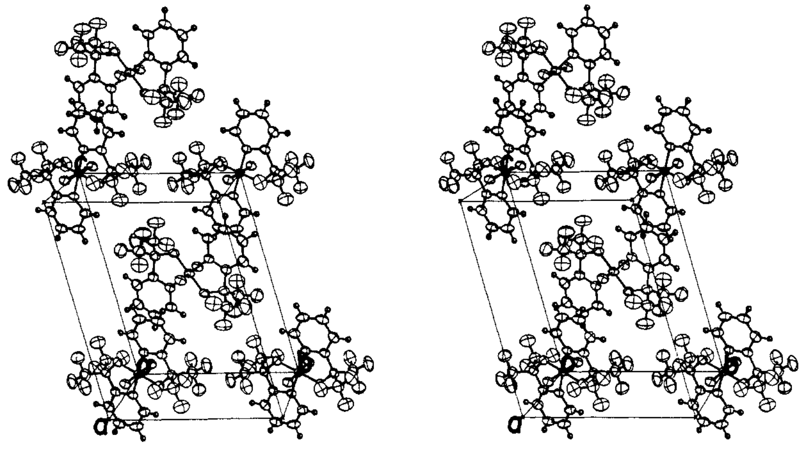


Figure 2. Stereoscopic view of the crystal structure of **2**.

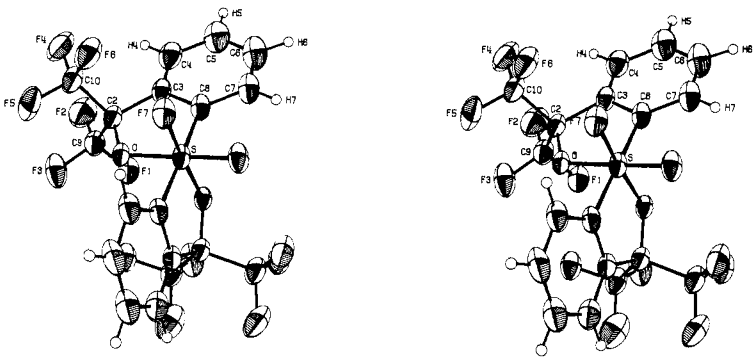


Figure 3. Stereoscopic view of the single molecule of isomer **3**.

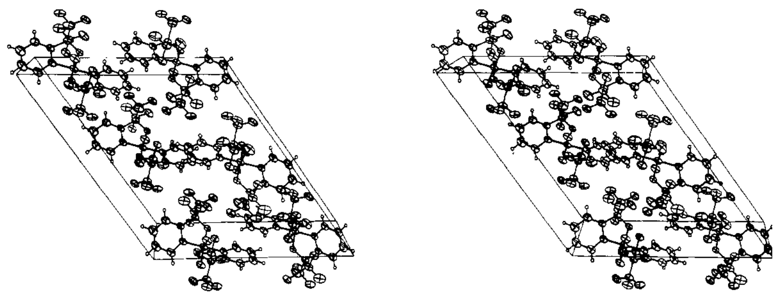


Figure 4. Stereoscopic view of the crystal structure of **3**.

Table III. Selected Bond Lengths and Angles for Persulfuranes 2 and 3[a]

	2	3
	Bond Length (Å)	
S–F	1.6492 (14), 1.6463 (14)	1.627 (2)
S–O	1.693 (2), 1.688 (2)	1.717 (2)
S–C	1.817 (2), 1.816 (2)	1.804 (3)
	Bond Angle (Deg)	
O–S–F	90.14 (8), 89.90 (7)	89.84 (9),[c] 175.74 (9)[d]
C–S–F	89.92 (9), 90.07 (9)	90.7 (1)
C–S–O	90.31 (10), 90.28 (9)	89.5 (1)
O–S–O	180.00 (8), 180.00 (8)	93.91 (9)
F–S–F	180.00 (7), 180.00 (7)	86.48 (9)
C–S–C	180.0 (1), 180.0 (1)	175.3 (1)
S–O–C_{sp^3}–C_{sp^2}	1.10, 1.04	5.81
S–C_{sp^2}–C_{sp^2}–C_{sp^3}	0.79, −1.58	−1.00
O–C_{sp^3}–C_{sp^2}–C_{sp^2}	−1.18, 0.44	−2.83

[a] Estimated standard deviation in parentheses. [b] Listed here are values for primed and unprimed molecules in the unit cell of 2. [c] The value of the cis O–S–F angle. [d] The value of the trans O–S–F angle.

