

THE EFFECT OF  $\text{Eu}(\text{DPM})_3$  ON THE NMR SPECTRA  
OF SULFHYDRYL COMPOUNDS

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A lot of recent reports have shown the ability of the shift reagent, tris(dipivalomethanato) europium (III),  $\text{Eu}(\text{DPM})_3$ , in spreading out and simplifying complicated NMR spectra.<sup>2</sup> The valuable utility of the technique is demonstrated by a number of structural problems which have been solved via its use.<sup>3-6</sup> A few attempts have been hitherto made at sulfur-containing compounds,<sup>7-11</sup> whereas there is no example of the application of the technique to sulfhydryl compounds.

In the course of our investigation on the chemical structures of natural sulfur-bearing compounds from asparagus,<sup>12, 13</sup> we observed that each proton signal due to two sulfhydryl groups in dihydroasparagusic acid methyl ester (I) was shifted downfield by  $\text{Eu}(\text{DPM})_3$ .<sup>14</sup> This finding led us to examine whether the downfield shift of proton signals in sulfhydryl compounds are generally induced by  $\text{Eu}(\text{DPM})_3$ . This communication describes some results concerning the effect of  $\text{Eu}(\text{DPM})_3$  on NMR spectra of mono- and di-sulfhydryl compounds.

The NMR spectra were obtained using a Varian T-60, A-60 D, and HA-100 spectrometers with Mr values between 0.045 and 0.50 (Mr = molar ratio of  $\text{Eu}(\text{DPM})_3$ /substrate).<sup>\*1</sup>  $\Delta\delta(\text{Hz})$  values, as defined by Demarco et al,<sup>15</sup> represent the difference in the resonance position for a given solute proton from that when an equimolar amount of  $\text{Eu}(\text{DPM})_3$  is present, and we estimated the value from the slope of the straight line obtained from plots of  $\Delta\delta(\text{Hz})$  vs Mr. The spectra were measured at five different molar ratios to obtain each slope.

Ethyl mercaptan showed overlapping signals due to methyl and sulfhydryl groups at  $\delta$  1.2-1.5 (Fig. 1a), which was changed to a simple triplet by an addition of  $\text{D}_2\text{O}$ . Addition of  $\text{Eu}(\text{DPM})_3$  to this compound in  $\text{CCl}_4$  with a molar ratio of 0.073 caused the signals to separate completely (Fig. 1b), where, all the signals shifted downfield and, interestingly, SH appeared as a doublet of doublet.<sup>16</sup> When  $\text{Eu}(\text{FOD})_3$  was added instead of  $\text{Eu}(\text{DPM})_3$ , the magnitude in proton shifts was small-

er than that with  $\text{Eu(DPM)}_3$  (Fig. 2).

From the  $\Delta\text{Eu}$  values in the Table, the followings can be seen: a. Protons in aliphatic compound are shifted much more than those in aromatic compounds. b. The additivities of the induced downfield shifts were not observed at  $\alpha$  and  $\beta$  protons when ethyl and propyl mercaptans were compared with the corresponding ethylene and trimethylene mercaptans. c. The sulfhydryl proton has a much smaller induced shift value than the hydroxyl proton. From the competition experiment<sup>17</sup> (an equimolar amount of ethyl mercaptan and ethyl alcohol was allowed to compete for  $\text{Eu(DPM)}_3$  in  $\text{CCl}_4$ ), we concluded that a sulfhydryl group coordinates with the shift reagent less effectively than a hydroxyl group by the factor of 1:9, this is in good agreement with the known relative basicity of thiol and alcohol.<sup>18, 19</sup>

Variation in induced shifts in different solvents ( $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$ ,  $\text{CDCl}_3$ , and  $\text{CCl}_4$ ) have been plotted (Fig. 3) and the relative shift power has been estimated from the gradient of the straight line. The order of the magnitude of the induced shifts was  $\text{CS}_2 > \text{CCl}_4 > \text{C}_6\text{H}_6 > \text{CDCl}_3$ . The larger shift was observed in  $\text{CS}_2$  and  $\text{CCl}_4$ , in particular,  $\text{CCl}_4$  is generally a good solvent for mercaptans because the induced shift increased linearly with an increment of Mr values.

The effect of  $\text{Eu(DPM)}_3$  on the NMR spectra of polyfunctional compounds, i.e., dihydroasparagusic acid methyl ester (I), asparagusic acid methyl ester (II), and trimethylene mercaptan (III) were shown in Fig. 4, in which each proton signal is shifted differently. Since it is known that a sulfide group shows negligible coordination with  $\text{Eu(DPM)}_3$ ,<sup>10</sup> the proton shift in compound II is essentially due to the coordination of the ester group. In compound I, however, the induced shifts of both  $\text{CO}_2\text{Me}$  and SH are relatively smaller than those of II ( $\text{CO}_2\text{Me}$ ) and III (SH). In addition to the smaller shift values, compound I caused clearly the increase in the solubility of  $\text{Eu(DPM)}_3$  in  $\text{CCl}_4$ , and the magnitude permitting the dissolution was the order of  $\text{I} > \text{II} > \text{III}$ . These evidence might suggest that sulfhydryl and ester groups of I coordinate cooperatively with the shift reagent.

