

SULFONIUM SALTS AS LANTHANIDE SHIFT
DONORS IN PMR AND CMR SPECTROSCOPY

R.L. Caret*[†], A. Vennos[†], M. Zapf[†], and J.J. Uebel[‡]

[†]Department of Chemistry, Towson State University, Towson, MD, 21204, USA;

[‡]Department of Chemistry, University of New Hampshire, Durham, NH, 03824, USA

Summary Lanthanide shift reagents (LSR) may be used in the structural elucidation of sulfonium salts by both PMR and CMR. In these investigations there is qualitative agreement with the McConnell-Robertson equation and complexation appears to occur at the anion.

The use of Lanthanide Shift Reagents (LSR) as probes in the structural elucidation of organic salts has been reported. ^{1, 2} Investigations of ammonium ^{1a, b, c, f}, sulfonium ^{1d, 2}, and phosphonium salts ^{1d}, as well as carboxylate ions ^{1e} are all known. These investigations have been limited by the lack of suitable solvents, solvents in which both the shift reagent and substrate are soluble, which are suitable for NMR investigations, and which will not bind with the shift reagents themselves. The investigations thus far have used aqueous systems, ^{1c, 6} melts of mixtures of the salts and LSR ^{1f}, and deuterated methylene chloride (CD₂Cl₂) ^{1d, 2}.

We recently reported that sulfonium salts do indeed give observable induced shifts when LSR [such as Eu(fod)₃ or Pr(fod)₃]³ are employed². A series of trialkyl- and dialkylaryl-sulfonium salts were synthesized and shift studies run⁴. Examples of the magnitudes of these shifts are provided in Figures 1 and 2 and Table 1. Note that qualitatively the relative shifts are in agreement with the McConnell-Robertson equation⁷ when the lanthanide is placed near the sulfonium sulfur.

To demonstrate the general applicability of these reagents to the structure elucidation of salts, we synthesized a series of dimethyl-p-tolylsulfonium salts in which the anion was varied. The LIS results of this series are also presented in Table 1. It appears that the magnitude of the induced shift is proportional to the size of the anion. This is consistent with findings of both ammonium and phosphonium halides ^{1d}. The origin of these shifts is

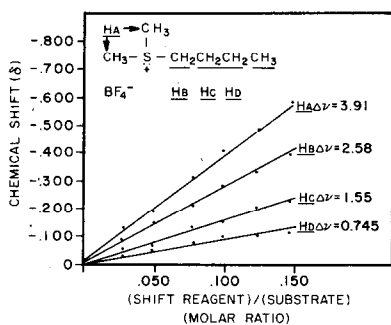


Figure 1. Lanthanide Induced Shift (LIS) of dimethyl-*n*-butylsulfonium tetrafluoroborate with $\text{Pr}(\text{fod})_3$. The chemical shifts of each group of protons is plotted as a function of the molar ratio of shift reagent to substrate. The induced shift at a 1:1 molar ratio of the shift reagent to substrate ($\Delta\nu$) for each line is given. The correlation coefficients of each line are 0.955 or better.⁵ (Perkin Elmer RL2-A, 60 MHz NMR).

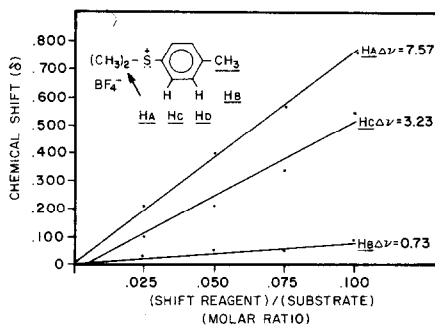
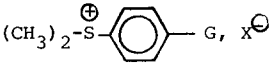
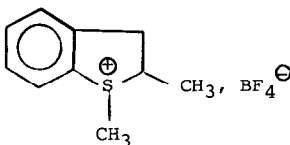


Figure 2. Lanthanide Induced Shift (LIS) of dimethyl-*p*-tolylsulfonium tetrafluoroborate with $\text{Pr}(\text{fod})_3$. The chemical shifts of each group of protons is plotted as a function of the molar ratio of shift reagent to substrate. The induced shift at a 1:1 molar ratio of the shift reagent to substrate ($\Delta\nu$) for each line is given. The correlation coefficients of each line are 0.942 or better.⁵ H_D protons gave a poor correlation (0.772) and are not plotted.

attributed to a pseudocontact interaction between the paramagnetic lanthanide shift reagent and the molecule under investigation⁸. It has been suggested that the observed chemical shifts for ammonium and phosphonium salts are a result of the binding of the LSR with the anion $\text{b}, \text{d}, 2$. With sulfonium salts, however, two sites of complexation are possible; the electron pair on sulfur and/or the anion. Work in our laboratories on the *cis* and *trans* isomers of 1,2-dimethyl-2,3-dihydrobenzothiophenium tetrafluoroborate indicates that the complexation occurs at the anion preferentially². The results in Table 1 substantiate this. With highly non-associative anions, for example tetraphenylborate, no shift is observed.

