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RECEIVED for review June 30, 1986. Accepted October 20, 1986.

Organic-Soluble Lanthanide Nuclear Magnetic Resonance Shift Reagents for Sulfonium and Isothiouronium Salts

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Lanthanide complexes of the formula $[\mathrm{Ln(fod)_4}]^-$ (fod, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione) are effective organic-soluble nuclear magnetic resonance shift reagents for sulfonium and isothiouronium salts. The shift reagent is formed in solution from $\mathrm{Ln(fod)_3}$ and Ag(fod) or K(fod). The selection of Ag(fod) or K(fod) in forming the shift reagent is dependent on the anion of the organic salt. Ag(fod) is more effective with halide salts, whereas K(fod) is preferred with tetrafluoroborate salts. Resolution of diastereotopic hydrogen atoms was observed in the shifted spectra of certain substrates. Enantiomeric resolution was obtained in the spectrum of *sec*-butylisothiouronium chloride with a chiral shift reagent. The reagents can be employed in solvents such as chloroform and benzene.

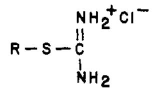
Lanthanide shift reagents are used to expand the utility of nuclear magnetic resonance (NMR) spectroscopy. In addition to their obvious application in stereochemical analysis, NMR shift reagents have often been employed in the analysis of mixtures. Lanthanide tris chelates have been used to analyze mixtures of straight chain alcohols (*1*), methylbenzyl alcohols (*2*), phenols (*3–5*), ketoterpenes (*6*), methyl esters (*7, 8*), fatty acid methyl esters (*9*), esters of tocopherols and retinols (*10*), cresol esters (*10*), methyl esters of toluic acids (*2, 11*), vitamin D_2 isomers (*12*), methylbenzylamines (*2*), toluamides (*2*), alkane- and alkenesulfonates (*13*), steroids (*14*), and triglycerides (*15, 16*). Binuclear lanthanide(III)–silver(I) shift reagents have been used to analyze mixtures of cis and trans olefins (*17–19*), xylenes (*20, 21*), and methylbenzenes in gasoline (*21*).

We have recently reported that the binuclear complex $\mathrm{Ag[Eu(fod)_4]}$ formed in solution from $\mathrm{Eu(fod)_3}$ and Ag(fod) (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione) is an effective organic-soluble NMR shift reagent for ammonium salts (*22*). The interaction between an ammonium salt and $\mathrm{Ag[Eu(fod)_4]}$ is believed to involve an ion pair between the ammonium cation and $[\mathrm{Eu(fod)_4}]^-$. The equilibrium representative of this process is shown in eq 1. Precipitation

$$\mathrm{R_4N^+X^- + Ag[Eu(fod)_4] = R_4N^+[Eu(fod)_4]^- + AgX(s)} \tag{1}$$

of the silver salt favors formation of the ion pair between the organic cation and the lanthanide tetrakis chelate anion. The shifts in the spectrum of $\mathrm{R_4N^+}$ with $[\mathrm{Eu(fod)_4}]^-$ were significantly larger than those with $\mathrm{Eu(fod)_3}$ (*22*).

We have since determined that the species $[\mathrm{Ln(fod)_4}]^-$ is an effective NMR shift reagent for sulfonium and isothiouronium salts (I) (isothiouronium salts are often prepared as



$$\mathrm{R{-}S{-}}\underset{\underset{\displaystyle \mathrm{NH_2}}{|}}{\overset{\overset{\displaystyle \mathrm{NH_2^+Cl^-}}{\|}}{\mathrm{C}}}$$

I

derivatives of alkyl halides) as well (*23–25*). The species $[\mathrm{Ln(fod)_4}]^-$ would therefore appear to be a useful anionic organic-soluble NMR shift reagent applicable to a wide range of cations. Other workers have noted that the spectra of sulfonium salts are shifted in the presence of $\mathrm{Eu(fod)_3}$ (*26–28*). We have found that the shifts in the spectra of sulfonium and isothiouronium salts with $[\mathrm{Eu(fod)_4}]^-$ are significantly larger than those with $\mathrm{Eu(fod)_3}$. The shifts in the spectra of sulfonium salts with $[\mathrm{Ln(fod)_4}]^-$ are also appreciably larger than those in the spectra of the corresponding sulfides with $\mathrm{Ln(fod)_3}$. The shifts in the spectra of isothiouronium salts with $[\mathrm{Ln(fod)_4}]^-$ are larger than those for the corresponding alkyl halide with $\mathrm{Ln(fod)_3}$ (*29*) or the binuclear reagent $\mathrm{Ag[Ln(fod)_4]}$ (*17, 30*).

EXPERIMENTAL SECTION

Reagents. The compounds 1-iodobutane, iodomethane, 1-bromopentane, 1-bromononane, 1-chlorobutane, benzyl chloride, 2-bromobutane, 2-chlorobutane, methyl sulfide, *n*-butyl sulfide, tetrahydrothiophene, benzothiophene, and diphenyl sulfide were purchased from commercial sources and used as received. Silver tetrafluoroborate was purchased from Aldrich Chemical Co. and stored in a desiccator over P_4O_{10}. Trimethyloxonium tetrafluoroborate was purchased from Alfa Products Co. and stored at 0 °C prior to use. Methylene chloride was distilled from P_4O_{10} under an atmosphere of dry nitrogen and stored over K_2CO_3. Nitromethane was stored over K_2CO_3. All other solvents were used as received.

