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NMR SPECTRA OF THIOLSULFINATES CONTAINING HETEROSTERIC[1] GROUPS. USE OF A CHEMICAL SHIFT REAGENT.

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Chemical shift non-equivalence of heterosteric groups has been reported for a number of organosulfur compounds, including sulfinates[2-4], sulfites[2,3,5-8], sulfinamides[9], sulfoxides[5,10-14], sulfide-borane adducts[10], sulfonium salts[15], and sulfonium ylids[16,17].

Several recent reports have described the ability of the lanthanide shift reagents to simplify complex NMR spectra[18,19]. In organosulfur chemistry, the shift reagent tris (dipivalomethanato)-europium (III), Eu $(DPM)_3$, has been used to assist in the assignment of configuration in several sulfoxides and a cyclic thiolsulfinate[22]. This same reagent has also been used to great advantage in revealing the presence of heterosteric protons in some sulfoxides[23].

In this communication, we report the use of the shift reagent, tris (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-d_6-4,6-octanedione-d_3)-europium (III), Eu-FOD-d_{27}, in simplifying the complex NMR spectra of some thiolsulfinates containing heterosteric protons or methyl groups.

Ethyl ethanethiolsulfinate and isopropyl isopropanethiolsulfinate were prepared by photosensitized oxidation of the corresponding disulfides as previously described[24]. Benzyl toluenethiolsulfinate was prepared by the m-chloroperbenzoic acid oxidation of dibenzyl disulfide (white crystals, m.p. 82-82.5°, lit.[25] m.p. 84-86°, yield 44%; IR (nujol) 1042 cm^{-1} (s=o); mass spectral peak at m/e 262, parent).

The best results were obtained in the isopropyl isopropanethiolsulfinate case (Fig. 1). The unshifted spectrum (C_6D_6) contains a multiplet centered at 1.18 δ due to the methyl groups and two multiplets at 3.38 and 2.84 δ due to the methine protons. In the presence of Eu-FOD-d_{27} (.2987 moles thiolsulfinate,

.1689 moles shift reagent) the spectrum consists of four separate doublets at 4.38, 3.70, 2.87 and 2.55 δ for the methyl groups and two multiplets at 7.10 and 6.08 δ for the methine hydrogens. The presence of four doublets for the methyl groups indicates that both isopropyl groups contain heterosteric methyl groups due to the presence of the sulfinyl function. Using the LAOCOON program[26], the unshifted methyl spectrum could be simulated using J=7 Hz and δ=1.08, 1.13, 1.20 and 1.25[27].

The spectrum of the disulfide remains unchanged in the presence of Eu-FOD-d_{27} indicating that complexing occurs through the sulfinyl group. In $CDCl_3$ solvent the chemical shifts of the thiolsulfinate increase linearly with Eu-FOD-d_{27} concentration up to a molar ratio of ca. 0.6 after which the dependence was non-linear. The magnitude of the shift was not dependent upon the concentration (as opposed to molar ratio) of shift reagent. It has been suggested[28] that the quantity Δ(Eu), defined as the difference in chemical shifts between the proton resonance in $CDCl_3$ and in the same solvent containing an equimolar amount of $Eu(DPM)_3$, be used as a measure of the strength of the paramagnetic induced shifts. Andersen and Uebel have calculated a Δ(Eu) value of ca. 8.9 for the methyl groups in dimethyl sulfoxide[23]. Applying a similar definition to the Eu-FOD-d_{27} reagent, we are able to calculate Δ(Eu) values of 1.97, 2.05, 4.19, and 4.60 for the methyl groups of isopropyl isopropanethiolsulfinate[29].

For ethyl ethanethiolsulfinate the unshifted spectrum (C_6D_6) consists of a multiplet centered at 1.07 δ due to the methyl groups and a multiplet centered at 2.68 δ for the methylene groups. In the presence of Eu-FOD-d_{27} (.2003 moles thiolsulfinate, .1448 moles shift reagent) the spectrum consisted of two triplets at 5.18 and 3.24 δ and two multiplets at 8.87 and 6.35 δ. The multiplets are not simple quartets, indicating the presence of heterosteric protons. On this basis, each of the triplets could be interpreted as being composed of two overlapping doublets. Addition of more shift reagent failed to further resolve the triplets. The unshifted (C_6D_6/CCl_4-3/1) spectrum of benzyl toluenethiolsulfinate consisted of a doublet at 3.92 δ due to the benzyl protons and a singlet at 7.07 δ due to the aromatic protons. With Eu-FOD-d_{27} added (.1451 moles thiolsulfinate,

.03881 moles shift reagent) the spectrum consisted of two partially-resolved doublets at 6.00 and 5.55δ for the benzyl protons and a widespread complex multiplet for the aromatic protons. The partially-resolved doublets are presumably the central two peaks of AB quartets due to the heterosteric protons. Addition of more shift reagent shifts the doublets underneath the aromatic proton absorption.

