Correspondence

Intramolecular Ligand Rearrangements in Four- and Five-Coordinate Sulfur Compounds

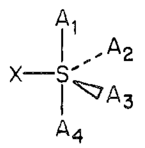
AIC501055

Sir:

There is a surfeit of examples of intramolecular ligand rearrangements of five- and six-coordinate compounds and ions in the literature.[1] Much less attention has been paid to the intramolecular rearrangements of other polyhedra. However, the recent demonstration by dynamic NMR (DNMR) spectroscopy that the fluorine-exchange process in SF_4 is intramolecular[2,3] (as opposed to intermolecular[4] or impurity catalyzed[5]) prompts us to consider the rearrangement modes[6] and observable processes[7] in a variety of four-coordinate sulfur compounds (sulfuranes). In the interest of completeness the rearrangements in the corresponding five-coordinate sulfur oxides (sulfurane oxides) are also considered.

At the outset it should be stressed that the ligand rearrangements of pentacoordinated species may proceed via an infinite variety of mechanisms including intramolecular,[1c,1f,1g,8] intermolecular[4,9,10] solvent-assisted exchange,[5d,11] exchange via dimeric intermediates,[12] and impurity-catalyzed exchange.[5,10] However, since DNMR data are interpreted within the framework of the "jump model", they cannot provide mechanistic information; rather, such data are best discussed with reference to the pertinent rearrangement modes[6] which are, of course, merely permutational in character. Furthermore, due to the DNMR spectroscopic indistinguishability of several of the rearrangement modes it is convenient to effect a further classification into observable processes.[7] For example, the DNMR data for the trigonal-bipyramidal molecule $(CH_3)_2NPF_4$[13] can be accommodated by either the aeae (mode M_1) or aexae (mode M_5) intramolecular fluorine rearrangement. The DNMR experiment provides no way of distinguishing between these two rearrangements; hence modes M_1 and M_5 are included in the same observable process (OP_1).

Sulfur tetrafluoride[14] and sulfur oxytetrafluoride[14,15] have been shown to possess basic trigonal-bipyramidal structures, **1**, in which one of the equatorial sites, X, is occupied by a lone pair of electrons or an oxygen atom. Assuming the persistence of these basic geometries the introduction of two different ligands, A and B, into the coordination sphere results in structures **2**–**5**. Note that, due to the absence of a plane of symmetry **5** and **5'** constitute an enantiomeric pair.



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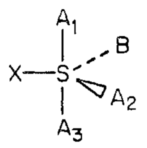

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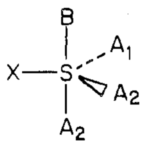

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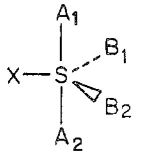

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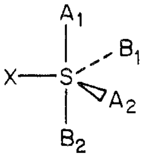

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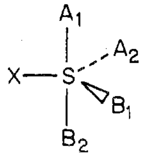
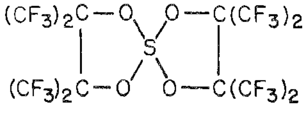


5'

A summary of the rearrangement modes,[6] M_i, and observable processes,[7] OP_i, pertaining to intramolecular exchange in **1**–**5** is presented in Table I.

Consider first molecules of the classes SA_4 and $(O)SA_4$. The only molecule to receive detailed study is SF_4.[2] Basically, SF_4 could undergo exchange by any of three observable processes, viz., OP_0, OP_1, or OP_2 (Table I). By means of line shape analysis of the second-order spectra it has been demonstrated that the ^{19}F DNMR spectra of SF_4 are consistent only with a process in which both axial–equatorial pairs are interchanged, i.e., modes M_1 and M_5. In a permutational sense the ligand rearrangement in SF_4 resembles closely that in $(CH_3)_2NPF_4$ (vide supra).[13] It is probable that other molecules of the general types SA_4 and $(O)SA_4$ also undergo positional interchange of the A ligands via the observable process OP_1.