Chloroform-*d* was purchased from Aldrich Chemical Co. and stored over molecular sieves. Deuterium oxide, benzene-d_6, and 3-(trimethylsilyl)propanesulfonic acid sodium salt (DSS) was purchased from Wilmad Glass Co., Inc. Acetone-d_6 was purchased from Norell, Inc. Acetonitrile-d_3 was purchased from Stohler Isotope Chemicals. The Ln(fod)$_3$ (31), Ag(fod) (32), Ag(ptb) (*33*) (ptb = 4,4,4-trifluoro-1-phenyl-1,3-butanedione), and K(fod) (*34*) chelates were synthesized by literature methods and stored in a desiccator over P_4O_{10}. The H(fod) ligand, Pr(facam)$_3$, Pr(hfbc)$_3$, Eu(facam)$_3$, and Eu(hfbc)$_3$ (facam = 3-trifluoroacetyl-*d*-camphor, hfbc = 3-heptafluorobutyryl-*d*-camphor) were purchased from Aldrich Chemical Co. All chiral shift reagents were stored in a desiccator over P_4O_{10} prior to use.

Apparatus. All NMR spectra were recorded on a Varian EM-360L 60-MHz instrument at ambient probe temperature.

Synthetic Preparations. The procedures employed in the preparation of sulfonium (*35–44*) and isothiouronium salts (*23–25*) were modifications of literature methods. Representative examples of each will be described.

Conversion of Sulfides into Sulfonium Salts. Method 1. Direct methylation with iodomethane

$$R{-}S{-}R' + CH_3I = RR'S{-}CH_3^+I^-$$

This procedure has been described in the literature for the preparation of trimethylsulfonium iodide (*35–37*). It is only suitable for the derivatization of highly nucleophilic sulfides. Trimethylsulfonium iodide, *S*-methyltetrahydrothiophenium iodide, and di-*n*-butylmethylsulfonium iodide were prepared by this method.

(*A*) *Preparation of S-Methyltetrahydrothiophenium Iodide.* Tetrahydrothiophene (2.20 g, 0.0211 mol) and iodomethane (3.00 g, 0.0211 mol) were added to a small Erlenmeyer flask that was stoppered and allowed to stand overnight. The solid that formed was removed and recrystallized from ethanol. After washing with cold ethanol the light yellow solid was washed with anhydrous ether. It was then dried in vacuo over P_4O_{10} for 18 h: mp 201–206 °C (sealed capillary) (sublime) [lit. (*45*) mp 185–190 °C (sublime)]; NMR (D_2O) δ 3.50 (m, 4), 2.85 (s, 3, CH_3), 2.30 (m, 4).

(*B*) *Preparation of Di-n-butylmethylsulfonium Iodide.* After 24 h an orange oil that had settled to the bottom of the flask was removed and triturated three times with anhydrous ether. The oil remaining after trituration was dried for 24 hours in vacuo over P_4O_{10}. A waxy orange solid formed on drying: NMR ($CDCl_3$) δ 3.80 (m, 4 CH_2), 3.25 (s, 3, CH_3), 1.1–2.0 (broad, 8), 0.95 (t, 6, CH_3).

Method 2. Methylation with iodomethane in the presence of silver tetrafluoroborate (*37–42*)

$$R{-}S{-}R' + CH_3I + AgBF_4 = RR'S{-}CH_3^+BF_4^- + AgI$$

In comparison to method 1, this procedure can be used for the derivatization of less nucleophilic sulfides. Ethyldiphenylsulfonium tetrafluoroborate and *S*-methyltetrahydrothiophenium tetrafluoroborate were prepared by this method.

(*A*) *Preparation of S-methyltetrahydrothiophenium Tetrafluoroborate.* To a flame-dried three-necked flask equipped with a nitrogen inlet, reflux condenser, and magnetic stirrer was added a solution of iodomethane (0.36 g, 0.00254 mol) and tetrahydrothiophene (0.45 g, 0.00511 mol) in 15 mL of dry nitromethane. Silver tetrafluoroborate (1.00 g, 0.005 14 mol) was added to the solution as a solid over several minutes. The reaction was stirred at room temperature under an atmosphere of nitrogen for 6 h. An additional 15 mL of dry nitromethane was added and the solution was filtered by gravity. The nitromethane was removed by rotary evaporation and the resulting brown solid was washed with anhydrous ether and collected by suction filtration. It was then dried in vacuo over P_4O_{10} for 24 h: mp 239–245 °C [lit. (*46*) mp 250–251 °C]; NMR (D_2O) δ 3.48 (m, 4), 2.81 (s, 3, CH_3), 2.36 (m, 4).

(*B*) *Preparation of Ethyldiphenylsulfonium Tetrafluoroborate.* The reaction of phenyl sulfide and iodoethane with silver tetrafluoroborate in dry methylene chloride resulted in a brown oil that did not solidify on drying in vacuo: NMR ($CDCl_3$) δ 7.2–7.6 (broad, 10, aryl), 3.48 (q, 2, CH_2), 1.18 (t, 3, CH_3).

