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Fluorine-19 Nuclear Magnetic Resonance Spectrum of Trifluoromethyl(pentafluoroethyl)sulfur Difluoride

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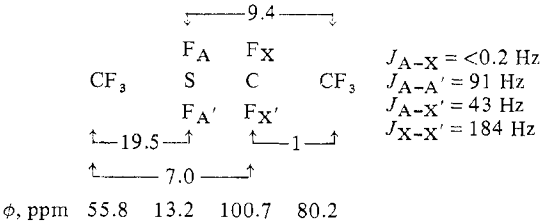
A study of the ^{19}F nuclear magnetic resonance spectrum of trifluoromethyl(pentafluoroethyl)sulfur difluoride, $CF_3SF_2CF_2CF_3$, shows that the geminal fluorine atoms of the methylene group as well as the geminal fluorine atoms bonded to sulfur are magnetically nonequivalent. Thus this molecule may be described in terms of an $AA'XX'Y_3Z_3$ system. Chemical shifts and coupling constants of all fluorine nuclei are reported.

There are many reports of magnetic nonequivalence of geminal nuclei on vicinal atoms, such as in $CF_2{=}CH_2$ which is the classical example of an AA'XX' spin system.[2] However, we report here the first example of magnetic nonequivalence of two geminal fluorine atoms bonded to S(IV) and the concomitant magnetic nonequivalence of the geminal fluorine atoms on the adjacent methylene carbon in trifluoromethyl(pentafluoroethyl)sulfur difluoride, $CF_3SF_2CF_2CF_3$. The chemical shifts of the members of each pair of nuclei are identical and are in the region characteristic for fluorine bonded to S(IV) or to methylene carbon.

Results

The trifluoromethyl(pentafluoroethyl)sulfur difluoride was prepared by the literature method[3] and the ^{19}F nuclear resonance spectral studies were obtained using a Varian HA-100 nmr spectrometer operating at 94.1 MHz. Freon 11 was the internal reference. The chemical shift and spin–spin coupling data are as indicated. This molecule gives a typical spectrum for an $AA'XX'Y_3Z_3$ system which can be analyzed by examining the CF_2 and SF_2 regions separately. Basically these two portions of the spectrum are identical with those described for such a system[4] but appear to be dissimilar due to the different spin–spin couplings with the fluorine atoms of CF_3 and CF_3S, e.g., between $CF_3S{-}SF_2$ (J = 19.5 Hz) and $CF_3S{-}CF_2$ (J = 7.0 Hz) and between $CF_3C{-}SF_2$ (J = 9.4 Hz) and $CF_3C{-}CF_2$ (J = 1 Hz). The experimentally and computer-generated CF_2 portions of the spectrum are identical. As is expected, the peaks at the center of the spectrum are much more intense than the components of the basic quartets farthest removed from the center. Although the pair of quartet of quartets separated by 195 Hz was sufficiently intense to be recorded during a normal scan, it was necessary to use time-averaging techniques to observe the pair separated by 552 Hz. That the quartets are not ^{13}C satellites follows from two observations: (1) the structure is the expected quartet of quartets, rather than the more complicated pattern expected of ^{13}C satellites; (2) there is self-consistency within the AA'XX' scheme, which determines four coupling constants from five pieces of data.



J_{A-X} = <0.2 Hz
$J_{A-A'}$ = 91 Hz
$J_{A-X'}$ = 43 Hz
$J_{X-X'}$ = 184 Hz

Table I

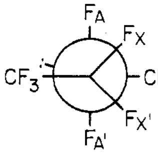
Compd	Chem shift SF$_{ax}$	Chem shift SF$_{eq}$
CF_3SF_3[7]	−47	49
$(CF_3)_2CFSF_3$[6]	−61	54
$CF_3SF_2CF_3$[3]	14	
$CF_3SF_2C_2F_5$[3]	13	
$CF_3SF_2CF_2CF_2CF_3$[3]	11	
$CF_3SF_2CF(CF_3)_2$[6]	14	
$[(CF_3)_2CF]_2SF_2$[6]	11	
c-$C_4F_8SF_2$[8]	11	

Discussion

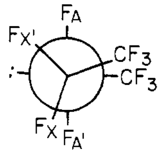
As expected, the ^{19}F NMR spectra of the bis(perfluoroalkyl) sulfides, e.g., CF_3SCF_3,[5] $CF_3SCF_2CF_3$,[3] and $CF_3SCF_2CF_2CF_3$,[3] are straightforward textbook examples. These sulfides which are likely to have a skewed tetrahedral structure with the unshared electron pairs at two of the apices are easily fluorinated with chlorine monofluoride at −78° to the respective bis(perfluoroalkyl) sulfur difluorides, $R_fSF_2R_f'$. The ^{19}F NMR spectrum of the sulfur difluoride where $R_f = R_f' = CF_3$ is again simple with no evidence for either magnetic or chemical nonequivalence of the fluorine bonded to sulfur. However, when $R_f = R_f' = C_2F_5$, the spectrum is much more complex and has not been completely interpreted.

