UV absorption of 1-indanone (in 96 % ethanol): λ_{max} 2460 Å (ε 11 963); 2940 (ε 2634).

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Lanthanide-Induced Shifts in Proton Magnetic Resonance Spectra of Some Simple Di-, Tri-, and Tetracoordinate Sulfur Compounds

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Lanthanide "shift reagents", introduced by Hinckley in 1969,[1] have been rapidly and widely adopted as powerful tools in the analysis of proton magnetic resonance spectra of several classes of organic molecules possessing Lewis base character.[2,3] Sulfur-containing substrates studied are as yet few, comprising sulfoxides,[4-8] thioamides,[9] and thionocarbamates,[10] besides a number of somewhat more special cases including sulfone,[8] thioether,[8,11] p-toluenesulfonyl,[12] thioketal,[13,14] hemithioketal,[14] phosphorothiolate,[15] phosphorodithiolate,[15] and thiolohypophosphite [16] groupings.

In connection with current work in this laboratory, we have measured the paramagnetic shifts induced by tris(7,7-dimethyl-1,1,1,2,2,3,3-heptafluoro-4,6-octane-dionato)europium(III), (Eu(fod)$_3$),[17] in the ${}^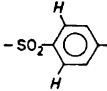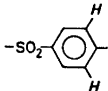1$H-spectra of deuteriochloroform solutions of a series of di-, tri-, and tetracoordinate dimethyl sulfur compounds. The data are presented in Table 1. All measurements were performed at constant substrate concentration, with increasing amounts (up to 30 mol %) of Eu(fod)$_3$ added. The induced shifts, believed to be pseudocontact in nature,[2] were extrapolated to 100 mol % Eu(fod)$_3$ by the least-squares method (from observed shifts at 0, 10, 20, and 30 mol %) and are presented as $\Delta_{Eu(fod)_3}$-values, as defined by Demarco et al.[18]

The correlation between the electronegativity of the functional group (expressed as δ_0-values) and the induced shifts is obvious (compare compounds Nos. 1, 2, 4, 5, and 6). Qualitative application of the simplified third-order distance dependence equation,[2] $\Delta_{Eu(fod)_3} \propto r^{-3}$, to the N-p-toluenesulfonyl derivatives 3, 7, and 8, reveals the oxygen atoms of the sulfonyl-groups as the predominant coordination sites, competitively affected though by the introduction of an oxygen atom or, even more, an NH-group on the dimethylated sulfur atom. The competitive effect is reflected also in the aromatic moiety.

The present data suggest that rare-earth chemical-shift reagents may prove useful as a diagnostic tool in future studies of tri- and tetra-coordinate sulfur compounds.

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Table 1. Eu(fod)$_3$-Induced pseudocontact shifts, $\Delta_{\text{Eu(fod)}_3}$, of di-, tri-, and tetracoordinate sulfur compounds.[a]

Substrate	CH_3-S	$-SO_2-$⬡(H,H)	$-SO_2-$⬡(H,H)	Ar-CH_3	=NH
1. Me$_2$S	-1.0 ± 0.2[b] (2.12)[c]				
2. Me$_2$SO[d]	-5.8 ± 0.3 (2.61)				
3. Me$_2$SNTs	-1.90 ± 0.03 (2.68)	-6.5 ± 0.1 (7.72)	-1.37 ± 0.05 (7.22)	-0.77 ± 0.07 (2.39)	
4. Me$_2$SO$_2$	-8.5 ± 0.3 (2.98)				
5. Me$_2$S(O)NH	-9.1 ± 0.3 (3.08)				$ca. -70$[e] (2.65)
6. Me$_2$S(NH)$_2$[f]	-12.05 ± 0.03 (3.11)				$ca. -50$[e] (2.01)
7. Me$_2$S(O)NTs[g]	-3.4 ± 0.3 (3.33)	-5.0 ± 0.3 (7.82)	-1.0 ± 0.2 (7.25)	-0.62 ± 0.07 (2.38)	
8. Me$_2$S(NH)NTs[g,h]	-5.7 ± 0.1 (3.33)	-4.8 ± 0.1 (7.82)	-0.68 ± 0.07 (7.25)	-0.30 ± 0.03 (2.39)	[i]

[a] All measurements were performed at ordinary probe temperature on a Varian HA-60D instrument using 0.33 M CDCl$_3$-solutions of substrate, unless otherwise stated. [b] $\Delta_{\text{Eu(fod)}_3}$-Values are given in ppm, along with the 95 % confidence limits derived from the least-squares analyses Correlation coefficients >0.990. [c] Values in parentheses are chemical shifts, δ_0, without Eu(fod)$_3$, given in ppm downfield from internal tetramethylsilane. [d] Previously studied in tetrachloromethane solution, with tris(dipivaloylmethanato)europium (III) as the shift reagent.[4] [e] By linear extrapolation from 0 and 10 mol % Eu(fod)$_3$. Shifts at higher Eu(fod)$_3$ concentrations were not recorded due to considerable signal broadening. [f] Addition of more than 20 mol % Eu(fod)$_3$ caused precipitation. Hence, the measurements were repeated and the least-squares analysis was performed on six points (twice, each at 0, 10, and 20 mol % Eu(fod)$_3$). [g] 0.083 M solutions, due to low solubility of substrate. [h] Previously described by Appel and Lassmann.[19] [i] Not observed.

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