Method 3. Methylation with trimethyloxonium tetrafluoroborate (*41, 43, 44*)

$$R{-}S{-}R' + (CH_3)_3O^+BF_4^- = RR'S{-}CH_3^+BF_4^- + CH_3OCH_3$$

This procedure is recommended for the least nucleophilic sulfides and was employed successfully with *n*-butyl sulfide and thianaphthene.

(*A*) *Preparation of Di-n-butylmethylsulfonium Tetrafluoroborate.* To a flame-dried three-necked flask equipped with a magnetic stirrer, rubber septum, nitrogen inlet, and reflux condenser was added trimethyloxonium tetrafluoroborate (1.00 g, 0.006 76 mol) and 20 mL of dry methylene chloride. A solution of *n*-butyl sulfide (0.99 g, 0.0068 mol) in 5 mL of methylene chloride was added via syringe. The reaction was stirred at room temperature for 4 h and then filtered by gravity. The filtrate was triturated with 40 mL of anhydrous ether. An oil formed at the bottom of the flask and was removed and dried in vacuo over P_4O_{10} for 24 h. No visible changes occurred during this time: NMR ($CDCl_3$) δ 3.32 (t, 4, CH_2), 2.85 (s, 3, CH_3), 1.1–2.0 (broad, 8), 0.95 (t, 6, CH_3).

(*B*) *Preparation of S-Methylbenzothiophenium Tetrafluoroborate.* The mixture of reactants was heated under reflux for 2 h and then stirred at room temperature for 60 h. Trituration with anhydrous ether resulted in the formation of a red oil. Drying the oil in vacuo over P_4O_{10} for 18 h resulted in a red-brown solid. The solid softened at 70 °C and melted from 110 to 112 °C [lit. (*41*) mp 72–73 °C]: NMR ($CDCl_3$) δ 7.6–7.9 (broad, 6), 3.50 (s, 3, CH_3).

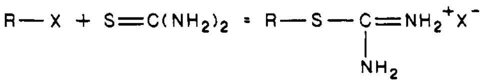
Conversion of Alkyl Halides into Sulfonium Salts. Sulfonium salts of alkyl halides such as iodomethane, 1-iodobutane, and benzyl chloride were prepared by modifying methods 1 and 2 (*35–37*). In these reactions the alkyl halide was derivatized with methyl sulfide.

(*A*) *Preparation of n-Butyldimethylsulfonium Iodide by Method 1.* A light brown solid formed from a mixture of 1-iodobutane and methyl sulfide that was allowed to stand over a period of 4 days. It was collected, washed with anhydrous ether, recrystallized from acetone, and dried in vacuo over P_4O_{10} for 18 h: mp 81–82 °C [lit. (*47*) mp 82 °C]; NMR ($CDCl_3$) δ 3.85 (t, 2, CH_2), 3.42 (s, 6, CH_3), 1.4–2.0 (broad, 4), 1.05 (t, 3, CH_3).

(*B*) *Preparation of n-Butyldimethylsulfonium Tetrafluoroborate by Method 2.* The reactants (1-iodobutane, methyl sulfide, and silver tetrafluoroborate) were stirred in dry methylene chloride at room temperature for 18 h. The yellow solid obtained from the workup of the reaction was dried in vacuo over P_4O_{10}: mp 70–72 °C [lit. (*48*) mp 67.5–68 °C]; NMR ($CDCl_3$) δ 3.28 (t, 2, CH_2), 2.84 (s, 6, CH_3), 1.2–1.9 (broad, 4), 0.91 (t, 3, CH_3).

(*C*) *Preparation of Benzyldimethylsulfonium Tetrafluoroborate by Method 2.* The reactants (benzyl chloride, methyl sulfide, and silver tetrafluoroborate) were stirred in nitromethane at room temperature for 60 h. After suitable workup, and recrystallization from 2-propanol, the white solid was dried in vacuo over P_4O_{10}: mp 96–100 °C [lit. (*49*) mp 99–101 °C]; NMR ($CDCl_3$) δ 7.3–7.6 (broad, 5, aryl), 4.61 (s, 2, CH_2), 2.86 (s, 6, CH_3).

Conversion of Alkyl Halides into Isothiouronium Salts.



$$R{-}X + S{=}C(NH_2)_2 = R{-}S{-}\underset{\displaystyle NH_2}{\underset{|}{C}}{=}NH_2^+X^-$$

The isothiouronium salts were prepared by a modification of literature methods (*23–25*). This procedure was used in the derivatization of 1-chlorobutane, 1-bromopentane, 1-bromononane, 1-iodobutane, benzyl chloride, 2-chlorobutane, and 2-bromobutane.

(*A*) *Preparation of n-Pentylisothiouronium Bromide.* A mixture of 1-bromopentane (5.00 g, 0.0331 mol), thiourea (2.52 g, 0.0331 mol), and 20 mL of 95% ethanol was heated under reflux, with stirring, for 24 h. The course of the reaction can be monitored by the disappearance of the slightly soluble thiourea. The reflux condenser was removed and the volume of solution was reduced until the first sign of solid material. The mixture was then cooled in an ice bath. The resulting solid was collected by suction filtration and recrystallized from 95% ethanol. A waxy material was obtained that was dried in vacuo over P_4O_{10} for 18 h (33% yield, mp 78–84 °C): NMR ($CDCl_3$) δ 3.36 (t, 2, CH_2), 1.1–2.0 (broad, 6), 0.94 (t, 3, CH_3).