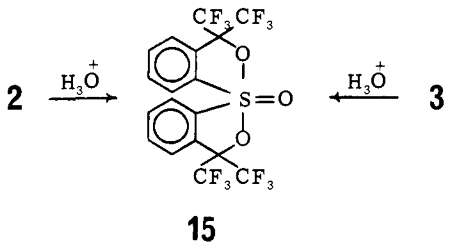
from octahedral geometry is in the O–S–O and F–S–F angles, which are 93.91 and 86.48°, respectively. The five-membered rings of **3**, unlike those of the more symmetrical **2**, are not planar. The oxygen atom is the largest contributor to the deviation from planarity. Similar nonplanar five-membered rings have been observed in 10-S-4 species.[16] There are no intermolecular contacts within the van der Waals radii of the atoms in the crystal structures of **2** and **3**.

The difluoropersulfurane is indefinitely stable under basic conditions. It does not react with hydroxide, nor with any of several amines. These reactions are monitored by ^{19}F NMR, with no change seen in the spectra of solutions of **2** upon additon of the various amines.

$$\mathbf{2} \xrightarrow[\text{RNH}_2]{^-\text{OH}} \text{No Reaction}$$

R = H, Me, $PhSO_2$, t-butyl

Acid-catalyzed hydrolyses of **2** and **3** proceed rapidly to give a common product, sulfurane oxide **15**. Calorimetry was used to measure the difference in the heats of hydrolysis of the isomers to give **15**. The enthalpy difference between the cis and trans



15

isomers, ΔH, is determined as the difference in the heats of hydrolysis of the isomers to give **15**. The heat of solution of the solid isomers was measured in toluene, giving values for the cis and trans isomers of 4.90 ± 0.1 and 4.27 ± 0.2 kcal/mol, respectively. The heats of hydrolysis of crystalline cis and trans isomers, measured in 30% CF_3CO_2H/toluene, containing 1% water, are −5.55 ± 0.1 and −8.18 ± 0.3 kcal/mol, respectively. When eq 2 is subtracted from eq 1, the value of ΔH is

$$3 + H_2O \rightarrow 15 + 2HF + (\Delta H^{cis}_{hydrolysis} - \Delta H^{cis}_{soln}) \quad (1)$$

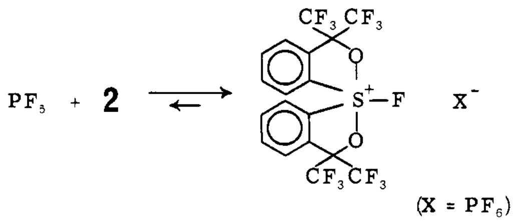
$$2 + H_2O \rightarrow 15 + 2HF + (\Delta H^{trans}_{hydrolysis} - \Delta H^{trans}_{soln}) \quad (2)$$

$3 - 2 = 2.00 \pm 0.5$ kcal/mol[a]

[a] Standard deviation.

When a catalytic amount of antimony pentafluoride is added to a solution of **2** in CH_2Cl_2, isomerization is rapid to give the thermodynamically more stable cis persulfurane **3**, as determined by ^{19}F NMR. The cis isomer constitutes 94 ± 1% of the equilibrium mixture. This was determined by measuring the relative areas of the peaks for the fluorines attached to sulfur of **2** and **3**. The relative thermodynamic stability of the cis isomer, calculated from the Gibbs free energy equation, $\Delta G = -RT \ln K_{eq}$, is 1.6 ± 0.1 kcal/mol at 25 °C. The larger uncertainty in our measured value for ΔH does not allow for a reliable estimate of the entropy of the system. Peaks for the persulfonium hexafluoroantimonate can be seen in the ^{19}F NMR spectra in solutions of both difluoropersulfuranes in the presence of small amounts of antimony pentafluoride. Two quartets for the CF_3 groups of the persulfonium hexafluoroantimonate occur at δ −70.9 and −72.0.