Table 1. Sulfonium Salts

<u>Structure</u> ⁶	<u>Yield, %</u>	<u>MP (°C)</u>	<u>Δν</u> ^(a)
$(\text{CH}_3)_2\text{-S}^{\oplus}\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3, \text{BF}_4^{\ominus}$	34	60-63	3.91
			
(G = CH ₃ , X = BF ₄)	86	102-103	7.6/27.4 ^(c)
(G = CH ₃ , X = SbCl ₆)	54	151-153	<u>(b)</u>
(G = CH ₃ , X = CF ₃ COO)	45	108-109.5	6.46
(G = CH ₃ , X = FSO ₃)	95	111-115	11.4
(G = CH ₃ , X = Ph ₄ B)	78	175-177	<u>(b)</u>
	45	177-178	6.09 (<u>cis</u>) 6.56 (<u>trans</u>)

a. Induced shift of S-CH₃ at a 1:1 molar ratio of shift reagent to substrate; obtained by extrapolation. b. No shift observed. c. Independent shift studies.

The use of carbon-13 as an alternative NMR probe was also investigated. As expected, induced shifts are observed. The induced shifts for dimethyl-p-tolylsulfonium tetrafluoroborate at a 1:1 molar ratio of shift reagent to substrate are provided in Figure 3. The CMR shifts also give qualitative agreement with the McConnell-Robertson equation.

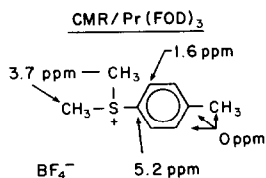


Figure 3. LIS of dimethyl-*p*-tolylsulfonium tetrafluoroborate as measured by carbon-13 NMR. (JOEL FX-90Q, 90 MHz NMR).

In summary, LSR may be used in the structural elucidation of sulfonium salts by both PMR and CMR. In these investigations there is qualitative agreement with the McConnell-Robertson equation and complexation appears to occur at the anion.

References and Notes

1. a. I.M. Walker and D.H. Weeden, *Inorg. Chem.*, **12**, 772 (1973); I.M. Walker and M.S. Quereshi *ibid.*, **13**, 2896 (1974); b. J.I. Seeman and R.L. Bassfield, *J. Org. Chem.*, **42**, 2337 (1977); c. G. Elgavish and J. Reuben, *J. Amer. Chem. Soc.*, **99**, 1762 (1977); d. K.B. Lipkowitz, T. Chevalier, B.P. Mundy and J.J. Theodore, *Tetrahedron Lett.*, 1297 (1980); e. J. Reuben, *J. Amer. Chem. Soc.*, **102**, 2232 (1980); f. R.A. Friedman, E.G. Malawer, Y.W. Wong and B.R. Sundheim, *ibid.*, **102**, 925 (1980).
2. R.L. Caret and A. Vennos, *J. Org. Chem.*, 361 (1980).
3. It is imperative that the solvent be kept dry, that the LSR be freshly sublimed, and that the substrate be dried under vacuum to obtain reproducible results. Otherwise, large variations in the observed induced shifts are possible. $\text{Fod} = \text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{CHC}(\text{O})\text{C}(\text{CH}_3)_3$.
4. Typically, 0.5 ml of a 0.4 M solution of the sulfonium salt in methylene chloride- d_2 was placed in an oven-dried NMR tube which had been flushed with nitrogen while cooling. The NMR spectrum was recorded; 0.05 ml (0.005 mmol) of a 0.1 M solution of solution of the shift reagent (in CD_2Cl_2) was added by means of a microliter syringe, and the NMR spectrum was again recorded. The process was repeated with 4-6 aliquots of the shift reagent.
5. A Least-squares analysis was performed on five to seven points, twice, each at varying percentages of the shift reagent to substrate between 0 and 15 mol% of $\text{Pr}(\text{Fod})_3$.
6. All of the salts were synthesized as described in K. K. Andersen, R. L. Caret, and I. K. Nielsen, *J. Amer. Chem. Soc.*, **96**, 8026 (1974). All of the salts were purified for elemental analysis by recrystallization from ethanol and all gave results within the publishable guidelines ($\pm 0.3\%$ for C, H, and S).
7. H.M. McConnell and R.E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).
Computer aided methods for solving the equation have been published, e.g. see M.R. Willcott, and R.E. Davis, *Science*, **190**, 850 (1975) and R.M. Wing, J.J. Uebel and K.K. Andersen, *J. Amer. Chem. Soc.*, **95**, 6046 (1973); and a graphical method has been described, R.M. Wing, T. Early and J.J. Uebel, *Tetrahedron Lett.*, 4153 (1972).
8. R.E. Cramer, R. Dubois, and K. Seff, *J. Amer. Chem. Soc.*, **96**, 4125 (1974).

(Received in USA 17 September 1980)