(*B*) *Preparation of n-Nonylisothiouronium Bromide.* Thiourea and 1-bromononane were heated under reflux for 18 h. The desired product was obtained in 78% yield (mp 84–87 °C) as a white, waxy material: NMR ($CDCl_3$) δ 3.35 (t, 2, CH_2), 1.1–2.0 (broad, 14), 0.90 (t, 3, CH_3).

(*C*) *Preparation of Benzylisothiouronium Chloride.* Benzyl chloride and thiourea were heated under reflux for 24 h. The product was obtained in 97% yield as a white, waxy material (mp 136-137 °C): NMR (D_2O) δ 7.51 (s, 5, aryl), 4.43 (s, 2, CH_2).

(*D*) *Preparation of n-Butylisothiouronium Iodide.* Thiourea and 1-iodobutane were heated under reflux for 1 h. After reduction of the volume and cooling, anhydrous ether was added and a white precipitate formed. Recrystallization from 95% ethanol afforded the product in 60% yield as a fine white powder (mp 95–101 °C): NMR (D_2O) δ 3.13 (t, 2, CH_2), 1.1–2.0 (broad, 4), 0.92 (t, 3, CH_3).

(*E*) *Preparation of n-Butylisothiouronium Chloride.* Thiourea and 1-chlorobutane were heated under reflux for 24 h. After reduction of the volume and cooling, the product was obtained as a precipitate by the addition of anhydrous ether. The crude product was recrystallized from 95% ethanol and obtained in 73% yield as fine white crystals (mp 69–75 °C): NMR (D_2O) δ 3.16 (t, 2, CH_2), 1.1–2.0 (broad, 4), 0.92 (t, 3, CH_3).

(*F*) *Preparation of sec-Butylisothiouronium Bromide.* Thiourea and 2-bromobutane were heated under reflux for 2.5 h. After the product was isolated by removal of the solvent, it was dissolved in ethanol and triturated with anhydrous ether. The sticky white material was collected and dried in vacuo over P_4O_{10} for 12 h. Its appearance did not change on drying: NMR (D_2O) δ 3.66 (m, 1, CH), 1.77 (m, 2, CH_2), 1.43 (d, 3, CH_3), 1.01 (t, 3, CH_3).

(*G*) *Preparation of sec-Butylisothiouronium Chloride.* Thiourea and 2-chlorobutane were heated under reflux for 144 h. The solution was cooled and unreacted thiourea was removed by gravity filtration. The filtrate was triturated with ether and reducing the volume resulted in a light brown solid. The solid was collected, recrystallized from 100% ethanol, and washed with anhydrous ether. The desired product was obtained as an off-white solid in 6.4% yield (mp 75–80 °C): NMR (D_2O) δ 3.66 (m, 1, CH), 1.76 (m, 2, CH_2), 1.43 (d, 2, CH_3), 1.02 (t, 3, CH_3).

Procedures. To record the spectrum of a substrate in the presence of $[Ln(fod)_4]^-$, the appropriate amount of $Ln(fod)_3$, M(fod) (M = Ag or K), and substrate were weighed into a test tube. The correct amount of solvent was added and the test tube was stoppered and shaken vigorously for a period of 2 min. In instances when the substrate was sparingly soluble in $CDCl_3$, the mixture was periodically shaken over the course of an hour to ensure solubilization of the cation. Insoluble material, including the silver halide or potassium tetrafluoroborate salt, was removed by centrifugation and decantation of the supernatant. Prior to recording of the spectrum, the test tube and NMR tube were covered with foil to exclude light.

Table I. Lanthanide Induced Shifts (ppm) in the Proton NMR Spectra of Butyl Sulfide (0.1 M), Di-*n*-butylmethylsulfonium Iodide (0.1 M), and Di-*n*-butylmethylsulfonium Tetrafluoroborate (0.1 M) in $CDCl_3$ with Various Shift Reagents (0.05 M)

$$\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_2})_2S$$

shift reagent	1	2	3	4
$Eu(fod)_3$	0.07	0.10	0.10	0

$$(\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_2})_2SCH_3{}^+I^-$$

shift reagent	CH_3	1_a[a]	1_b	2	3	4
$Eu(fod)_3$	0.15	0.09	0.09	–[b]	–	0
$Eu(fod)_3$–K(fod)	0.17	0.34	0.34	0.30	0.30	0.09
$Eu(fod)_3$–Ag(fod)	14.35	4.37	3.77	2.32	1.13	0.75

$$(\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_2})_2SCH_3{}^+BF_4{}^-$$

shift reagent	CH_3	1_a	1_b	2	3	4
$Eu(fod)_3$	0.88	0.44	0.44	0.30	0.10	0.05
$Eu(fod)_3$–K(fod)	12.43	4.28	3.65	2.01	0.95	0.58
$Eu(fod)_3$–Ag(fod)	0.25	0.09	0.09	0.10	0.10	0

[a] With certain shift reagents, the resonances of the diastereotopic hydrogen atoms at position 1 were resolved.

[b] Masked by the shift reagent resonance.