The SF chemical shifts of known R_fSF_3 and $R_fR_f'SF_2$ compounds are given in Table I. Muetterties et al.[6] have argued that because the observed resonance of $R_fR_f'SF_2$ compounds is intermediate between the axial and equatorial positions of the R_fSF_3 compounds, a rapid axial–equatorial exchange may be occurring in the $R_fR_f'SF_2$ compounds. By contrast, intermolecular exchange of axial (but not equatorial) fluorine atoms is suggested for SF_4[9] and was extended by Seel[10] to other three- and four-coordinated sulfur(IV) atoms. Seel[10] has also shown in his systems that the chemical shift of axial fluorine atoms changes much more with changing temperature than is the case for the equatorial fluorines. For $CF_3SF_2SCF_3$, the chemical shift change for $-SF_2-$ is ~4 ppm in the range −100 to 0°. We observe a chemical shift of ~1–2 ppm over the same temperature range for $CF_3SF_2CF_3$ and $CF_3SF_2C_2F_5$. The peaks are sharp and well resolved at room temperature; there is some line broadening at the temperatures near −100°. We cannot say if the broadening indicates an exchange process like those described above or perhaps an internal rotation barrier. But an intramolecular axial–equatorial exchange seems unlikely. In $c\text{-}C_4F_8SF_2$, the S–F chemical shift is the same as for other $R_fR_f'SF_2$ compounds, but the rigid cyclic structure should preclude axial–equatorial exchange. Thus, the intermediate position of the $R_fR_f'SF_2$ shifts is more likely due to a change in chemical environment arising from the presence of the second R_f group. The temperature dependence of the chemical shift indicates a basically axial position. These axial fluorine atoms could still undergo intermolecular exchange. Preliminary examination of the Raman and infrared spectra of these $-SF_2-$ compounds, also, supports an axial arrangement of the fluorine atoms bonded to sulfur. This work will be reported subsequently. Thus, the sulfur–fluorine atoms in $CF_3SF_2CF_2CF_3$ are most likely in the axial positions having identical chemical shifts but having nonidentical coupling interactions with the geminal fluorine atoms of the vicinal methylene group.

The sharpness of the spectral lines at room temperature indicates that the barrier to rotation about the F_2C-SF_2 bond will be small so free rotation occurs. As noted above, the effect of a barrier may be appearing at low temperatures. Thus, there is chemical equivalence between the two fluorines of $-SF_2-$ and between the two fluorines of $-CF_2-$. The magnetic nonequivalence arises from the fact that the relationship between SF_A and CF_X (see below) does not average out to be the same as between SF_A and $CF_{X'}$, making $J_{AX} \neq J_{AX'}$. In rotamer I, F_A is cis to F_X and S-CF_3 is trans to C-CF_3. But in II, with F_A cis to $F_{X'}$, S-CF_3 is cis to C-CF_3. Therefore, F_A does not perceive $F_{X'}$ in II in the same way as F_A perceives F_X in I, although the relationship between the fluorines is cis in each case.



I



II

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Proton Affinity and Gas-Phase Ion Chemistry of Hydrogen Fluoride

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The gas-phase ion chemistry of HF is investigated using the techniques of ion cyclotron resonance spectroscopy. The only observed reaction of the parent ion is $HF^+ + HF \rightarrow H_2F^+ + F$ for which a bimolecular rate constant $k = (9 \pm 3) \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1} is determined. Proton-transfer reactions in mixtures of HF with N_2, CH_4, and CO_2 are examined to determine the proton affinity of HF. While HF is found to be substantially less basic than CH_4 and CO_2, the proton affinities of HF and N_2 are comparable. From the measured equilibrium constant and estimated entropy change a value of $\Delta H = -1.1 \pm 0.2$ kcal/mol is calculated for the reaction $H_2F^+ + N_2 \rightleftarrows N_2H^+ + HF$. From previous studies of PA(N_2) this allows an absolute value of PA(HF) = 112 ± 2 kcal/mol to be determined. The disparate base strength of HF relative to the other hydrogen halides is discussed.

I. Introduction

The proton affinity of a species M, defined as the enthalpy change for reaction 1, represents a quantitative measure of

$$MH^+ \rightarrow M + H^+ \qquad \Delta H = PA(M) \tag{1}$$

the intrinsic basicity of the molecule in the gas phase. For two species M_1 and M_2, a knowledge of the preferred direction of the proton-transfer reaction 2 establishes the sign of the free

$$M_1H^+ + M_2 \rightleftarrows M_2H^+ + M_1 \tag{2}$$

energy change for the reaction, ΔG. If reaction 2 describes a system at thermal equilibrium, then the measured equilibrium