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THE EFFECT OF SHIFT REAGENT ON THE CONFORMATIONAL EQUILIBRIUM OF 3,3'-DISUBSTITUTED DIPHENYLSULFINES

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Shift reagents have widely been used in NMR spectroscopy, particularly in the determination of molecular geometry. So far little attention has been given to its use in the study of mobile conformational equilibria. The use of shift reagents in such mobile systems can give rise to NMR spectra which are difficult to interpret. Some authors recognized the possibility that complexation with shift reagents can change the conformational preference, others neglected such effects. In one instance, viz, of the conformational equilibrium of cyclic phosphonates, the perturbation caused by added shift reagents has been treated quantitatively. The sum of the percentages of uncomplexed and complexed conformers was obtained from an analysis of coupling constants.

In this paper we wish to present an analysis of the conformer populations of 3,3'-disubstituted diphenylsulfines (I) in the complexed state by means of chemical shift differences and to compare these conformer populations with those in the uncomplexed state. In addition, the solvent dependency on the conformational equilibrium in the complexed state is being compared with that in the uncomplexed state.

The system of 3,3'-disubstituted diphenylsulfines can be described as an equilibrium between the two rotamers P and Q, which differ in the relative orientation of the group dipole moments of the substituent X and the CSO group (μ_{CSO} = 3.62 D, directed towards the sulfine oxygen with an angle of 25° with the carbon sulfur bond). The proportions of these rotamers in different media have been obtained by an evaluation of the difference in anisotropic deshielding effect of the CSO system on the protons H1 and H5. It was found that the rotational equilibrium strongly depends on the polarity of the solvent in the sense that the
population of the more polar rotamer (P for X = Cl or NO₂ and Q for X = OCH₃ or CH₃) increases with increasing solvent polarity.

The shift reagent, Eu(dpm)₃, complexes with sulfines at the sulfone oxygen. Consequently the LI shifts for the ortho protons of the A-ring will be much larger than for those of the B-ring. Furthermore, complexation of Eu(dpm)₃ with rotamer P will show a much larger downfield shift for proton H₁, which is situated closest to the CSO system, than for proton H₅. The reverse will be true for the complexed rotamer Q.

The proportions of the rotamers P and Q in the complexed state can be obtained as follows. When z equiv. of shift reagent are added, we assume that for a 1:1 complexation a fraction z of the total amount of sulfine is in the complexed state. This fraction z consists of a proportion a of rotamer P and a proportion b of rotamer Q. The LI shifts of protons H₁ and H₅ (Δ₁ and Δ₅) are expressed by the equations

\[ Δ₁ = \delta(H₁)_{\text{exp}} - \delta(H₁)_{\text{free}} = z \left( aP^\text{max} + bQ^\text{max} \right) \]

\[ Δ₅ = \delta(H₅)_{\text{exp}} - \delta(H₅)_{\text{free}} = z \left( aP^\text{max} + bQ^\text{max} \right) \]

By making the assumptions that P^\text{max}_1 = Q^\text{max}_5 and P^\text{max}_5 = Q^\text{max}_1, which means that the effect of the position of the substituent X on the coordination of Eu(dpm)₃ with the CSO group is being neglected, the expression \( P_1/(P_1 + Q_5) \) becomes a measure for the proportion a (equation 3).

\[ \frac{P_1}{P_1 + Q_5} = \frac{\Delta₁ - zbQ¹^\text{max}}{\Delta₁ - zbQ¹^\text{max} + \Delta₅ - zaQ₅^\text{max}} = a \]

\[ \frac{P_1}{P_1 + Q_5} = \frac{\Delta₁ - zaQ₁^\text{max}}{\Delta₁ + \Delta₅ - 2zaQ₁^\text{max}} = a \]

P₁ stands for the LI shift of proton H₁ in the conformer P upon addition of one equiv. of Eu(dpm)₃. Q₅ represents the LI shift of proton H₅ in conformer Q for a given amount of shift reagent. However, the parameters to calculate a from equation (3) are experimentally only partly available. The expression (4) also equals a provided that the assumptions P^\text{max}_1 = Q^\text{max}_5 and P^\text{max}_5 = Q^\text{max}_1 are incorporated.

In good approximation, for the quantity \( zaQ₁^\text{max} \) may be taken the shift difference for the ortho protons H₆ and or H₁₀ of ring B resulting from complexation of the sulfine with one equiv. of Eu(dpm)₃. By means of equation (4) the proportion of rotamer P in the complexed state can be obtained from the observed LI shifts. The figure shows these shifts as they were found for sulfine Ib in CDCl₃. The results thus obtained for the four sulfines in different solvents are listed in the Table, which also includes the rotamer populations in the uncomplexed state.
The data in the Table reveal that in the three different solvents studied the proportion of conformer P in the complexed state is much smaller\textsuperscript{17} than in the uncomplexed state. Thus, as well for sulfines Ia and Ib for which rotamer P is the more polar one, as for sulfines Ic and Id for which rotamer Q is the more polar one, complexation with Eu(dpm)\textsubscript{3} leads to a larger preference for rotamer Q. This effect cannot be due to changes in polarity of the medium caused by the presence of the shift reagent because the behaviour of the sulfines Ia and Ib towards changes in medium polarity is opposite to that of the sulfines Ic and Id (vide supra). A likely explanation for the effect of Eu(dpm)\textsubscript{3} on the conformational

