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# SPECIFIC BROADENING OF THE METHYL GROUPS SIGNALS IN $^1$H NMR SPECTRA OF TERTIARY SILANOLS IN THE PRESENCE OF TRIS(DIPIVALOMETHANE)EUROPIUM CHELATE

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## Summary

Specific proton signal broadening observed for methyl groups of methylphenylsilanols in the presence of tris(dipivalomethane)europium chelate, is absent in the spectra of analogous carbinols under the same conditions. This unexpected behaviour is probably caused by restricted rotation of the methyl groups, due to steric hindrance of the t-butyl groups of a molecule of the dipivalomethane chelate, intermolecularly associated to the silanol complex through a coordinative bond of the carbonyl oxygen and the silicon atom. The lower relative "bound" shifts of the methyl-silanol groups in comparison with the same shifts of the carbinols, are additional effects of the proposed intermolecular association.

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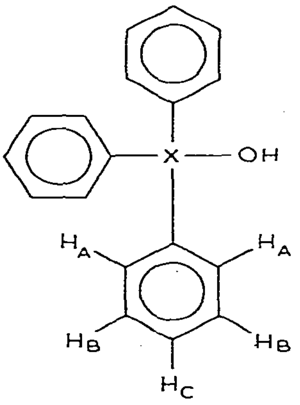
## Introduction

In a preliminary communication [1] we reported the effect of tris(dipivalomethane)europium chelate Eu(DPM)$_3$ on the proton spectra of CCl$_4$ and CDCl$_3$ solutions of tertiary silanols $(C_6H_5)_x(CH_3)_n \cdot SiOH$ ($x = 3 - n$; $0 \leqslant n \leqslant 2$) at 25°C.

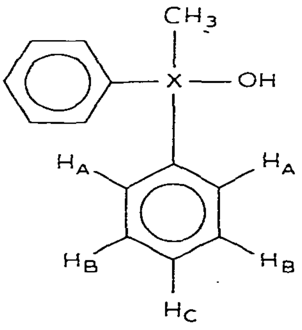
Compared with the protons of the phenyl groups, the methyl groups showed larger induced shifts and considerable concentration dependent lanthanide shift reagent signal broadening. Specific signal broadening has been recorded in lanthanide shifted NMR spectra for flavonemethoxyl signals [2] and for 4-methyl group signal of *N*-butyl-*N*-(4-methoxylazol-2-yl)-2-methylpropionamide [3]. These compounds are capable of bifunctional, 6-membered ring chelation to the lanthanide atom. In the case of monofunctional tertiary silanols the specific broadening of methyl groups signals must obviously have a different origin.

## Experimental

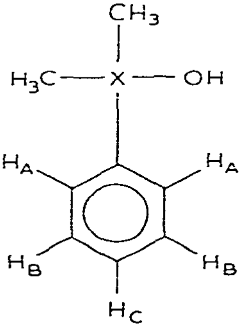
Triphenylsilanol (I), methyldiphenylsilanol (II), dimethylphenylsilanol (III) [4], triphenylcarbinol (IV) [5], methyldiphenylcarbinol (V) [6], and dimethylphenylcarbinol (VI) [7] were prepared by published procedures. Eu(DPM)$_3$ was used as purchased from Merck Sharp and Dohme. Carbon tetrachloride was kept over a molecular sieve prior to use. Proton spectra of 0.1 *M* solutions of silanols and carbinols in $CCl_4$ with small stepwise addition of Eu(DPM)$_3$ (reagent to substrate ratios 0.1—0.6) were recorded at 25°C on a JEOL JNM-3 H-60 spectrometer and referred to TMS ($\delta$ 0.00 ppm).



(I) X = Si
(IV) X = C



(II) X = Si
(V) X = C



(III) X = Si
(VI) X = C

The values of $\rho$ were determined by least-squares method as the slopes of plots $\Delta\delta$ versus [Eu(DPM)$_3$]/[substrate] according to eq. 1 [8] where $\delta$(S) are

$$\delta(\mathrm{Eu}) - \delta(\mathrm{S}) = \frac{[\mathrm{Eu(DPM)_3}]}{[\mathrm{substrate}]} \cdot \rho \qquad (1)$$

the chemical shifts of proton signals in the NMR spectra of substrates and $\delta$(Eu) are the chemical shifts in the NMR spectra of substrates after addition of the Eu(DPM)$_3$.