Apart from SF_4 the only characterized acyclic examples of the classes SA_4 and $(O)SA_4$ comprise SCl_4,[16] $S(C_6F_5)_4$,[17] $S(OC_6H_5)_4$,[18] and $(O)SF_4$.[19] The cyclic compound **6** is also known.[20]



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The ranges of sulfuranes and sulfurane oxides can, in principle, be expanded to include A or B = H, R_f, NR_2, OR, OR_f, SR, etc. Plausible synthetic approaches might involve the use of silyl or stannyl reagents (eq 1), radical plasmas[21] (eq 2), or oxidative fluorination (eq 3).

$$R_3MX + SF_4 \text{ (or other fluorosulfurane)} \rightarrow SF_3X + R_3MF \qquad (1)$$
$$R = \text{alkyl};\ M = \text{Si or Sn};\ X = H,\ NR_2,\ OR,\ SR$$

$$SX_4\ [\text{or } (R_f)_nSX_{4-n}] + \dot{C}F_3 \rightarrow (CF_3)_4S + CF_3X \qquad (2)$$
$$X = \text{halogen}$$

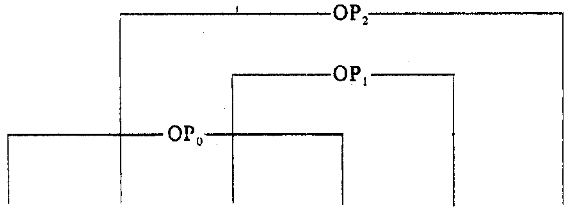
$$(O)S(OR)_2 + ClF \rightarrow (O)S(OR)_2F_2 \qquad (3)$$

The presently known sulfuranes and sulfurane oxides of the composition SA_3B and $(O)SA_3B$ are shown in Table II. ^{19}F NMR spectral data suggest that $(CH_3)_2NSF_3$,[22] CF_3SF_3,[23] $i\text{-}C_3F_7SF_3$,[24] $C_6H_5SF_3$,[25] $C_6F_5SF_3$,[26] and $(CH_3)_2NS(O)F_3$[27] adopt **2** as the ground-state geometry and it is likely that this structure persists for the other SA_3B and $(O)SA_3B$ species which are known presently. One should perhaps point out, however, that unlike the corresponding phosphoranes,[28] nothing is known about the apicophilicity[1f] of substituent groups in sulfuranes.

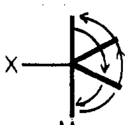
At this point no information is available concerning the ligand permutational processes in compounds of the type SA_3B or $(O)SA_3B$.[29] Assuming the ground-state geometry **2** reference to Table I indicates that there are only two possibilities for intramolecular exchange: either (i) the compound exhibits no temperature sensitivity of the NMR spectra (OP_0) or (ii) if changes do take place in the DNMR spectra, intramolecular exchange must proceed by the observable process OP_1 which comprises mode M_1 (ae) or M_2 (aee) (or combinations thereof). In a sense trifluorosulfuranes and trifluorosulfurane oxides resemble trifluorophosphoranes. DNMR studies of the trifluorophosphoranes $R_1R_2PF_3$, with $R_1 = R_2 = C_6H_5$,[30] CH_3,[10] CF_3,[32] and $R_1 = CF_3$, $R_2 = H$,[32] indicate that the intramolecular fluorine exchange proceeds by the OP_1 process and it is probably safe to assume that a similar situation prevails for the trifluorosulfuranes and trifluorosulfurane oxides.

Finally, consideration is given to the general classes of compounds SA_2B_2 and $(O)SA_2B_2$. Examples of these structural types are rather sparse and apart from the per-

Table I. Summary of Rearrangement Modes, M_i, and Observable Processes, OP_i, for Sulfuranes and Sulfurane Oxides

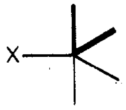


Compd	M_0[a]	M_1	M_2	M_3	M_4	M_5	Total modes	Total OP's
$(X)SA_4$[b] (1)	1	1	4	1	4	1	12	3
$(X)SA_3B$ (EQ)[c] (2)	1	0	2	1	2	0	6	2
$(X)SA_3B$ (AX)[c] (3)	1	0	2	1	2	0	6	2
$(X)SA_2B_2$ (EQ)[c] (4)	1	0	0	1	0	0	2	1
$(X)SA_2B_2$ (AX) (EQ)[c] (5)	1	1	1	2	2	1	8	3



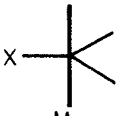
M_1

aeae



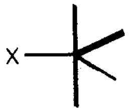
M_2

ae



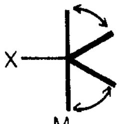
M_3

aa



M_4

aae



M_5

aexae

[a] Identity operation. [b] X = lone pair or oxygen atom. [c] AX or EQ indicates the position of the B ligands.