Persulfonium hexafluorophosphate **16** ($X = PF_6$) was formed by allowing the difluoropersulfurane to react with an excess of phosphorus pentafluoride at −80 °C. The product isolated from the reaction rapidly loses phosphorus (as gaseous PF_5), and when *tert*-butylamine is allowed to react with **16** ($X = PF_6$), regeneration of the *trans*-difluoropersulfurane is seen by ^{19}F NMR. Nucleophilic attack occurs at phosphorus of the PF_5 rather than at the persulfonium sulfur. The ^{19}F NMR spectrum of **16** ($X = PF_6$, SbF_6) shows two unresolved multiplets for the nonequivalent CF_3 groups at −70.9 and −72.0 ppm. The single fluorine attached to sulfur appears at 89.5 ppm. The identical ^{19}F chemical shifts for the cation in hexafluorophosphate and hexafluoroantimonate salts provide evidence against the formulation of **16** as the complex of **2** with PF_5.

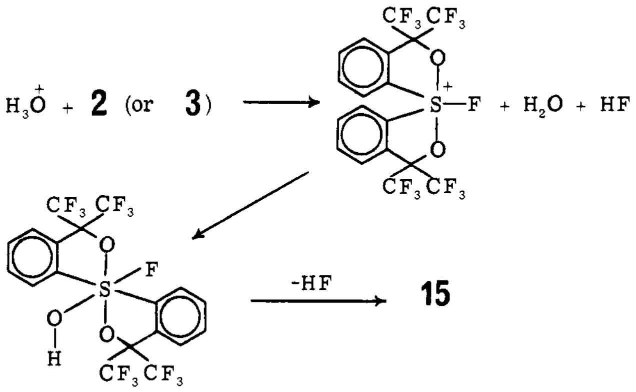


16

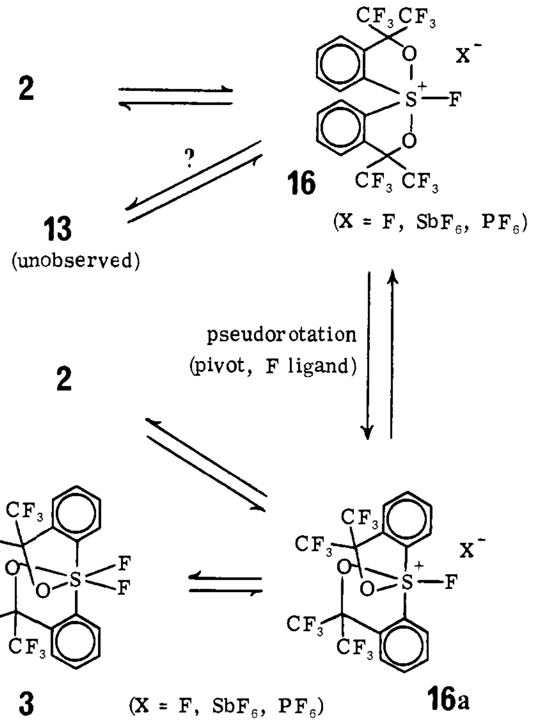
Heating a solution of *trans*-difluoropersulfurane **2** at 238 °C for 254 h in quinoline did not cause any detectable isomerization to give **3**. The lower limit of the activation barrier ($\Delta G^*_{238\,°C}$) for isomerization is 50 kcal/mol under these nonacidic conditions. Disappearance of **2** to form any other products was not detected under these conditions.

Discussion

Dissociative Reactions Involving 2 and 3. The rapid hydrolysis of **2** and **3** under acidic conditions to give **15**, together with their unreactivity toward water in the absence of acid, suggested to us that the acid-catalyzed hydrolysis proceeds by a dissociative mechanism via a persulfonium ion intermediate. This persulfonium ion was subsequently isolated as its hexafluorophosphate salt, **16** ($X = PF_6$).[1] Since Lewis acids convert the difluoropersulfurane to the persulfonium salt, we may safely assume that the rapid, acid-catalyzed isomerization of **2** to give **3** occurs by a dissociative mechanism. The isolation of cis isomer **3**, rather than trans isomer **2**, in the fluorination of sulfurane **1** with excess fluorinating agent can be attributed to equilibration catalyzed by Lewis acid bromine trifluoride or perhaps by traces of hydrogen fluoride generated from a small amount of substitutive fluorination. Formation of the thermodynamically favored cis isomer by attack of fluoride on the persulfonium ion is not a simple process. A possible route begins with pseudorotation of the persulfonium ion to give a high energy TBP conformer, **16a**, with equatorial oxygen and apical carbon substituents, followed or accompanied by attack of fluoride ion (or a fluoride ion equivalent such as hexafluoroantimonate ion) in the equatorial plane to provide either **2** or **3**. Fluoride attack in the equatorial plane of **16** provides either **2** or the unobserved cis isomer **13**.



