Tetrahedron Letters No.60, pp. 5253-5255, 1970. Pergamon Press. Printed in Great Britain.

USE OF TRISDIPIVALOMETHANATOEUROPIUM(III) AS A NUCLEAR RESONANCE CHEMICAL SHIFT REAGENT IN THE ANALYSIS OF THE SPECTRA OF SOME SULFOXIDES

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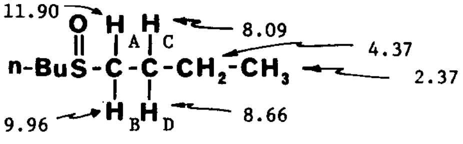
(Received in USA 13 November 1970; received in UK for publication 25 November 1970)

Pseudocontact effects between a paramagnetic metal ion and its ligands have proven helpful in the past in interpreting the nmr spectrum, in particular the proton n.m.r. spectrum, of the ligands.[1] Unusually large chemical shifts spread out a spectrum, simplify it, and often make it amenable to first order analysis. Recently, Hinckley[2,3] has pointed out that the dipyridine adduct of trisdipivalomethanatoeuropium(III), Eu(DPM)$_3$•2Py, when added to solutions of alcohols, ketones, and other molecules capable of complexing with the europium, caused downfield shifts of the protons which were a function of the distance of the proton from the europium and which consequently simplified the spectral analyses. Sanders and Williams[4] showed that Eu(DPM)$_3$ is preferable to the pyridine complex and gave examples of the usefulness of the former as a chemical shift reagent. Demarco and coworkers[5] have published two communications on the use of Eu(DPM)$_3$ as a shift reagent for use in the analysis of conformationally-fixed alcohols, steroids, and terpenoids. Hart and coworkers[6] demonstrated that Pr(DPM)$_3$ causes even larger chemical shifts, but in an upfield direction.

This communication describes some of our results with Eu(DPM)$_3$ and sulfoxides. Most striking perhaps is the case of dibutyl sulfoxide in which a CCl$_4$ solution (0.5 ml) of sulfoxide (0.32 mmol) and Eu(DPM)$_3$ (0.32 mmol) gave not only large chemical shifts, but as a result of a difference in their chemical shifts and coupling constants, clearly revealed the diastereotopic nature of the β-protons. The structural formula below indicates the chemical shifts of the various protons with and without Eu(DPM)$_3$ obtained at 60 MHz and their differences, all in ppm, downfield from TMS. The coupling constants were obtained by computer analysis of the spectrum using the LAOCOON program.[7]



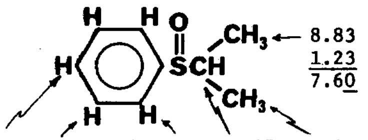
$n\text{-BuS}(=O)\text{-CH}_A\text{H}_B\text{-CH}_C\text{H}_D\text{-CH}_2\text{-CH}_3$

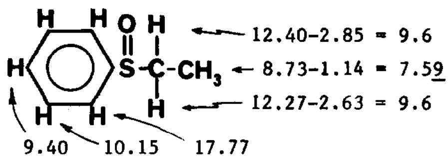
J_{AB} = -13.6
J_{CD} = -14.0
J_{AC} = 9.9
J_{BC} = 6.4
J_{AD} = 5.3
J_{BD} = 10.3

Without Eu(DPM)$_3$: δ 2.61 (rough t, J≃7Hz, SC$\underline{H}_2$); 1.6 (m, (C$\underline{H}_2$)$_2$CH$_3$); 0.98 (t, C$\underline{H}_3$)

The spectra of ethyl phenyl sulfoxide and 2-propyl phenyl sulfoxide were also obtained (0.66 ml CCl_4, 0.64 mmol sulfoxide, 0.32 mmol $Eu(DPM)_3$). The results are shown below.

