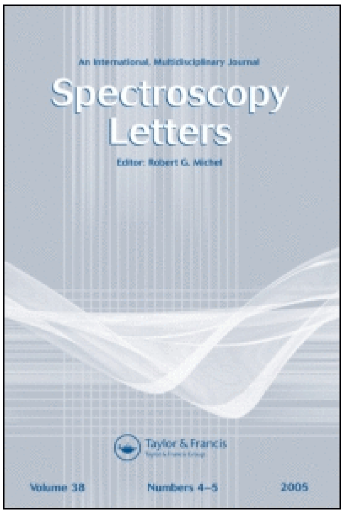

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Lanthanide Shift Reagents II: Pr(TTA)$_3$ a "Two-Way" Shift Reagent for the Ring Protons of Benzylic Systems

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LANTHANIDE SHIFT REAGENTS II: Pr(TTA)$_3$ A "TWO - WAY" SHIFT REAGENT FOR THE RING PROTONS OF BENZYLIC SYSTEMS

KEY WORDS: NMR, Two - Way Shift Reagent, Pr(TTA)$_3$, benzylic System

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In our search for new lanthanide shift reagents, we have recently reported[1] the use of tris(acetylacetonato)ytterbium(III), Yb(acac)$_3$, in producing downfield shifts of PMR signals of benzyl alcohol. During this study, it was noted that the corresponding Pr(acac)$_3$ failed to produce the expected shifts analogous to those by other Pr(III)-complexes[2]. In examining a series of acetylacetonate complexes of the lanthanides and an analysis of the data already available in the literature, it was concluded[1] that the ability of a lanthanide complex to act as a shift reagent is strongly dependent on the nature of the ligand in its coordination shell. Hence, we have started exploring complexes of lanthanide ions with different donor atoms that would act as shift reagents.

In this paper we wish to report the remarkable ability of tris-(thenoyltrifluoroacetonato)Praseodymium(III), Pr(TTA)$_3$, as a shift reagent and, in particular, its pulling-apart effect on aromatic proton signals in benzylic systems. The usual behaviour of Pr(III)-shift reagents is to shift all peaks <u>upfield</u>, while Eu(III)-complexes generally shift all peaks <u>downfield</u>. Pr(TTA)$_3$ is remarkable in the sense that: (a) it produce both upfield and downfield shifts of the ring proton signals in a benzylic

