

Received: March 21, 1983; accepted: July 7, 1983

SOLVENT EFFECTS IN FLUORINE-19 NMR SPECTROSCOPY: NONUNIFORM SHIFTING OF THE AXIAL AND EQUATORIAL FLUORINE RESONANCES OF THE PENTAFLUOROSULFANYL GROUP

JOSEPH S. THRASHER*, JON L. HOWELL, DONALD E. MAURER and ALAN F. CLIFFORD

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24061 (U.S.A.)

SUMMARY

The chemical shifts of the fluorine resonances of $SF_5N=SF_2$ are given in fourteen different solvents. A change in solvent polarity was found to affect the axial fluorine of the SF_5 group more substantially than the equatorial fluorines. This nonuniform shifting of the axial and equatorial fluorine resonances of the SF_5 group is best explained as a trans effect and can sometimes be used to simplify complex spectra as shown in the examples $SF_5NHC(O)F$ and $SF_5NHC(O)CF_3$.

INTRODUCTION

Differential solvent effects have widely been observed in NMR spectroscopy and have often been used to simplify spectra, elucidate structure, and study stereochemical changes, no matter what the nucleus [1-3]. We recently reported the nonuniform shifting of axial and equatorial fluorine resonances in $[SF_5NHC(O)]_2$ as an effect of solvent [4]. We have also observed this effect in our study of the fluorine-19 NMR chemical shifts of $SF_5N=SF_2$ in fourteen different solvents [5]. The results of this study are reported herein along with several examples of where this solvent effect has been used to simplify complex AB_4 patterns arising in SF_5N - compounds.

*Current address: Department of Chemistry, Clemson University, Clemson, S.C. 29631, U.S.A.

RESULTS AND DISCUSSION

To study the solvent dependence of the fluorine resonances in $SF_5N=SF_2$, solutions of approximately equal concentration were used in order to preclude concentration effects. The spectra were also referenced to an internal standard (Freon 11) so that no correction would be needed for bulk susceptibilities [1-3]. The results, shown in Table 1, clearly demonstrate that the choice of solvent does have a pronounced effect, and there appears to be a rough correlation between the observed chemical shifts and the polarity of the solvent. The A and X fluorines of the AB_4X_2 pattern observed for $SF_5N=SF_2$ are substantially more affected by the changes of solvents than are the B fluorines. And, it should be pointed out that the sulfur(VI) fluorines are deshielded when changing from non-polar to polar solvents, while the sulfur(IV) fluorines are shielded. No explanation for this trend can be given at this time, but the relative changes in the chemical shifts of the A and B fluorines (6.5 to 1 ppm) coincide well with the fact that in SF_5R compounds the axial fluorine is often more influenced by changes in the substituent R [4,6]. This nonuniform shifting of the axial and equatorial fluorine resonances most likely results from a trans effect. It is therefore obvious that solvent choice is critical when attempting to compare substituent effects on the fluorine-19 NMR resonances of the SF_5 group.

However, this nonuniform solvent effect on the axial and equatorial fluorines of the SF_5 group can sometimes be used to one's advantage. The fluorine-19 NMR spectrum of $SF_5NHC(O)F$ has an atypical AB_4X spin pattern due to the small chemical shift difference between the A and B nuclei [4]. It was hoped that by using the solvent effect just described that a more nondegenerate AB_4X pattern could be obtained for $SF_5NHC(O)F$. Even though the chemical shifts would differ from those of the neat solution (or CCl_3F solution) of the carbamyl fluoride, the coupling constants could then be obtained without the use of complex calculations and computer simulations. The solvent acetone not only pulled apart the A and B fluorine resonances but also effectively dehydrofluorinated the carbamyl fluoride. Thus, interpretation of the

TABLE 1

Effect of solvent on the ^{19}F NMR chemical shifts of $\text{SF}_5\text{N}=\text{SF}_2$

F-SF ₄ -N-SF ₂ A B ₄ X ₂ Solvent	Dielectric Constant ^b	Chemical Shifts ^a (ppm)		
		δA	δB	δX
1 Dimethylsulfoxide	46	76.2	84.5	46.7
2 Dimethylformamide	37.6	75.8	84.2	47.5
3 1,4-Dioxane	2.22	73.7	84.2	48.5
4 Acetonitrile	35.1	73.1	84.0	49.5
5 Nitromethane	35.0	73.1	84.2	49.9
6 Boron Trifluoride Etherate		72.7	84.0	50.1
7 Trifluoroacetic Acid	8.2	70.2	83.8	52.6
8 Neat		70.3	83.7	52.7
9 m-Bromo- <i>a,a,a</i> -Trifluorotoluene		71.2	84.0	52.6
10 Trifluoroacetic Anhydride	2.7	70.3	83.7	52.8
11 Benzene	2.26	71.7	83.9	52.8
12 Hexafluorobenzene		70.1	83.7	53.1
13 Freon 113	2.41	70.0	83.6	53.2
14 Freon 11	2.28	70.1	83.6	53.3
15 n-Hexane	1.90	69.7	83.5	53.6
Change: All Solvents		Δ=6.5	Δ=1.0	Δ=6.9

^aReferenced to internal Freon 11.^bDielectric constants [2,7,8] at ambient temperature (25-40°C).