RESULTS AND DISCUSSION

The reason for the superior effectiveness of $[Ln(fod)_4]^-$ compared to $Ln(fod)_3$ as a shift reagent for organic salts is not known with certainty. It has been postulated that the mechanism by which $Ln(fod)_3$ complexes cause shifts in the spectra of organic salts involves the formation of the anionic species $[Ln(fod)_3X]^-$ (X = original anion of the organic salt) (eq 2) (*26–28*, *50–56*). The binding constants of the anions of organic salts with $Ln(fod)_3$ to form $[Ln(fod)_3X]^-$ are of intermediate values (*26*). The binding constant of Ag(fod) with $Ln(fod)_3$ (eq 3) has a calculated value of 500 M^{-1} (*57*). This reaction is in the slow exchange region below 20 °C and discrete resonances for the binuclear species $Ag[Ln(fod)_4]$ are observed (*57*). The values reported in the literature for the association constants of X^- (chloride or bromide) with $Ln(fod)_3$ (eq 2) range from 27 to 954 M^{-1} (*26*, *50*). A further consideration with $[Ln(fod)_4]^-$, however, is that the anion of the organic salt precipitates with the Ag^+ or K^+ (eq 4). The

$$R^+X^- + Ln(fod)_3 = R^+[Ln(fod)_3X]^- \qquad (2)$$

$$Ag(fod) + Ln(fod)_3 = Ag[Ln(fod)_4] \qquad (3)$$

$$R^+X^- + Ag[Ln(fod)_4] = R[Ln(fod)_4] + AgX(s) \qquad (4)$$

formation of such a precipitate was obvious from both the volume of insoluble material and unmistakable appearance of the silver halide. The formation of a precipitate was verified by adding a solution of *N*-methylnicotinium iodide in chloroform to a filtered solution of $Ag[Eu(fod)_4]$ in chloroform. A gray-white solid formed on mixing the two solutions. This precipitation forces the association of the organic cation with the shift reagent and seems to be the most plausible reason for the enhanced shifts with $[Ln(fod)_4]^-$ compared to $Ln(fod)_3X^-$.

Other mechanisms cannot be ruled out, however, in explaining the relative effectiveness of $[Ln(fod)_4]^-$ and $Ln(fod)_3$ as shift reagents for organic cations. The shifts in the spectrum of an organic cation in the presence of an anionic shift reagent are probably predicted by the dipolar shift equation (*58*). It may be that the geometric term of the dipolar shift equation (distance and angle terms) with $[Ln(fod)_4]^-$ results in larger shifts than for $[Ln(fod)_3X]^-$.

Sulfonium Salts. The NMR spectra of sulfonium salts with halide or tetrafluoroborate counterions exhibit large shifts in the presence of $[Eu(fod)_4]^-$. The shifts recorded in the spectra of di-*n*-butylmethylsulfonium iodide and -tetrafluoroborate with several shift reagents are listed in Table I. The shifts in the NMR spectra of both salts with $Eu(fod)_3$ are included in the table for comparison. The effectiveness of the species $[Eu(fod)_4]^-$ relative to $Eu(fod)_3$ as a shift reagent for sulfonium salts is apparent. One interesting observation is that the resonances of the diastereotopic hydrogen atoms of the methylene group α to the sulfur atom are resolved in the spectra with $[Eu(fod)_4]^-$. No resolution of these diastereotopic protons was observed in the presence of $Eu(fod)_3$.

The selection of M(fod) to use in the formation of $[Eu(fod)_4]^-$ depends on the identity of the counterion of the sulfonium salt. The data presented in Table I for di-*n*-butylmethylsulfonium iodide and di-*n*-butylmethylsulfonium tetrafluoroborate illustrate this conclusion. The species $[Eu(fod)_4]^-$ formed from $Eu(fod)_3$–Ag(fod) was more effective as a shift reagent for the sulfonium halide than $[Eu(fod)_4]^-$ formed from $Eu(fod)_3$–K(fod). The opposite was found for the sulfonium tetrafluoroborate salt. A similar pattern was noted for the shifts in the spectra of the halide and tetrafluoroborate salts of the *S*-methyltetrahydrothiophenium and *n*-butyldimethylsulfonium cations with $Eu(fod)_3$–Ag(fod) and $Eu(fod)_3$–K(fod).

The influence of M(fod) on the magnitude of the shifts most likely reflects differences in the solubility of the K^+ and Ag^+ salts with the halide and tetrafluoroborate ions. This was shown by adding a solution of the chloroform-soluble salt benzyldimethylsulfonium tetrafluoroborate to solutions of $Ag[Eu(fod)_4]$ and $K[Eu(fod)_4]$. With the silver reagent no precipitation was observed until high substrate concentrations were employed. With the potassium reagent a precipitate (presumably KBF_4) was noted on the first addition of substrate. By an analogous study the reverse properties were shown using a solution of *N*-methylnicotinium iodide in chloroform. The first introduction of substrate to the silver reagent resulted in a precipitate, presumably AgI. With the potassium reagent, the solution only developed a slight cloudiness until high concentration of substrate were added. If the anion of the organic salt does not precipitate with the cation of the shift reagent, the association of the organic cation with the shift reagent will be reduced and smaller shifts will result. The use of K(fod) is therefore recommended with tetrafluoroborate salts and Ag(fod) is recommended for halide salts.