The persulfonium hexafluorophosphate is in mobile equilibrium with small amounts of persulfuranes **2** and **3**. Samples of the salt therefore lose volatile phosphorus pentafluoride under vacuum. When *tert*-butylamine is allowed to react with **16** ($X = PF_6$) persulfurane **2** is the only observed product. This is explained by postulating that rapid reaction between phosphorus pentafluoride and the amine removes phosphorus pentafluoride from the equilibrating mixture to leave the kinetically favored per-

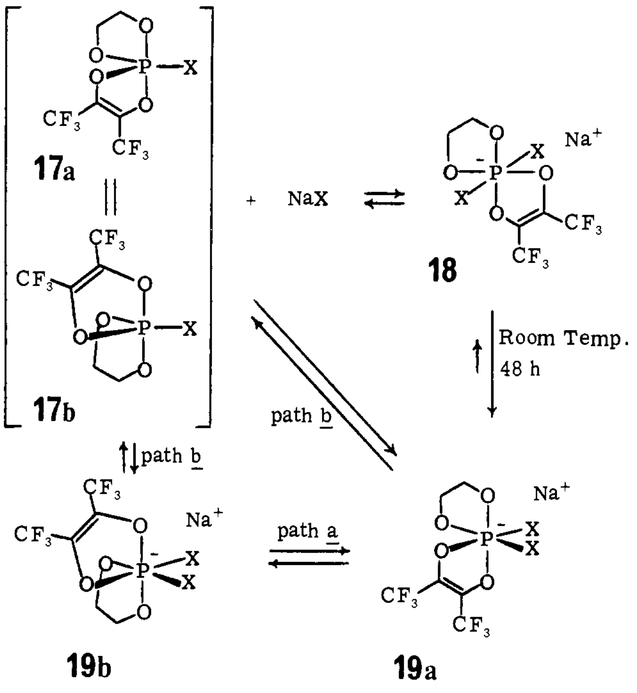


sulfurane **2**. The persulfonium hexafluoroantimonate, **16** (X = SbF$_6$) derived from the reaction of either of the difluoropersulfuranes with the stronger Lewis acid antimony pentafluoride,[31] undergoes nucleophilic attack at the sulfur atom. These reactions will be discussed in a future paper.[32] Frontier orbital considerations suggest that kinetically favored attack to give trans **2** occurs from a direction determined by the shape of the LUMO. If the LUMO is adequately approximated as the σ^* orbital of the S–F bond of the persulfonium cation, this explains the kinetically favored approach of fluoride along a path leading to **2**[33] from **16**.

Nondissociative Isomerization. Geometrical isomers of hexacoordinate metal complexes incorporating a variety of metals have been extensively studied. Hexacoordinate metal complexes follow two main pathways for their permutational isomerization processes.[34] One is dissociative, proceeding through a trigonal-bipyramidal (TBP) or square-pyramidal intermediate; the other is intramolecular, involving no bond rupture. Nondissociative mechanisms are collectively known as twist mechanisms. Two types have been proposed—the Bailar twist[35] (a process maintaining local C_3 symmetry) and the Ray and Dutt twist[36] (local C_2 symmetry). Twist mechanisms have been established for a variety of metal complexes. Ground-state structures with trigonal-prismatic geometry (the transition state of a Bailar twist) have been identified.[37]

