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

I. KARUP NIELSEN and ANDERS KJÆR

Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

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 Sulfur-containing substrates studied are as yet few, comprising sulfoxides,3 thiocyanates,6 thioureas,6 and thionocarbonates,6 besides a number of somewhat more special cases including sulfones,5 thioethers,11 p-toluenesulfonyl,12 thioalkanes,13,14 methiothioalkanes,14 phosphorothiolates,15 phosphorodithiolates,15 and triololypophosphates16 groupings.

In connection with current work in this laboratory, we have measured the paramagnetic shifts induced by tris(7,7,8,8-tetramethyl-1,1,2,2,3,3,5,5-octanedionato)europium(III), (Eu(fod)3),17 in the \(^1\)H-spectra of deuteriochloroform solutions of a series of di-, tri-, and tetracoordinate dimethylsulfur 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 pseudo-contact 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 \(\Delta_{\text{Eu(fod)3}}\)-values, as defined by Demarco et al.18

The correlation between the electronegativity of the functional group (expressed as \(\delta\)-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 \(\Delta_{\text{Eu(fod)3}} \propto r^{-3}\), 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 tetracoordinate sulfur compounds.

Table 1. Eu(fod)$_2$-Induced pseudocontact shifts, $\Delta_{\text{Eu(fod)$_2$}}$, of di-, tri-, and tetracoordinate sulfur compounds.a

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\text{CH}_3\text{S}$</th>
<th>$-\text{SO}_2\text{R}$</th>
<th>$-\text{SO}_2\text{R}$</th>
<th>$\text{Ar-CH}_3$</th>
<th>$=\text{NH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Me$_2$S</td>
<td>$-1.0 \pm 0.2^b$ (2.12)$^c$</td>
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<tr>
<td>2. Me$_3$SO</td>
<td>$-5.8 \pm 0.3$ (2.61)</td>
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<tr>
<td>3. Me$_2$SNT$_S$</td>
<td>$-1.90 \pm 0.03$ (2.68)</td>
<td>$-6.5 \pm 0.1$ (7.72)</td>
<td>$-1.37 \pm 0.05$ (7.22)</td>
<td>$-0.77 \pm 0.07$ (2.39)</td>
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<tr>
<td>4. Me$_3$SO$_2$</td>
<td>$-8.5 \pm 0.3$ (2.98)</td>
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<tr>
<td>5. Me$_2$S(O)NH</td>
<td>$-9.1 \pm 0.3$ (3.08)</td>
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<tr>
<td>6. Me$_3$S(NH)$_3$</td>
<td>$-12.05 \pm 0.03$ (3.11)</td>
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<tr>
<td>7. Me$_2$S(O)NT$_S$</td>
<td>$-3.4 \pm 0.3$ (3.33)</td>
<td>$-5.0 \pm 0.3$ (7.52)</td>
<td>$-1.0 \pm 0.2$ (7.25)</td>
<td>$-0.62 \pm 0.07$ (2.35)</td>
<td></td>
</tr>
<tr>
<td>8. Me$_2$S(NH)NT$_S$</td>
<td></td>
<td>$-5.7 \pm 0.1$ (3.33)</td>
<td>$-4.8 \pm 0.1$ (7.82)</td>
<td>$-0.68 \pm 0.07$ (7.25)</td>
<td>$-0.30 \pm 0.03$ (2.39)</td>
</tr>
</tbody>
</table>

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. $^a$Values are given in ppm, along with the 95% confidence limits derived from the least-squares analyses. Correlation coefficients $>0.990$. $^b$Values in parentheses are chemical shifts, $\delta$, without Eu(fod)$_2$, given in ppm downfield from internal tetramethylsilane. $^c$Previously studied in tetrachloromethane solution, with tris(dipivaloylmethanato)europium (III) as the shift reagent. $^d$By linear extrapolation from 0 and 10 mol % Eu(fod)$_2$. Shifts at higher Eu(fod)$_2$ concentrations were not recorded due to considerable signal broadening. $^e$Addition of more than 20 mol % Eu(fod)$_2$ caused precipitation. Hence, the measurements were repeated and the least-squares analysis was performed on six points (twice, at each 0, 10, and 20 mol % Eu(fod)$_2$). $^f$0.083 M solutions, due to low solubility of substrate. $^g$Previsously described by Appel and Lassmann. $^h$Not observed.


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