As can be seen from the data in Table I, the shifts in the spectrum of di-*n*-butylmethylsulfonium tetrafluoroborate with $Eu(fod)_3$–K(fod) are similar in magnitude to those of di-*n*-butylmethylsulfonium iodide with $Eu(fod)_3$–Ag(fod). The same shifts would result if the anion of the salt precipitated with the cation of the shift reagent. Each sample would then contain an ion pair of the sulfonium cation with $[Eu(fod)_4]^-$. Identical observations have been noted with the tetrafluoroborate and iodide salts of the *S*-methyltetrahydrothiophenium and *n*-butyldimethylsulfonium cations.

The shifts in the spectrum of butyl sulfide with $Eu(fod)_3$ are also presented in Table I. These shifts are small and agree with a previous conclusion that chelates of fod are relatively ineffective as NMR shift reagents for organosulfides (*59*). Chelates with 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonanedione were reportedly more effective NMR shift reagents for organosulfides (*59*), but the magnitudes of the shifts do not compare with those in the spectra of sulfonium cations in the presence of $[Ln(fod)_4]^-$.

The proton NMR spectra of the *S*-methyltetrahydrothiophenium cation with and without $[Eu(fod)_4]^-$ are shown in Figure 1. This compound has four different ring protons, the resonances of which were completely resolved in the shifted spectrum. No resolution of the geminal pairs (H_a from H_b and H_c from H_d) was observed in the unshifted spectrum recorded at 60 MHz. Only small shifts were recorded in the spectrum of the *S*-methyltetrahydrothiophenium cation with $Eu(fod)_3$. This confirms that $[Eu(fod)_4]^-$ forms an ion pair with the cation rather than associating with the cation at the lone pair of electrons of the sulfur atom. Assuming that the $[Eu(fod)_4]^-$ associates near the sulfur atom, the shifts of H_a and H_b would be larger than those of H_c and H_d. Resolution of the four different hydrogen atoms of the ring indicates that $[Eu(fod)_4]^-$ must be preferentially located toward one face of the ring. This would place the shift reagent closer to either the methyl group or the lone pair of electrons of the sulfur atom. The exact geometry of the shift reagent–substrate complex cannot be determined from the shift data and unequivocal assignment of the H_a,H_b and H_c,H_d pairs cannot be made at this time.

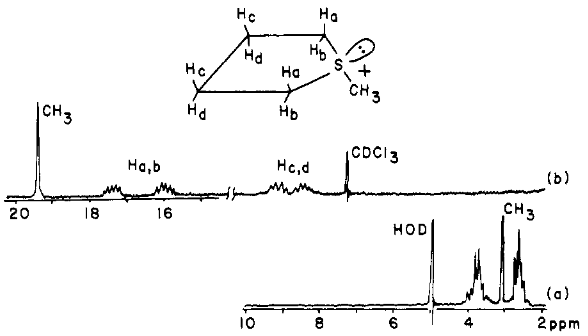
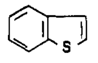


Figure 1. Proton NMR spectrum of *S*-methyltetrahydrothiophenium iodide (0.1 M) in (a) D_2O and (b) in $CDCl_3$ with $[Eu(fod)_4]^-$ (0.05 M). $[Eu(fod)_4]^-$ was formed in solution from $Eu(fod)_3$ and Ag(fod).

The spectra of sulfonium salts of aromatic sulfides such as phenyl sulfide and benzothiophene (II) are shifted in the presence of $[Ln(fod)_4]^-$. The shifts in the spectrum of ethyldiphenylsulfonium tetrafluoroborate with $[Eu(fod)_4]^-$ were too small to be of practical utility. In a solution containing $[Yb(fod)_4]^-$ (0.1 M) and this substrate (0.1 M) the resonances of the protons ortho to the sulfur atom were shifted by 1.60 ppm. The protons meta and para to the sulfur atom were unresolved and exhibited shifts of approximately 0.5 ppm. The shifts for the methylene resonance of the ethyl group were less than 0.5 ppm. The steric encumbrance of this substrate probably reduces the association constant with the shift reagent causing the small shifts. A similar conclusion was postulated to explain the small shifts in the spectrum of diphenylamine hydrochloride with $[Eu(fod)_4]^-$ (*22*).



II

In the spectra of benzothiophene and the *S*-methylbenzothiophenium ion at 60 MHz, none of the aromatic protons exhibit unique resonances. Essentially no shifts are observed in the spectrum of benzothiophene with $Eu(fod)_3$. Shifts are observed in the spectrum of benzothiophene with binuclear shift reagents (*18, 60*). By use of $Pr(fod)_3$–ag(tfa) (0.15 M) first-order spectrum was obtained at 250 MHz for benzothiophene (0.1 M) (*18*). The largest shift with this reagent was −2.87 ppm for the H-2 resonance. The spectrum of *S*-methylbenzothiophenium tetrafluoroborate (0.1 M) with $[Eu(fod)_4]^-$ (0.05 M) is shifted and three doublets and one complex multiplet are observed between 7 and 10 ppm. The three doublets are probably the resonances for the protons at the 2, 3, and 7 positions. Assuming the resonance furthest shifted is that of H-2, a shift of 2.57 ppm was obtained. Unfortunately the resonances were too close together in the shifted spectrum to permit decoupling experiments and assignment.