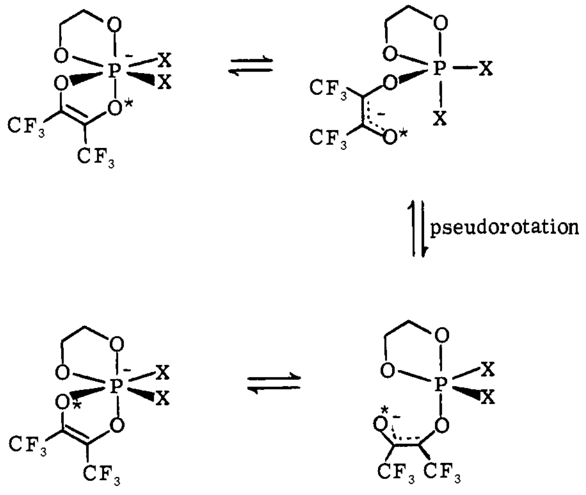
The difluoropersulfuranes are very unreactive toward nucleophiles in basic media. The sulfur atom is expected to have a greater concentration of positive charge in a 12-S-6 system than in a 10-S-4 system,[38] and some 10-S-4 species have been shown[39] to undergo associative nucleophilic attack. The sterically congested environment about the sulfur atom of **2**, however, prevents associative nucleophilic attack, just as it does in the very unreactive SF$_6$.[38] This unreactivity was exploited to determine a lower limit for the activation barrier of a twist mechanism for the permutational isomerization of trans isomer **2** to the thermodynamically favored cis isomer, **3**. Our failure to observe isomerization upon boiling a solution of **2** in quinoline at 238 °C for 254 h showed that the free energy of activation for any nondissociative route for permutational isomerism of **2** to **3** is greater than 50 kcal/mol at 238 °C. The relative stereochemical rigidity of another 12-S-6 system, C$_6$H$_5$SF$_5$, was established on the NMR time scale by observing an unaltered AB$_4$ pattern for the fluorine atoms up to 215 °C.[40] The difference in time scale for this NMR experiment, however, prevents one from setting a lower limit for the barrier nearly so large as the 50 kcal/mol established in the present work.

A related transformation of the all-trans 12-P-6 species **18** to the more stable cis isomer, **19**, has recently been described.[12] Coalescence at elevated temperatures of ^{19}F NMR peaks for **19** was attributed to a nondissociative interconversion of **19a** and **19b** (path a). The free energies of activation for the exchange of the CF$_3$ groups and the para-fluorophenoxy groups were reported to be 17.2 and 16.5 kcal/mol, respectively. Since separate signals were observed for the CF$_3$ groups of phosphorane **17** and anion **19** at temperatures above the coalescence temperature, an isomerization mode for the interconversion of **19a** and **19b** involving dissociative to give **17** was considered to play an insignificant role.



X = OC$_6$H$_4$F

An alternative intramolecular mechanism, pictured below, involving dissociation of another P-O bond followed by a pseudorotation, has not been ruled out. The high free energy of activation reported here for a twist mechanism in the isoelectronic 12-S-6 systems which we have studied makes such a dissociative mechanism seem more likely for the isomerization of **19** than the postulated twist mechanism but more work will be required before generalizations are justifiable.



Either this dissociative mechanism or the nondissociative mechanism favored in the earlier paper[12] could give different activation energies for the coalescence of ^{19}F NMR peaks resulting from the exchange of CF$_3$ or X groups.

Relative Stability of Persulfurane 2 and 3. Trans isomer **2** is the kinetically favored product from attack of fluoride on the persulfonium ion, and **3** is the thermodynamically favored product. It is tempting to discuss the thermodynamic stability of **3** relative to **2** as a gas-phase stability, even though the measurements were done by using toluene and methylene chloride solutions. The possibility that the thermodynamic preference for the cis isomer is attributable to preferential solvation of the cis isomer (trans isomer **2** has no dipole moment) must be considered. If the enthalpy of solvation of the dipolar isomer, **3**, in toluene is correctly

---

(32) Michalak, R. S.; Martin, J. C., manuscript in preparation.

(33) Semiempirical calculations at the MINDO/3 level indicate that in the LUMO the antibonding contribution of carbon orbitals adjacent to sulfur are directed toward the sulfur and are in phase with the back lobe of the S–Fσ^* orbital. This would further enhance that position as being favored for kinetic attack.

(34) For reviews of twist mechanisms involving metal species see: (a) Fortman, J. J.; Sievers, R. E. *Coord. Chem. Rev.* **1971**, *6*, 331. (b) Serpone, N.; Bickley, D. G. *Prog. Inorg. Chem.* **1972**, *17*, 391.

(35) Bailar, J. C., Jr. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165.

(36) Rây, P. Dutt, N. K. *J. Indian Chem. Soc.* **1943**, *20*, 81.