\begin{table}[h]
\centering
\begin{tabular}{|c|ccc|ccc|ccc|}
\hline
\multirow{2}{*}{Compd.} & \multicolumn{3}{c|}{Ia} & \multicolumn{3}{c|}{Ib} & \multicolumn{3}{c|}{Ic} \\
\cline{2-10}
 & A\textsubscript{1} & A\textsubscript{5} & A\textsubscript{6,10} & A\textsubscript{1} & A\textsubscript{5} & A\textsubscript{6,10} & A\textsubscript{1} & A\textsubscript{5} & A\textsubscript{6,10} \\
\hline
Solvent & & & & & & & & & \\
CC\textsubscript{14} & 5.57 & 9.35 & 2.70 & 9.40 & 6.80 & 2.90 & 7.81 & 8.79 & 3.00 \\
CCl\textsubscript{3} & 3.47 & 5.72 & 1.60 & 2.14 & 5.05 & 1.40 & 5.16 & 6.03 & 1.90 \\
CH\textsubscript{2}Cl\textsubscript{2} & 2.80 & 4.30 & 1.25 & 1.21 & 2.55 & 0.70 & 3.46 & 3.17 & 1.15 \\
\hline
% P\textsubscript{c} & % P\textsubscript{u} & % P\textsubscript{c} & % P\textsubscript{u} & % P\textsubscript{c} & % P\textsubscript{u} & % P\textsubscript{c} & % P\textsubscript{u} & \\
CC\textsubscript{14} & 29 & 45 & 63 & 100 & & & & 45 & 72 \\
CCl\textsubscript{3} & 31 & 19 & 54 & 83 & & & & 43.5 & \\
CH\textsubscript{2}Cl\textsubscript{2} & 34 & 70\textsuperscript{a} & 22 & 40\textsuperscript{a} & & & & & 41 \\
CH\textsubscript{3}COCH\textsubscript{3} & 100 & 80 & & & & & & & 56 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a} % P\textsubscript{c} = percentage of conformer P in the complexed state; % P\textsubscript{u} = percentage of conformer P in the uncomplexed state. A-values in ppm obtained upon addition of 0.8 equiv. of Eu(dpm)\textsubscript{3}. Spectra recorded at 60 Mhz. Conc. 20 mg/0.5 ml. a: see note 16.
equilibrium is that steric interactions between the meta substituent X and the coordinated shift reagent result in a larger proportion of rotamer Q in which such interactions are minimized. The data in the Table show further that in the complexed sulfines the proportion of the more polar conformer (P for Ia and Ib, Q for Ic and Id) becomes larger in a solvent of a higher dielectric constant. Thus, in the complexed as well as in the uncomplexed state the conformational equilibrium shifts to the more polar rotamer with increasing solvent polarity. For the sulfines Ic and Id the difference in solvent effect on the conformer population in the complexed and uncomplexed state is small. However, in the uncomplexed sulfines Ia and Ib the effect of solvent polarity on the conformational equilibrium is large while in the complexed state this effect has become much smaller. Apparently, in the latter sulfines the steric effects caused by complexation with the shift reagent are dominating over the solvent effect.

In conclusion this study shows that mobile conformational equilibria can considerably be perturbed by complexation with lanthanides and that utmost care should be taken in studying such equilibria with the use of shift reagents.

REFERENCES AND NOTES

1. Part 26 in the series "Chemistry of Sulfines", part 25, see ref. 9.
10. The position of phenyl ring B cannot be specified, because H5 and H10 do not show up sufficiently different in the spectra for reasons that the anisotropic effect of the OSO system on these protons is negligible.
13. Δ1 reflects the LI shift of proton H1 for the same proportion of rotamers in the uncomplexed and complexed state, which a priori will not be the case. However, the formulation as given in the equations (1) and (2) is allowed, because in comparison with the magnitude of the LI shift δ(H1)free will vary only little when the rotamer ratio in the uncomplexed state becomes different from that in the complexed state.
14. The distance of the coordinated Eu(dpm)3 to proton H1 in the Q conformer or to proton H5 in the P conformer is about the same as the distance of Eu(dpm)3 to the ortho protons of ring B. Moreover, the value of Qfmax is small in comparison with that of pfmax or Qfmax, which means that a rather large deviation in Qfmax leads to only a small change in a.
15. The percentage of P in the complexed state has been calculated for different amounts of added shift reagent. The same value was obtained as is predicted from equation (4).
16. These percentages are derived from the spectra in dichloromethane in the manner as described in ref. 9 without making a correction for the solvent effects.
17. An exception is sulfine Ib in CDCl3 which has already predominantly conformation Q in the uncomplexed state.