## Results and discussion

For the absolute ($\rho$) and relative ($\rho_0$) values of bound shifts see Table 1.

The values $\rho$ of phenyl protons lie within the range for analogous compounds reported in literature [9] (phenol: $H_A$ ···12.6; $H_B$···4.0, $H_C$···3.1; benzyl alcohol: $H_A$···11.6; $H_B$···3.8; $H_C$···3.0; $CH_2$···24.9).

The lower $\rho$ values for silanols relatively to analogous carbinols correspond to larger distances of individual protons from europium atoms in silanols. Indeed, the ratio of calculated $\rho$ values for $H_C$ of compound IV (*r* 8.0 Å; angle Eu, O, $H_C$ 41°) and for $H_C$ of compound I (*r* 9.48 Å; angle Eu, O, $H_C$ 35°) is only 3% higher than the observed ratio (1.23).

TABLE I

VALUES OF "BOUND" SHIFTS $\rho$ AND OF RELATIVE "BOUND" SHIFTS $\rho_0$ [a] FOR STEPWISE ADDITION OF $Eu(DPM)_3$ TO 0.1 $M$ SOLUTIONS OF THE SILANOLS I—III AND CARBINOLS IV—VI IN CARBON TETRACHLORIDE AT 25°C

| Compound | Registry number | $H_A$ |  | $H_B$ |  | $H_C$ |  | $CH_3$ |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | $\rho$ | $\rho_0$ | $\rho$ | $\rho_0$ | $\rho$ | $\rho_0$ | $\rho$ | $\rho_0$ |
| I | 791-31-1 | 7.60 | 1.00 | 1.00 | 0.13 | 1.00 | 0.13 | — | — |
| II | 778-25-6 | 9.60 | 1.00 | 1.88 | 0.20 | 1.88 | 0.20 | 10.67 | 1.11 |
| III | 5272-18-4 | 11.26 | 1.00 | 2.70 | 0.24 | 2.70 | 0.24 | 12.47 | 1.11 |
| IV | 76-84-6 | 9.80 | 1.00 | 1.27 | 0.13 | 1.27 | 0.13 | — | — |
| V | 599-67-7 | 12.31 | 1.00 | 2.60 | 0.21 | 2.10 | 0.17 | 17.09 | 1.39 |
| VI | 617-94-7 | 14.57 | 1.00 | 3.17 | 0.22 | 2.53 | 0.17 | 19.29 | 1.32 |

[a] The ratio of $\rho$ for each compound to that of proton $H_A$.

The progressive increase of the Eu···OH distance and decrease of the complex stability, associated with the increasing number of phenyl groups, probably is the reason for the parallel decrease of $\rho$ values in both silanols and carbinols. The decreasing stability of the complexes is not primarily due to the increasing acidity of the hydroxyl groups. The ratios of $\rho(H_A)$ for compound VI relative to III and of IV relative to I are 1.49 and 1.48, respectively, while the ratios for $H_B$ of t- and n-butanol relative to $H_A$ for phenol are only 1.27 and 1.10, respectively, despite 6 orders difference of $pK_a$ between butanol and phenol. Also a noteworthy fact is the constancy (±0.5%) of the $\rho(H_A)$ ratios for analogous pairs of carbinols and silanols, although identical effects of the increasing number of phenyl groups on the acidity of both silanols and carbinols is most unlikely.