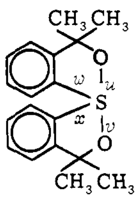
(37) Huheey, J. "Inorganic Chemistry: Principles of Structure and Reactivity"; Harper and Row: New York, 1972; p 386.

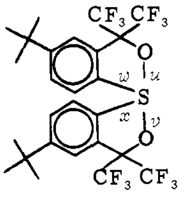
(38) We are unaware of any experimental studies of the effective positive charge on sulfur(VI) relative to sulfur (IV). The introduction of a second hypervalent bond with two additional electronegative substituents upon going from **1** to persulfuranes **6** and **12** suggests that the central sulfur atom has a greater effective positive charge in these molecules than the parent sulfurane. The central atom of a hypervalent bond is known to develope positive charge, with the apical ligands developing negative charge. See, e.g.: Musher, J. I.; Koutecky, V. B. *Theor. Chim. Acta* **1974**, *33*, 227.

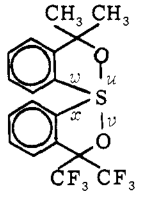
(39) Balthazor, T. M.; Martin, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 5634.

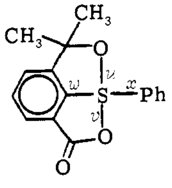
(40) Tebbe, F. N.; Meakin, P.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1970**, *92*, 1068.

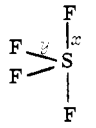
Table IV. Selected Bond Lengths in 10-S-4 and 12-S-6 Species