CHEMICAL SHIFTS OF SULFOXIDES WITH AND WITHOUT $EU(DPM)_3$





9.45	9.80	17.38	12.27	8.45	with $Eu(DPM)_3$	9.40	10.15	17.77
7.48	7.48	7.48	2.72	1.02	without $Eu(DPM)_3$	7.53	7.53	7.53
1.97	2.32	9.90	9.55	7.43		1.87	2.62	10.24

The aromatic protons give spectra which closely resemble the one obtained for benzyl alcohol plus $Eu(DPM)_3$ in that the ortho hydrogens form a doublet about 10 ppm downfield from their normal position while the para and meta hydrogens each give a triplet roughly 2.5 ppm downfield.[4] While the aromatic portion of the spectrum was simplified, the chemical shifts for the diastereotopic methylene protons moved closer together with a resultant complication of this part of the spectrum.

As expected, the chemical shifts increase linearly with $Eu(DPM)_3$ concentration for a given sulfoxide concentration. This was established for carbon tetrachloride solutions of dimethyl sulfoxide up to 0.467 M with $Eu(DPM)_3$/DMSO ratios between zero and one. Even though the solubility of $Eu(DPM)_3$ increases markedly in carbon tetrachloride upon the addition of sulfoxide, considerable difficulty was encountered in preparing the more concentrated solutions. The t-butyl proton absorptions of $Eu(DPM)_3$ were visible in these spectra at about 111 Hz upfield from internal cyclohexane and were quite concentration independent, i.e., ±3 Hz over the entire concentration range. Thus it should be possible in most cases to extrapolate back to zero $Eu(DPM)_3$ concentration to obtain the chemical shift in the absence of the complex. Figure 1 shows some of the plots which have been obtained with DMSO. Demarco[5] et al. have suggested the quantity $\Delta(Eu)$, as a measure of the strength of the paramagnetic induced shifts observed in alcohols. It is defined as the difference in chemical shifts between the proton resonance in deuteriochloroform and its position in the same solvent containing an equal molar amount of complex; i.e., $\Delta(Eu)=\delta(CDCl_3)-\delta(Eu(DPM)_2^{n=1})$. From figure 1 it can be seen that $\Delta(Eu)$ is not well defined for sulfoxides since the magnitude of the shift depends upon both the molar ratio and the concentration. However, at concentrations which are comparable to those used for the alcohols we calculate $\Delta(Eu)\approx 8.9$ for DMSO. For the comparable protons in open chain alcohols, the β protons, $\Delta(Eu)$ values of about 12-14 may be calculated.[4,5] Although sulfoxide shifts are 25-35% smaller than alcohol shifts, they are nevertheless quite large with $Eu(DPM)_3$ and apparently much larger than with $Eu(DPM)\cdot 2$ pyridine.[3]

Our work on the use of shift reagents in the analysis of the spectra of sulfoxides and related compounds is continuing.

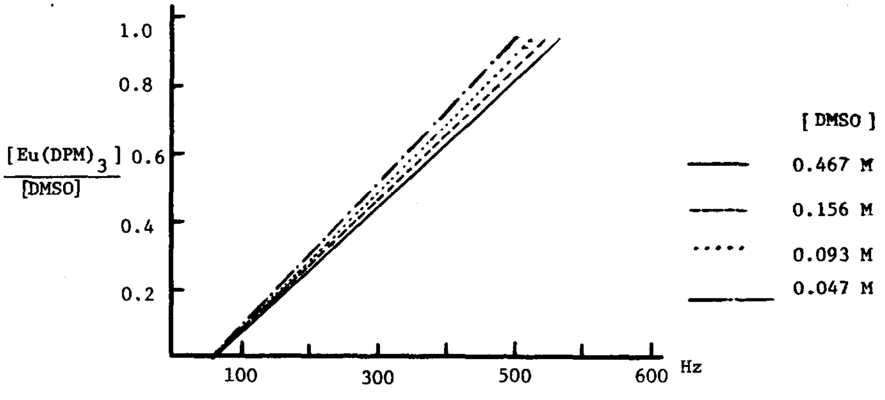


Figure 1. ^{a}Shifts are in Hz downfield from internal cyclohexane at 60 MHz.

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8. This research was sponsored in part by grants from the U. S. Public Health Service GM-10800 and the National Science Foundation, GP-8701 and GP-8136.