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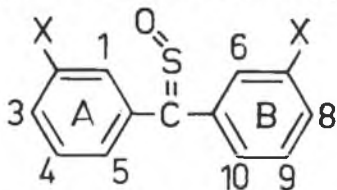
THE EFFECT OF SHIFT REAGENT ON THE CONFORMATIONAL EQUILIBRIUM
OF 3,3'-DISUBSTITUTED DIPHENYLSULFINES¹

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Shift reagents have widely been used in NMR spectroscopy², 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 interpret³. Some authors^{4,5} recognized the possibility that complexation with shift reagents can change the conformational preference, others^{6,7} neglected such effects. In one instance⁸, *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.

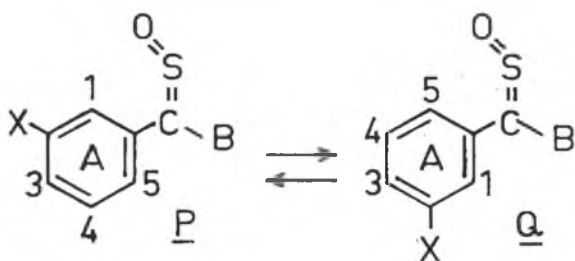


- Ia: X = Cl
- Ib: X = NO₂
- Ic: X = DCH₃
- Id: X = CH₃

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 described⁹ as an equilibrium between the two rotamers¹⁰ P and Q, which differ in the relative orientation of the group dipole moments of the substituent X and the CSO group ($\mu_{\text{CSO}} = 3.62$ D, directed towards the sulfine oxygen with an angle of 25° with the carbon sulfur bond¹¹).



The proportions of these rotamers in different media have been obtained⁹ 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 sulfine oxygen¹². 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 CSD 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 (Δ_1 and Δ_5) are expressed by the equations¹³ (1) and (2) in which $\delta(H_1)_{\text{free}}$ is the δ -value of proton H₁ in the spectrum without Eu(dpm)₃ and P_1^{max} is the LI shift of H₁ upon addition of one equiv. of Eu(dpm)₃ for *a* = 1. $\delta(H_5)_{\text{free}}$, Q_1^{max} , P_5^{max} and Q_5^{max} are defined analogously.

$$(1) \Delta_1 = \delta(H_1)_{\text{exp}} - \delta(H_1)_{\text{free}} = z (aP_1^{\text{max}} + bQ_1^{\text{max}})$$

$$(2) \Delta_5 = \delta(H_5)_{\text{exp}} - \delta(H_5)_{\text{free}} = z (aP_5^{\text{max}} + bQ_5^{\text{max}})$$

By making the assumptions that $P_1^{\text{max}} = Q_5^{\text{max}}$ and $P_5^{\text{max}} = Q_1^{\text{max}}$, which means that the effect of the position of the substituent X on the coordination of Eu(dpm)₃ with the CSD group is being neglected, the expression $P_1/(P_1 + Q_5)$ becomes a measure for the proportion *a* (equation 3).

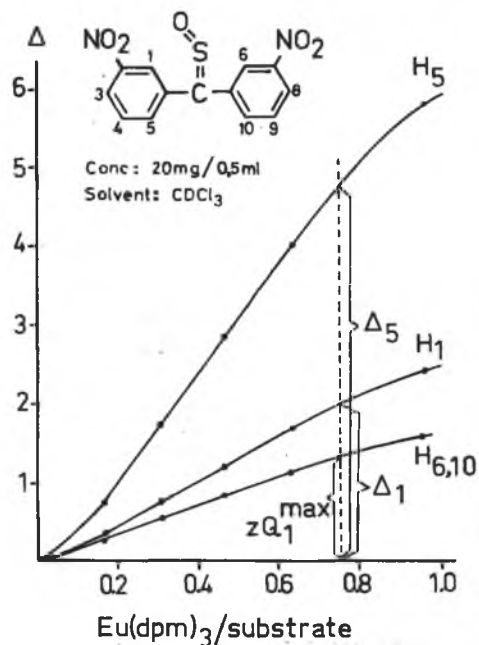
$$(3) \frac{P_1}{P_1 + Q_5} = \frac{\Delta_1 - zbQ_1^{\text{max}}}{\Delta_1 - zbQ_1^{\text{max}} + \Delta_5 - zaP_5^{\text{max}}} = a$$

P_1 stands for the LI shift of proton H₁ in the conformer P upon addition of *z* equiv. of Eu(dpm)₃. Q_5 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 to *a* provided that the assumptions $P_1^{\text{max}} = Q_5^{\text{max}}$ and $P_5^{\text{max}} = Q_1^{\text{max}}$ are incorporated.

$$(4) \frac{\Delta_1 - zQ_1^{\text{max}}}{\Delta_1 + \Delta_5 - 2zQ_1^{\text{max}}} = a$$

In good approximation¹⁴ for the quantity zQ_1^{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 *z* equiv. of Eu(dpm)₃. By means of equation (4) the proportion of rotamer P in the complexed state can be obtained¹⁵ from the observed LI shifts. The figure shows these shifts as they were found for sulfine Ib in CCl₄. 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 state⁹.



The data in the Table reveal that in the three different solvents studied the proportion of conformer P in the complexed state is much smaller¹⁷ 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)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)₃ on the conformational

TABLE

| Compd. | Ia | | | Ib | | | Ic | | | Id | | |
|-----------------------------------|----------------|------------------|-------------------|----------------|------------------|-------------------|----------------|------------------|-------------------|----------------|------------------|-------------------|
| | Δ ₁ | Δ ₅ | Δ _{6,10} | Δ ₁ | Δ ₅ | Δ _{6,10} | Δ ₁ | Δ ₅ | Δ _{6,10} | Δ ₁ | Δ ₅ | Δ _{6,10} |
| CCl ₄ | 5.57 | 9.35 | 2.70 | | | | 9.40 | 6.80 | 2.90 | 7.81 | 8.79 | 3.00 |
| COCl ₃ | 3.47 | 5.72 | 1.60 | 2.14 | 5.05 | 1.40 | | | | 5.16 | 6.03 | 1.90 |
| CH ₂ Cl ₂ | 2.80 | 4.30 | 1.25 | 1.21 | 2.55 | 0.70 | 3.46 | 3.17 | -1.15 | 3.80 | 4.77 | 1.45 |
| | | % P _c | % P _u | | % P _c | % P _u | | % P _c | % P _u | | % P _c | % P _u |
| CCl ₄ | | 29 | 45 | | | | | 63 | 100 | | 45 | 72 |
| CDCl ₃ | | 31 | | | 19 | 16 | | | | | 43.5 | |
| CH ₂ Cl ₂ | | 34 | 70 ^a | | 22 | 40 ^a | | 54 | | | 41 | |
| CH ₃ COCH ₃ | | | 100 | | | 80 | | | 83 | | | 56 |

% P_c = percentage of conformer P in the complexed state; % P_u = percentage of conformer P in the uncomplexed state. Δ-values in ppm obtained upon addition of 0.8 equiv. of Eu(dpm)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.

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10. The position of phenyl ring B cannot be specified, because H₆ and H₁₀ do not show up sufficiently different in the spectra for reasons that the anisotropic effect of the CSO system on these protons is negligible.
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13. Δ_1 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 $\delta(H_1)_{free}$ 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 Q_1^{max} is small in comparison with that of P_1^{max} or Q_5^{max} , which means that a rather large deviation in Q_1^{max} 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.