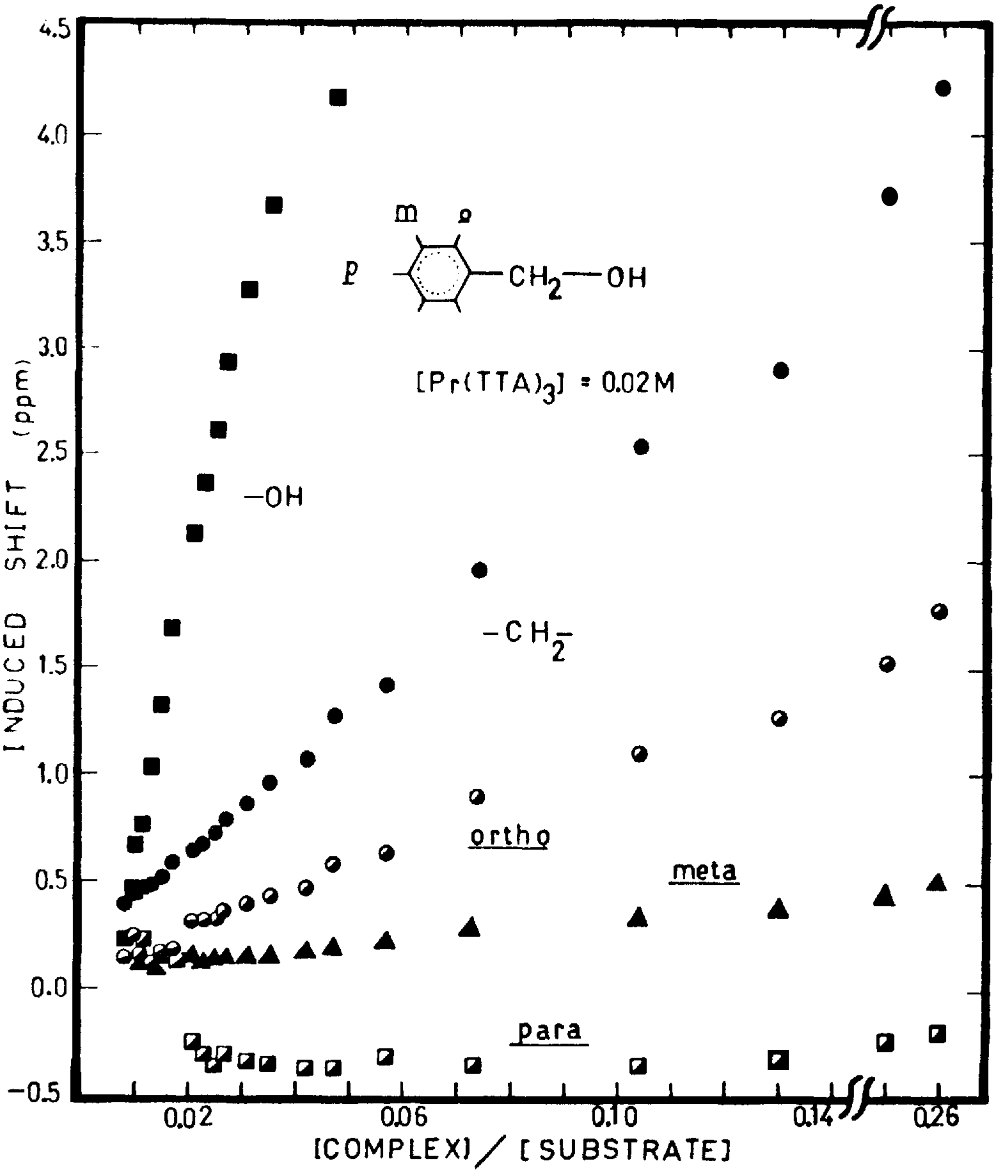

FIGURE 1. Dependence of the Induced Shifts of all Proton Signals in Benzyl Alcohol on the Ratios of Complex : Substrate

system, and (b) a complex: substrate molar ratio of as low as 0.2 produces recognizable shifts.

FIG. 1 shows the typical behaviour of all proton signals in benzyl alcohol for a wide variation in the complex: substrate ratio. In this particular experiment, the concentration of $Pr(TTA)_3$ was kept constant at 0.02 M. We also changed the concentration of the complex and smaller induced shifts were noted with lowering of the concentration of the complex.

It is obvious from FIG. 1 that the hydroxyl proton, CH_2-protons, ortho and meta proton signals undergo the expected upfield shift, while the para proton signal shifts downfield thus exhibiting a "two-way" shift for the ring protons.

This remarkable behaviour prompted us to examine several other benzylic systems and the effects of $Pr(TTA)_3$ on dibenzylether, benzylamine, dibenzylamine, and tribenzylamine are shown in FIG. 2. The separation of the ring protons into ortho, meta, and para peaks for benzylamine and dibenzylamine is easily adduced. However, the ring and CH_2 proton signals of dibenzylether and tribenzylamine remain practically unshifted on the addition of $Pr(TTA)_3$ (FIG. 2). This is rather surprising. Admittedly, there is some steric crowding around the donor nitrogen site of tribenzylamine, but models show that the rotamers of dibenzylether and tribenzylamine have plenty of room left for effective approach of a $Pr(TTA)_3$ molecule.

Several questions present themselves, the most important ones being: (a) whether the absence of shift is an indication of no complex formation between the shift reagent and the substrate (b) the function of H-atom on the donor sites and (c) why $Pr(TTA)_3$ acts as a "two-way" shift reagent. It has also been observed in this laboratory that Pr(III) ion produces a "two-way" shift for the protons of 2,2'-dipyridyl in methanolic solution[3].