Table II. Sulfuranes and Sulfurane Oxides of the Type SA_3B and $(O)SA_3B$

Compd	Ref
Sulfuranes	
CF_3SF_3	*a*
$C_2F_5SF_3$	*b*
$(CF_3)_2CFSF_3$	*c*
$C_6F_5SF_3$	*d*
$C_6H_5SF_3$ + (aryl)SF_3	*e, f*
$C_6H_5CF_2SF_3$	*e*
$CH_3CH_2CH_2CHFSF_3$	*d*
$(CH_3)_2NSF_3$	*g, h*
$(C_2H_5)_2NSF_3$	*h*
$(i\text{-}C_3H_7)_2NSF_3$	*i*
$ROSF_3$ (unstable), R = Me, Et	*j*
$FSSF_3$	*k*
$ClSSF_3$	*k*
$F_3SCF_2SF_3$	*l*
$F_3SCF_2SF_5$	*m*
F_3SCF_2COOH	*n*
$RSCl_3$, R = alkyl, aryl	*o*
$(C_6H_5O)_3SF$	*p*
Sulfurane oxides	
$(CH_3)_2NS(O)F_3$	*h*
$(C_2H_5)_2NS(O)F_3$	*h*

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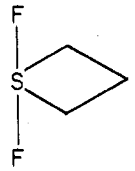
fluoroalkyl compounds $(CF_3)_2SF_2$,[24,33] $(C_2F_5)_2SF_2$,[33] $(i\text{-}C_3F_7)_2SF_2$,[24] $(CF_3)(i\text{-}C_3F_7)SF_2$,[33] $(CF_3)(n\text{-}C_3F_7)SF_2$,[33] and $(CF_3)(C_2F_5)SF_2$[33] the acyclic compounds are limited to dialkoxydiarylsulfuranes,[34] $(C_6H_5O)_2SF_2$,[18] and the methyl-substituted sulfuranes $(CH_3)_2SX_2$, X = F,[35] Cl,[35] and Br.[36] Recently the mono- and bis-chelated compounds **7–9** have been prepared.



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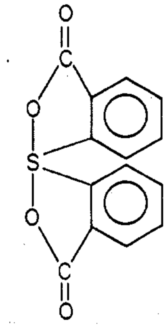

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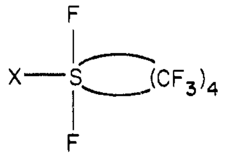

9,[39] X = O or lone pair

Compounds of the general types SA_2B_2 and $(O)SA_2B_2$ could have ground-state geometries **4** or **5** (or its enantiomer, **5'**). Considering first **4**, one notes (Table I) that the only possible intramolecular ligand rearrangement is aa, which is permutationally equivalent to the identity operation (i.e., OP_0). Providing that conversion to structure **5** (or **5'**) would require a prohibitively large amount of energy this implies that fluorosulfuranes possessing structure **4** (A = F) cannot exhibit temperature-dependent ^{19}F NMR spectra (unless, of course, intermolecular or impurity-catalyzed exchange is extant). A similar situation obtains in the case of fluorophosphoranes of the type R_3PF_2 and sulfuranes bearing AA or AB chelates. Since this point is apparently misunderstood it might, therefore, be worthwhile stressing that the temperature insensitivity of the NMR spectra of R_3PF_2 and R_2SF_2 molecules cannot be used to imply molecular rigidity because the aa rearrangement yields a product which is identical with the starting structure. If structure **5** (or its enantiomer **5'**) were the ground-state structure, all three observable processes are possible (Table I). This is an unlikely geometry if A and B are unidentate ligands; however it might be a feasible structure for chelating ligands.

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