Large shifts were observed in the spectra of *n*-butyldimethylsulfonium iodide and -tetrafluoroborate and benzyldimethylsulfonium tetrafluoroborate with $[Eu(fod)_4]^-$. The NMR spectra of benzyldimethylsulfonium tetrafluoroborate (0.1 M) with and without $[Eu(fod)_4]^-$ (0.1 M) are shown in Figure 2. In this example the shift reagent was formed from $Eu(fod)_3$ and K(fod). The spectrum with the shift reagent is first order. Both the *n*-butyldimethylsulfonium and benzyldimethylsulfonium salts were prepared by reacting the corresponding alkyl halide with methyl sulfide in the presence

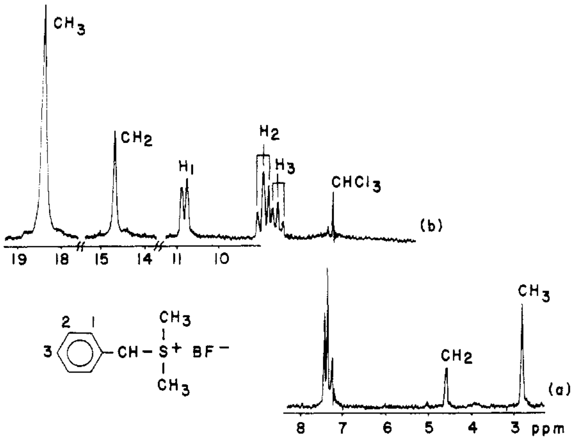


Figure 2. Proton NMR spectrum of benzyldimethylsulfonium tetrafluoroborate (0.1 M) in $CDCl_3$ with (a) no shift reagent and (b) $[Eu(fod)_4]^-$ (0.1 M). $[Eu(fod)_4]^-$ was formed in solution from $Eu(fod)_3$ and K(fod).

Table II. Lanthanide Induced Shifts (ppm) in the NMR Spectra of 1-Iodobutane (0.2 M), *n*-Butyldimethylsulfonium Iodide (0.1 M), and *n*-Butylisothiouronium Iodide (0.1 M) in $CDCl_3$

shift reagent (concn)	1	2	3	4
$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2I$				
$Yb(fod)_3$–Ag(fod) (0.1 M)	1.57[a]	1.00	0.64	0.47
$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2S(CH_3)_2{}^+I^-$				
$Eu(fod)_3$–Ag(fod) (0.05 M)	7.3	4.3	2.5	1.6
$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2S{-}\overset{NH_2}{\overset{\mid}{C}}{=}NH_2{}^+I^-$				
$Eu(fod)_3$–Ag(fod) (0.05 M)	3.8	2.7	1.9	1.2
$Yb(fod)_3$–Ag(fod) (0.05 M)	14.5	9.9	6.3	3.7

[a] From ref 9.

of $AgBF_4$. The spectra of alkyl chlorides, bromides, and iodides are not shifted in the presence of lanthanide tris chelates (*29*) and are shifted only slightly in the presence of binuclear lanthanide-silver reagents (*17*, *30*). Conversion of alkyl halides to their corresponding sulfonium salts represents a useful method to obtain a shifted NMR spectrum of the alkyl group. Unfortunately, only reactive alkyl halides can be converted into sulfonium salts. A more general scheme for the conversion of primary and secondary alkyl halides into salts is to prepare isothiouronium derivatives (*23–25*).

Isothiouronium Salts. Table II presents shift data for the spectra of 1-iodobutane, *n*-butyldimethylsulfonium iodide, and *n*-butylisothiouronium iodide with several shift reagents. The H_2 and H_3 resonances partially overlap in the unshifted spectra of 1-iodobutane and the two salts. The shifts observed in the spectrum of 1-iodobutane with $Yb(fod)_3$–Ag(fod) were small (*17*), and the H_2 and H_3 resonances were not fully resolved at 60 or 90 MHz. Previous reports have concluded that the binuclear reagents are marginally effective shift reagents for primary alkyl halides (*17*, *30*). The largest shifts are observed for iodo derivatives with the binuclear reagents (*17*).

As evidenced from the data in Table II, the shifts in the spectra of the sulfonium and isothiouronium salts with $[Ln(fod)_4]^-$ are significantly larger than those in the spectrum of the alkyl halide with $Ln(fod)_3$ (*29*) or $Ag[Ln(fod)_4]$ (*17*). Whereas the shifts in the spectra of sulfonium salts are adequate with $[Eu(fod)_4]^-$, the shifts in the spectra of isothiouronium salts with $[Eu(fod)_4]^-$ are not of much practical utility. This observation probably reflects the longer distance between the lanthanide ion and alkyl portion of the molecule in the isothiouronium derivatives. Employing $[Yb(fod)_4]^-$, a more powerful downfield shift reagent than $[Eu(fod)_4]^-$, results in larger and more useful shifts. The spectra of isothiouronium salts with $[Yb(fod)_4]^-$ exhibit more broadening than those observed with $[Eu(fod)_4]^-$. The broadening is within acceptable levels, however, and the fine structure due to coupling was usually present in the spectrum. The species $[Yb(fod)_4]^-$ is therefore recommended over $[Eu(fod)_4]^-$ for the study of isothiouronium salts.