In order to investigate whether the presence of H-atom on the donor site is a prerequisite for producing shifts, we have studied the shift in a

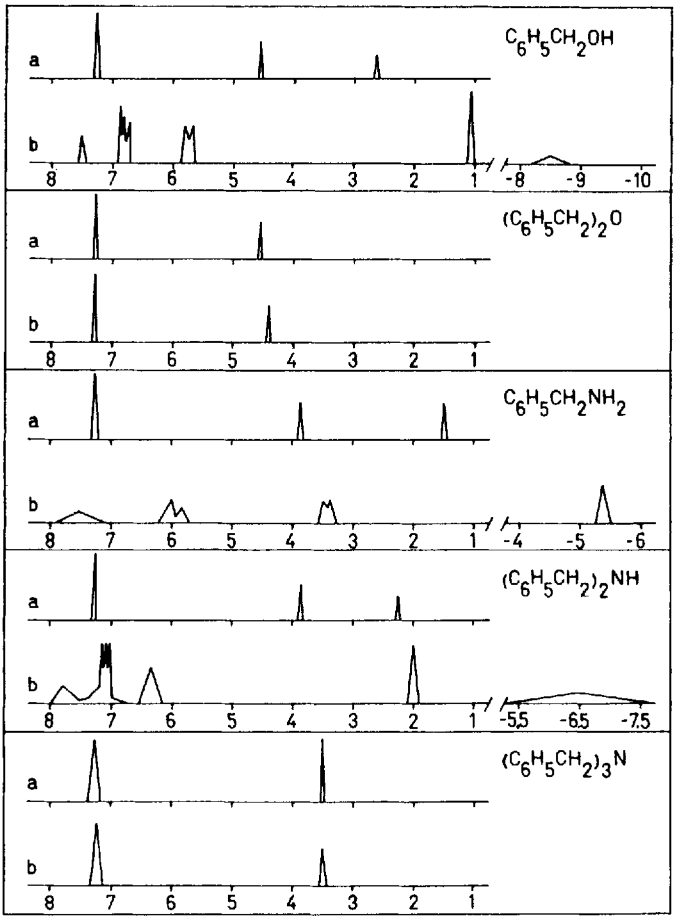

FIGURE 2. The "TWO-WAY" Shift of Benzylic Proton Signals in Several Systems: (a) the normal PMR spectra (b) with added Pr(TTA)3 (Complex:Substrate Ratio = 0.1 - 0.2)

pseudo-benzylic system i.e., benzophenone ($C_6H_5COC_6H_5$). Benzaphenone produces a complex spectrum between 7 and 9 ppm (relative to TMS) which is simplified and shifted upfield with progressive addition of $Pr(TTA)_3$. In the case of benzophenone the carbonyl oxygen is the donor atom and the ring protons are exactly the same distance away as in benzyl alcohol or amines. It then seems that there is no real need for the presence of H-atom on the donor sites. Many ketones and compounds containing halides and pseudohalides, however, were found[4] to produce observable shifts with the addition of a shift reagent[5] i.e. $Eu(FOD)_3$. It is more than obvious that the ether oxygen in dibenzylether and the tertiary nitrogen in tribenzylamine are better donors than the halogens in say $(C_6H_5)_3SnCl$ representing a system analogous to the benzylic ones.

At this stage one suggestion based on hydrogen bonding between the alcohol or amino protons and one of the oxygen atoms in the shift reagent complex may be put forward. This suggestion although looks very attractive in view of the fact that compounds without a proton on the donor site do not exhibit any shift suffers from the drawback that we have observed shifts of the protons in benzophenone with the same reagent e.g. $Pr(TTA)_3$.

$Pr(TTA)_3$ was also found to produce shifts in other organic systems i.e. Adamantan-1-ol and cholesterol. Adamantan-1-ol shows a cluster of lines between 1.40 and 2.20 ppm. On addition of $Pr(TTA)_3$ the resonances shifted upfield and the resonances due to (2,8,9) and (4,6,10) protons separated very nicely[3]. Moreover, the cis and trans configurations of the six protons in (4,6,10) position of adamantan-1-ol produced a simplified AB-spectrum. The sequence of shift is of the order $(3,5,7)H < trans, cis\ (4,6,10)H < (2,8,9)H \ll OH$.

All spectra were recorded in $CDCl_3$ with a Hitachi Perkin-Elmer R-20B NMR Spectrometer at 35°C. We wish to thank Dr. R.D. Green for interesting discussions.

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