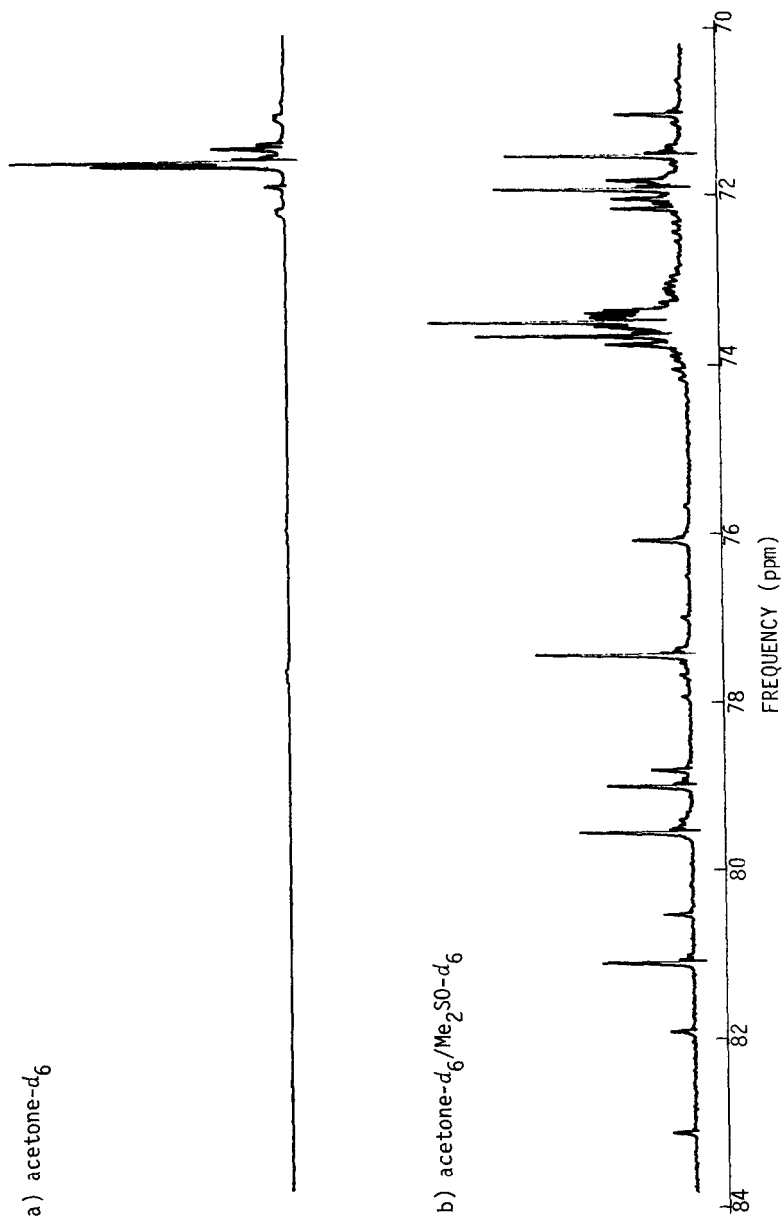


Fig. 1. Solvent Effect on the AB₄ Portion of the Fluorine-19 NMR Spectrum of SF₅NHC(O)CF₃.

spectrum was complicated by the presence of SF_5NCO , and an additional spectrum of SF_5NCO in acetone had to be obtained before the assignment could be made. The coupling constants obtained for $\text{SF}_5\text{NHC(O)F}$ were $J_{\text{AB}} = 160.0$ Hz and $J_{\text{BX}} = 12.1$ Hz. An example of this idea without added complications is shown in Figure 1 for different solutions of $\text{SF}_5\text{NHC(O)CF}_3$ [4].

These examples further display the differential solvent effect on the fluorine resonances of an SF_5 group as previously reported by us [4].

REFERENCES

- 1 J. Ronayne and D.H. Williams, in E.F. Mooney (Editor), Annual Review of NMR Spectroscopy, Vol. 2, Academic Press, New York, 1969, Chapter 3, pp. 83-124.
- 2 P. Laszlo, in J.W. Emsley, J. Feeney, and L.H. Sutcliffe (Editors), Progress in Nuclear Magnetic Spectroscopy, Vol. 3, Pergamon Press, New York, 1967, Chapter 6, pp. 231-402.
- 3 J.W. Emsley and L. Phillips, in J.W. Emsley, J. Feeney, and L.H. Sutcliffe (Editors), Progress in Nuclear Magnetic Resonance Spectroscopy, Vol. 7, Pergamon Press, New York, 1971, pp. 3-36.
- 4 J.S. Thrasher, J.L. Howell, and A.F. Clifford, Inorg. Chem., 21 (1982) 1616.
- 5 A.F. Clifford, J.S. Thrasher, C.R. Newman, D.E. Maurer, J.L. Howell, paper presented at the 178th National meeting of the American Chemical Society, Honolulu, HI, Aug. 1979.
- 6 a) N. Boden, J.W. Emsley, J. Feeney, and L.H. Sutcliffe, Trans. Faraday Soc., 59 (1963) 620.
b) K. Seppelt, Z. Anorg. Allg. Chem., 399 (1973) 65.
- 7 R.C. Weast (Editor), CRC Handbook of Chemistry and Physics, CRC Press, Inc., West Palm Beach, Florida, 58th edn., 1978, p. E-34,35.
- 8 J.M. Tedder, J. Chem. Soc. (1954) 2646.