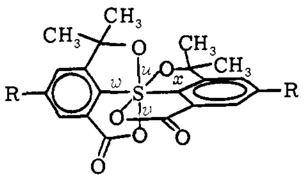

10

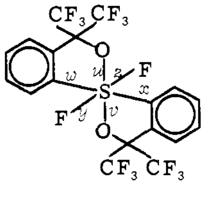

20

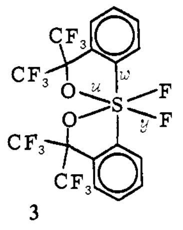

21

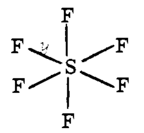

22




23

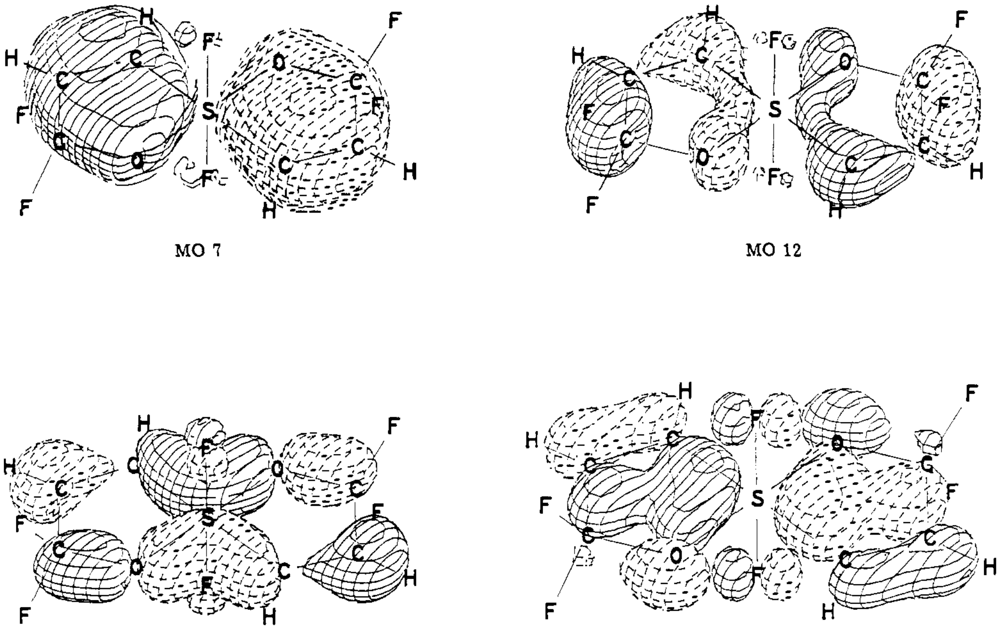

2


3



	10[a]	20[b]	21[c]	22[a]	23[a]	2[d]	3[d]	SF_4[e]	SF_6[f]
u	1.787 (2)	1.818 (5)	1.713 (2)	1.662 (2)	1.67 (1)	1.693 (2)	1.717 (2)	...	...
v	1.814 (2)	1.832 (5)	1.955 (2)	2.248 (2)	1.91 (1)	1.688 (2)	...	...	...
w	1.808 (3)	1.803 (8)	1.806 (3)	1.750 (2)	1.78 (2)	1.817 (2)	1.804 (3)	...	...
x	1.808 (3)	1.793 (8)	1.799 (3)	1.786 (2)	1.78 (2)	1.816 (2)	...	1.545	...
y						1.6463 (14)	1.626 (2)	1.648	1.58
z						1.6492 (14)	...	...	...

[a] Reference 10. [b] Reference 43. [c] Reference 10. [d] This work. [e] Kimura, K.; Bauer, S. H. *J. Chem. Phys.* 1963, *39*, 3172. [f] Gaunt, J. *Trans. Faraday Soc.* 1953, *49*, 1122.


MO 7

MO 12

MO 13

MO 16

Figure 5. Some calculated (MINDO/3) bonding molecular orbitals for **24**, showing π delocalization of fluorine lon pairs into skeletal orbitals.

correlated with empirical measures of solvent polarity such as the Kosower[41] *Z* values, one would expect little differential solvation of **3** relative to **2** since the *Z* value for benzene (54), a cose analogue of toluene, is identical with that of the gas phase (54).[41] It is therefore justifiable to speculate, at least in a limited manner, on possible molecular structure features which might be responsible for the greater stability of the more polar **3** relative to the less polar **2**.

The introduction of partial ionic character into a covalent bond between two atoms was suggested by Pauling[42] to lend stabilization to the bond in the form of resonance energy. For example, the unsymmetrical hydrogen halogenides all have greater bond energies than the average of the bond energies of hydrogen and molecular halogen.[42] Moreover, the magnitude of the difference increases as the electronegativity difference between the two atoms increases.[42]

If we consider the hypervalent bond joining three colinear atoms to be an extended analogue of a covalent bond between the two apical atoms, then unsymmetrical apical substitution of hypervalent bonds might also increase the resonance energy of that bond.

---

(41) Kosower, E. M. "An Introduction of Physical Organic Chemistry"; Wiley: New York, 1968; p 301.

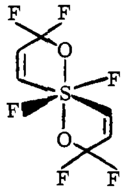
(42) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 3.

The X-ray structure determinations of sulfuranes **20**[43] and **21**[10] and persulfurane **22**[10] show that bond deformation of the hypervalent bond has occurred, in a manner consistent with large bond polarization. In a variety of sulfuranes and persulfuranes the longer of the two S–O bonds of unsymmetrically substituted O–S–O hypervalent bond systems joins the most electronegative alkoxy or acyloxy substituent to sulfur (**21**, **22**, and **23** in Table IV). Symmetrically substituted three-center bonds in **10**, **20**, and **2**, on the other hand, have nearly identical S–O bond distances. Further evidence in support of a marked polarizability of three-center bonds is found in stretching frequencies for the carbonyl groups of a series of sulfuranes. The increase in carbonyl stretching frequencies as substitution in the opposite apical position becomes more electronegative[44] is consistent with an increasing polarization of the hypervalent bond toward the more electronegative substituent. If a molecule which has two unsymmetrically substituted hypervalent bonds were more stable than the symmetrical isomer, we would expect cis isomer **3**, with two such unsymmetrical bonds, to be more stable than trans isomer **2**, as observed. On the other hand, **13** has a still more polarizable C–S–F bond, and **14** has three unsymmetrical hypervalent bonds. If polarization lends stabilization to the hypervalent bond why are **13** or **14** not formed? We have no evidence to indicate the presence of any other isomers, and the question remains unanswered as to whether these isomers are not seen because they are kinetically inaccessible or because they are still less stable than **2**.