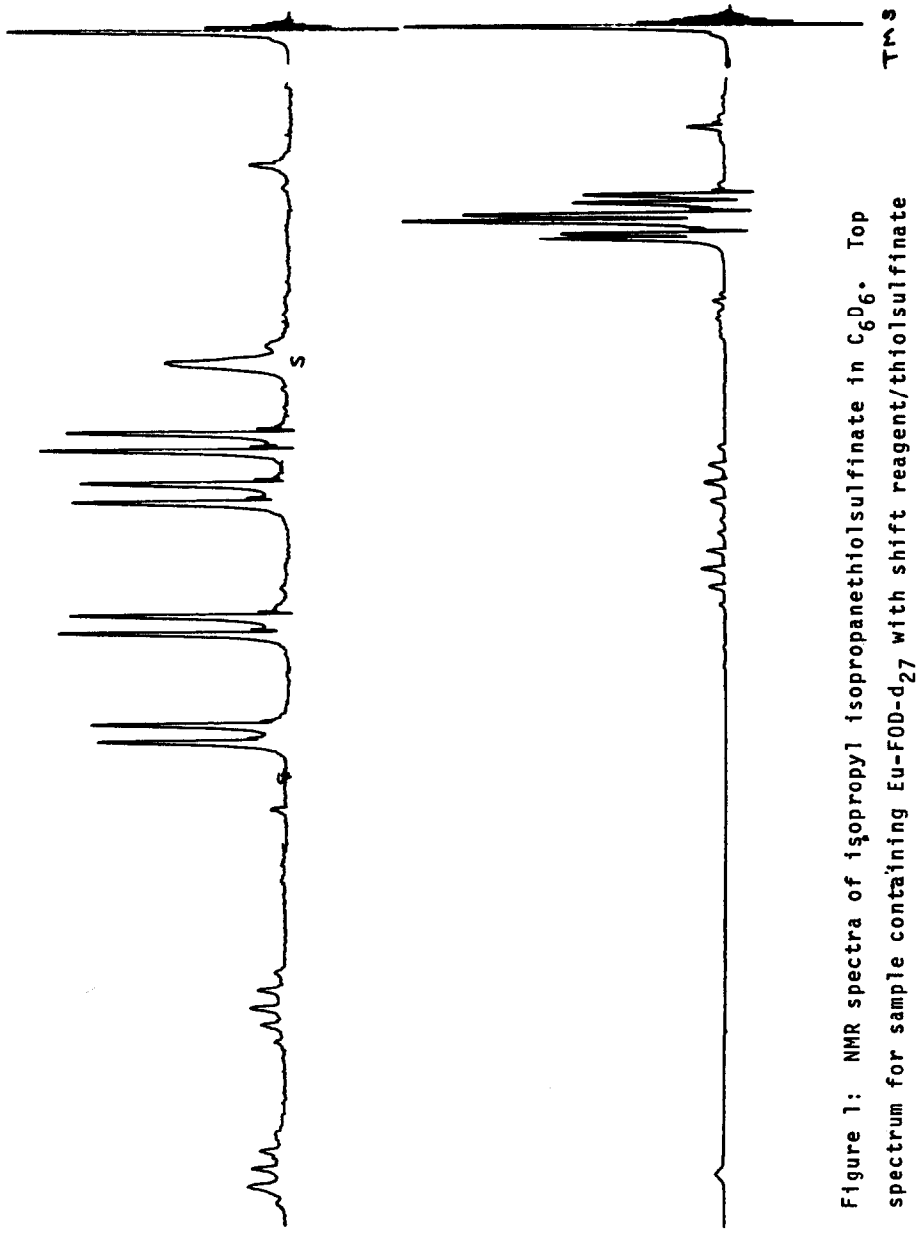

Figure 1: NMR spectra of isopropyl isopropanethiolsulfinate in C_6D_6. Top spectrum for sample containing Eu-FOD-d_{27} with shift reagent/thiolsulfinate molar ratio = .565. Bottom spectrum is for sample with no shift reagent. The Peak marked S is due to the shift reagent.

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