In conclusion, we have found that a sulfhydryl group coordinates with  $\text{Eu(DPM)}_3$  and the coordination simplifies the spectra of sulfhydryl compounds, even in the presence of other moiety having the Lewis basicity centre. These results show that the shift reagent can be applied to an NMR study of the structural elucidation of a sulfhydryl compound.

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## References

\*1 Due to the insolubility of  $\text{Eu}(\text{DPM})_3$ , spectra could not be measured at higher Mr values.

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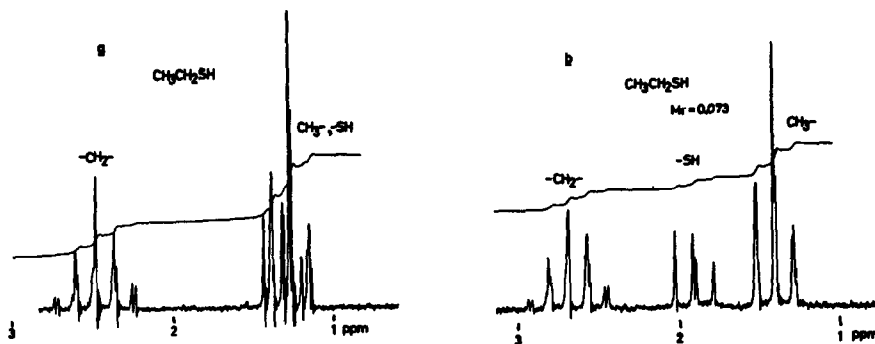


Fig. 1. NMR Spectrum of ethyl mercaptan in  $\text{CCl}_4$   
 a. Uncoordinated with  $\text{Eu}(\text{DPM})_3$       b. Coordinated with  $\text{Eu}(\text{DPM})_3$

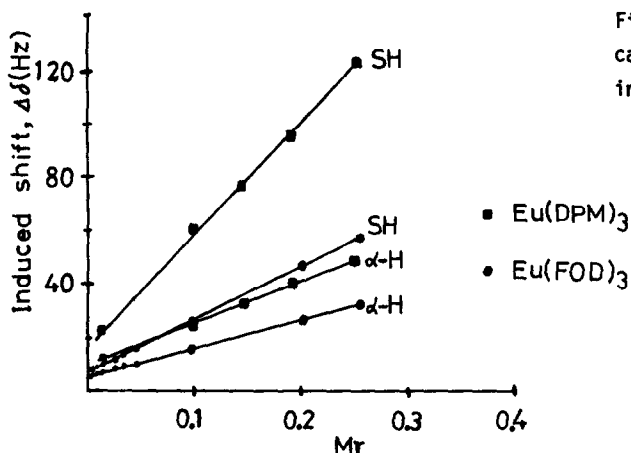


Fig. 2 Induced shift of ethyl mercaptan with  $\text{Eu}(\text{FOD})_3$  and  $\text{Eu}(\text{DPM})_3$  in  $\text{CCl}_4$  (60 MHz).

Table 1.  $\Delta\text{Eu}$  values (Hz) of different protons of mercaptans in  $\text{CCl}_4$  (60 MHz).

Compounds	S-H	$\alpha$ -H	$\beta$ -H	$\gamma$ -H	Others
$\text{CH}_3\text{CH}_2\text{SH}$	510	203	126		
$\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$	685	235	85	61	
$\text{HSCH}_2\text{CH}_2\text{SH}$	515	184			
$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{SH}$	480	219	188		
$\text{C}_6\text{H}_5\text{SH}$	183				64
$\text{CH}_3\text{CH}_2\text{OH}$	4650*	1150	690		

\* Hydroxyl proton

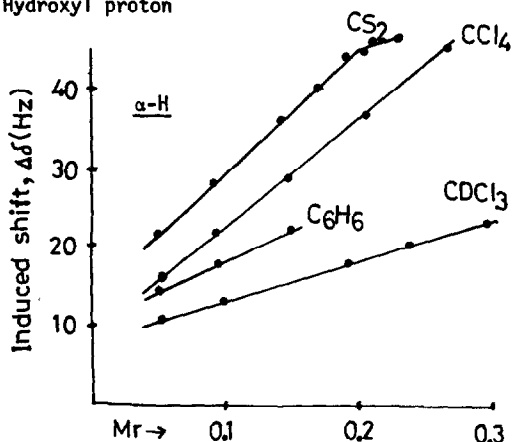


Fig. 3 Effects of solvents on the induced shifts of ethyl mercaptan (60 MHz).

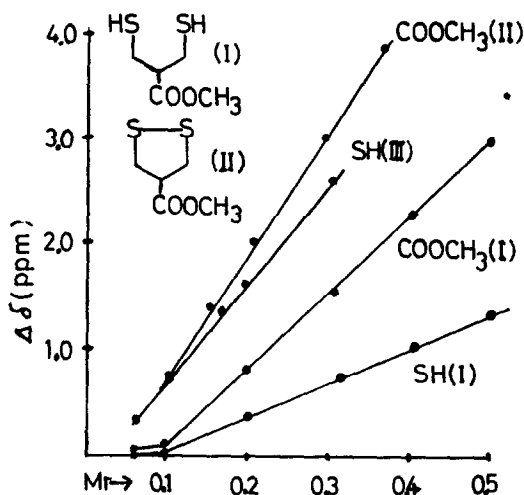


Fig. 4 Effect of  $\text{Eu}(\text{DPM})_3$  on the induced shifts of I, II, and III in  $\text{CCl}_4$  (100 MHz).