S–F and S–O Bond Lengths in 2 and 3. The S–F and S–O bond lengths are very similar in **2** and **3**. A prediction of longer S–F and shorter S–O bond distances in cis isomer **3** relative to **2** might be risked on the assumption that fluorine is effectively more electronegative than the hexafluoroalkyoxy ligand. This prediction is not supported by the fact that the S–F bond is **3** is shorter and the S–O bond longer, relative to **2**, by a small amount (ca. 0.02 Å). The observed near identity of bond lengths in **2** and **3** might be taken as evidence that both these substituents are comparable in electronegativity. Fluorine, however, has two lone pairs of electrons in orbitals of a symmetry which makes them available for π donation of electron density into antibonding orbitals of the sigma framework about sulfur. Alkoxy oxygen, on the other hand, has only one lone pair so situated. The fluorine substituents in **3** would therefore make a greater contribution to such a back-bonding effect than in the trans isomer since lone pairs of fluorine in **3** are not competing for the same antibonding orbitals about sulfur. In **2** they are competing for the same antibonding orbitals. This back-bonding effect, if important, could at least partially account for the longer than predicted S–F bond lengths of **2** and for the greater stability observed for **3** relative to **2**.

Semiempirical calculations at the MINDO/3 level[24] were performed for a simplified analogue of **2**, persulfurane **24**. Several of the bonding molecular orbitals calculated for **24** show such π delocalization of the lone pairs of fluorines into the σ-bond framework about sulfur (Figure 5).

S–C Bond Lengths in 2 and 3. Bond lengths for the nonhypervalent equatorial S–C bonds in 10-S-4 sulfuranes **9** and **20–22**



24

are nearly identical with the S–C distances in the 12-S-6 persulfuranes **2**, **3**, and **23**. A consideration of the greater concentration of positive charge in a sulfur(VI) species,[38] and the expected decrease in covalent radius as one goes from sulfur(IV) to sulfur(VI) might, however, lead one to predict shorter S–C distnaces in 12-S-6 species. One can make an argument based on perturbational molecular orbital theory to explain the longer than expected S–C bond lengths. The degree of mixing of the sulfur 2s orbital with the orbitals of the substituents on sulfur decreases in the order F > O > C as a consequence of the higher energy of the oxygen and carbon bonding orbitals. The result of this is an S–F bond with a greater amount of s character and an S–C bond with a greater amount of p character, leading to weaker and longer S–C bonds. The S–F bonds of SF_6 are 0.07 Å shorter than the equatorial S–F bonds of SF_4, in agreement with this prediction. The semiempirical calculations that were performed (MINDO/3,[24] CNDO,[25] and extended Hückel[26]) to compare the relative overlap populations of the S–X bonds did not consistently predict the ordering of the bonding orbitals. Mulliken overlap populations for the orbitals contributing to the S–C bonds are larger than those for the S–O or S–F bonds in all three methods. This order was reversed when nuclear–nuclear repulsion terms were excluded from the extended Hückel calculation.[26] The molecular orbital representations of Figure 5 must therefore be considered only as qualitatively informative.

Acknowledgment. This work was supported in part by the National Science Foundation (Grant CHE 7905692). The structure of **2** was solved by Dr. Eileen Duesler and that of **3** was solved by Dr. Scott Wilson. We thank Dr. Michael R. Ross for construction of the calorimeter which we used and Professor A. J. Arduengo for valuable consultation concerning the MO calculations. We also thank Professor S. Trippett for helpful comments. The mass spectrometry data processing equipment employed in this work was provided by NIH grants CA 11388 and GM 16864 from the National Cancer Institute and National Institute of General Medical Sciences, respectively.

Registry No. 1, 70091-68-8; **2**, 76652-53-4; **3**, 76704-64-8; **5**, 80662-97-1; **6**, 80662-99-3; **9**, 18810-55-4; **10**, 62750-58-7; **11a**, 80663-00-9; **11b**, 80662-78-8; **11c**, 80663-01-0; **11d**, 80663-02-1; **15**, 75194-66-0; **16**$\cdot PF_6^-$, 75238-06-1; **24**, 80663-03-2.

Supplementary Material Available: A listing of the thermal parameters for **2** (Table V) and **3** (Table VI), complete bond lengths and angles for **2** (Table VII) and **3** (Table VIII), and observed and calculated structure factor amplitudes for **2** (Table IX) and **3** (Table X) and complete results of the MINDO/3 calculations for **24** (82 pages). Ordering information is given on any current masthead page.

---

(43) Adzima, L. J.; Duesler, E. N.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4001.

(44) Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5761.