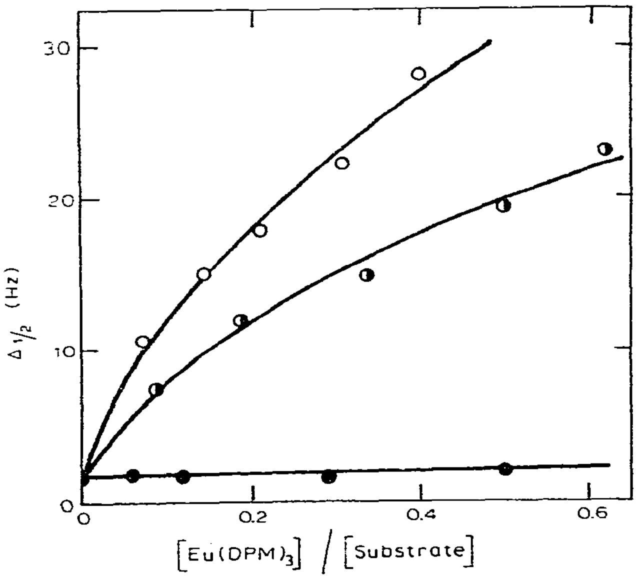
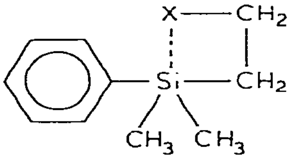


Fig. 1. Observed half-height linewidths of methyl signals as a function of the ratio $[Eu(DPM)_3]/[substrate]$. Substrates: ○ dimethylphenylsilanol (III); ◑ methyldiphenylsilanol (II); ● dimethylphenylcarbinol (VI).

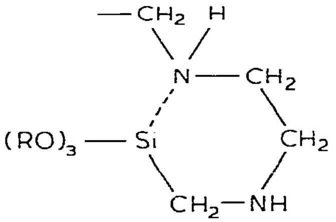
Thus, the progressive increase of Eu$\cdots$OH distances and the decrease of complex stability is probably the result of the increasing steric hindrance with the increasing number of phenyl groups in molecules.

In the light of the similar relative "bound" shifts $\rho_0$ values for the phenyl protons of silanols and carbinols, the large difference between the $\rho_0$ values of the methyl groups is very marked. The contrast is even more striking when the half-height linewidth of the methyl protons for the silanols are compared with those for the carbinols (see Fig. 1).

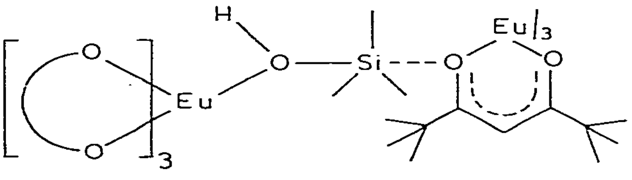
Some tentative calculations confirmed the supposition that this observed unusual broadening of the methyl signals could be brought about by hindered rotation of these groups. Each proton of fixed methyl groups is then exposed to a different pseudocontact influence of the europium atom. This hindered rotation must arise from some specific property of silicon atoms, since the methyl signals of analogous carbinol complexes are narrow. This could be the ability of the silicon atoms to coordinate 5 or 6 ligands, especially in cases where a ligand forms intramolecular bonds. Thus, the observed magnetic non-equivalence of methylene groups protons in the spectra of following compounds VII or VIII [10,11] can be plausibly interpreted in terms of a coordinative bond between the heteroatom and the silicon atom and thus fixation of the chain. However, the analogous intramolecular bond between silicon and oxygen atoms belonging to chelated DPM in the silanol complexes under study would not cause the methyl signal broadening, as can be shown by inspection of the appropriate models, and approximate calculations of pseudocontact influences on the individual protons of the methyl group. It thus seems necessary, to postulate intermolecular association of the type A with methyl groups partially immobilized by steric hindrance from the bulky t-butyl groups.



(VII) X = OH ; Cl



(VIII)



(A)

The observed differences between the methyl proton $\rho_0$ values for silanol complexes (1.11) and the analogous carbinol complexes (1.39) would then be the result of the variations in the geometry of silicon substituents, arising from the intermolecular association and of interference by the europium atom of the associated shift reagent molecules.

The assumption of the steric influence of the t-butyl groups upon the methyl groups mobility is corroborated by the absence of any broadening of the methyl groups signals of the silanols in the presence of fluorinated LSR [12]. Despite the coordinative bonding of this LSR molecule, as confirmed by the very low $\rho_0$ value for the methyl protons (1.00), the fluorinated chain does not restrict the rotation of the methyl groups because of its flexibility.

## References

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