The spectra of the isothiouronium salts of primary halides including 1-bromopentane, 1-bromononane, 1-chlorobutane, and benzyl chloride exhibited large shifts in the presence of $[Yb(fod)_4]^-$. The first five methylene resonances of *n*-nonylisothiouronium bromide (0.1 M) were fully resolved in the presence of $[Yb(fod)_4]^-$ (0.1 M). The proton NMR spectrum of benzylisothiouronium chloride (0.1 M) was first order in the presence of $[Pr(fod)_4]^-$ (0.05 M) and $[Yb(fod)_4]^-$ (0.05 M) at 60 MHz. The shifts in the spectrum of *n*-butylisothiouronium chloride with $[Yb(fod)_4]^-$ were essentially the same as those in the spectrum of *n*-butylisothiouronium iodide with $[Yb(fod)_4]^-$ (see Table II). Such an observation is consistent with precipitation of the halide counterion from solution as a silver halide salt.

Similar shifts were also noted in the spectra of *sec*-butylisothiouronium chloride and bromide in the presence of $[Yb(fod)_4]^-$. The hydrogen atoms of the methylene group of these substrates are diastereotopic and were fully resolved (shift difference of 1.2 ppm) in the presence of the shift reagent. The two secondary butylisothiouronium salts are chiral and attempts were made to resolve resonances of the dextro and levo enantiomers using chiral shift reagents. The chiral shift reagents formed from $Eu(facam)_3$–Ag(fod), $Eu(hfbc)_3$–Ag(fod), $Pr(hfbc)_3$–Ag(ptb), and $Pr(facam)_3$–Ag(fod) were evaluated. These particular binuclear reagents were selected because of their demonstrated effectiveness at causing enantiomeric resolution in the spectra of olefins and aromatics (*33*, *61–64*). Only with $[Eu(facam)_3(fod)]^-$ was any enantiomeric resolution obtained in the spectrum of *sec*-butylisothiouronium bromide. In this case the methyl resonance α to the asymmetric carbon was slightly resolved ($\Delta\Delta\delta$ = 0.05 ppm) when both the substrate and shift reagent were at 0.1 M.

Solvents. The effectiveness of $[Ln(fod)_4]^-$ as a shift reagent for organic salts was compared in chloroform-*d*, acetonitrile-d_3, acetone-d_6, and benzene-d_6. Essentially no shifts were observed in the spectra of benzyldimethylsulfonium tetrafluoroborate and *n*-butylisothiouronium iodide in the presence of $[Eu(fod)_4]^-$ in acetonitrile-d_3 and acetone-d_6. One possibility is that these solvents bond to the europium and prevent adequate formation of $[Eu(fod)_4]^-$ and/or the ion pair. An alternative explanation is that the anion of the organic salt may not precipitate with the cation of the shift reagent. In the case of the iodide salt, precipitation of silver iodide was apparent in both acetone and acetonitrile, ruling out the second mechanism. With the tetrafluoroborate salt, no precipitate was observed with the potassium reagent and both mechanisms may be operative. The shifts for the same two substrates in benzene-d_6 and chloroform-*d* were comparable in magnitude. Both solvents are suitable for use with the anionic shift reagents.

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RECEIVED for review July 14, 1986. Accepted October 29, 1986. We thank Bates College and Roger C. Schmutz for their support through a College Research Grant.

Supersonic Jet Spectroscopy with a Capillary Gas Chromatographic Inlet

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Supersonic jet spectroscopy is a highly selective molecular detection method that has suffered from relatively poor sensitivity. Sensitivity problems arise in part from the sample dilution effect of a free jet expansion. We report a new type of jet nozzle based upon sheath flow gas dynamic focusing that enriches the central core of the jet with analyte to provide better overlap with the incident laser beam. For a constant flow of analyte, the fluorescence intensity along the center line of a focused jet expansion is 30 times greater than that of an unfocused jet expansion. This method allows a detection limit of 50 pg ($S/N = 3$) to be achieved for naphthalene and provides a simple way to couple a capillary gas chromatograph to a supersonic jet expansion. The focusing and cooling properties of analyte enriched jets are presented, and spectral selectivity is illustrated for the detection of naphthalene in unleaded gasoline.

The selectivity of supersonic jet spectroscopy as a potential analytical tool is now well established. In this method, the analyte is seeded into a free jet expansion of a rare gas (He, Ar, Xe) from a high-pressure region into a vacuum. Isentropic cooling of the gas during the expansion reduces the thermal population of excited rotational and vibrational levels in the analyte. As a result, molecular absorption and/or excitation spectra are remarkably free of spectral congestion due to hot band transitions (*1*). The ability of supersonic jet spectroscopy to distinguish among similar compounds, thereby allowing a qualitative identification of an unknown sample, has been the subject of several recent publications (*2–9*). In contrast, only a few quantitative studies have been reported (*8, 10*). In each case, the sample was injected into a packed-column gas chromatograph. A small pinhole at the end of the column served as the supersonic jet orifice. The gas chromatograph served only as a quantitative injection device and was not designed for optimum separation efficiency. Detection limits were found to be in the 20–200 ng range.

The sensitivity of analytical jet spectroscopy is ultimately limited by the characteristics of the jet expansion itself. To achieve maximum cooling, the sample must be probed in the free-flow region of the jet, typically 50 nozzle diameters downstream from the jet orifice. At this position, the sample partial pressure is reduced by ca. 10^4 from its value prior to

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