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TRIS (DIPIVALOMETHANATO) YTTERBIUM - INDUCED SHIFTS IN PMR AMINES

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The influence of tris(dipivalomethanato)ytterbium (2)(3) on the PMR spectra of amines arises from its interactions with nitrogen lone pair electrons. Such effects could be anticipated from numerous applications of Eu(DPM)$_3$ to compounds with lone pairs on oxygen, as in alcohols (4) and epoxides (5), and are related to a change in the coordination geometry of the chelate upon association (6).

The results presented here were obtained at 60 MHz for 10% CCl_4 solutions after extrapolation to an equimolar ratio of Yb(DPM)$_3$ to amine, $\Delta Yb = (\delta - \delta_{CCl_4})$ppm. (Table 1). Amines were anhydrous and purified by gas chromatography. The PMR spectra are remarkably expanded and first-order analysis becomes possible, for example, for aniline, quinoline or benzylamine, although line-broadening does not allow the identification of long-range couplings. Investigated compounds were primary, secondary and tertiary amines in which the nitrogen lone pair is subject to different electronic and steric environments. The lanthanide chelate can be considered as a weak acid with very marked steric hindrance, so that the basicityscale of amines, described by protonation, fails in general. Steric factors related to the accessibility and inversion of the lone pair are important, as can be seen in decreasing shifts for quinuclidine, mono-, di- and triethylamine. Pyridine, quinoline and 2,4,6-collidine present similar effects. When steric conditions are comparable, the charge on the nitrogen atom determines the shift magnitude. A manifest example is that of pyrrolidine and pyrrole: the latter, with a positive nitrogen, has practically no affinity. A parallel can be drawn for furan (unperturbed) and tetrahydrofuran, carrying a "basic" oxygen and therefore strongly shifted.

The induced shifts were related to a specific geometry of the complexed organic molecule by acknowledging a pseudocontact interaction with predominant distance factor (8), and testing it for two rigid molecules, pyridine and quinuclidine. The coordinated ytterbium atom locates itself on the symmetry axis of these molecules, in the direction of the protruding nitrogen lone pair. For nitrogen-ytterbium distances from 1 to 5Å, the R values (distance between Yb and shifted protons) were measured on molecular models, and Δ Yb shifts related to $1/R^3$. A very satisfactory agreement was thus obtained as a straight line for protons of each molecule when the N-Yb distance was equal 3±0.3 Å, which seems quite acceptable (8). This empirical agreement can be expressed (Fig. 1)

$$\log \Delta Yb(ppm) = -3 \log R(Å) + k \quad (I)$$

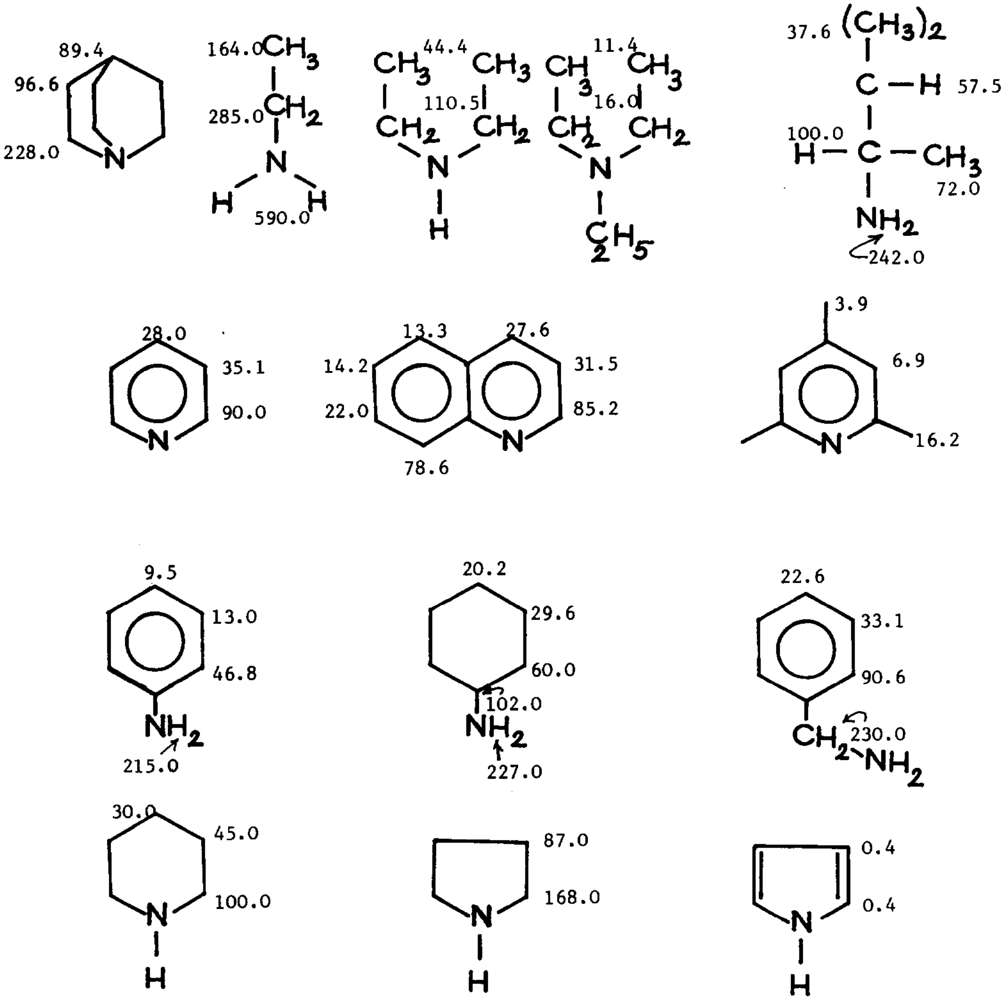
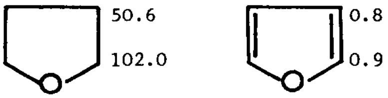


Table 1. ΔYb ($Yb(DPM)_3$-induced shifts) in ppm



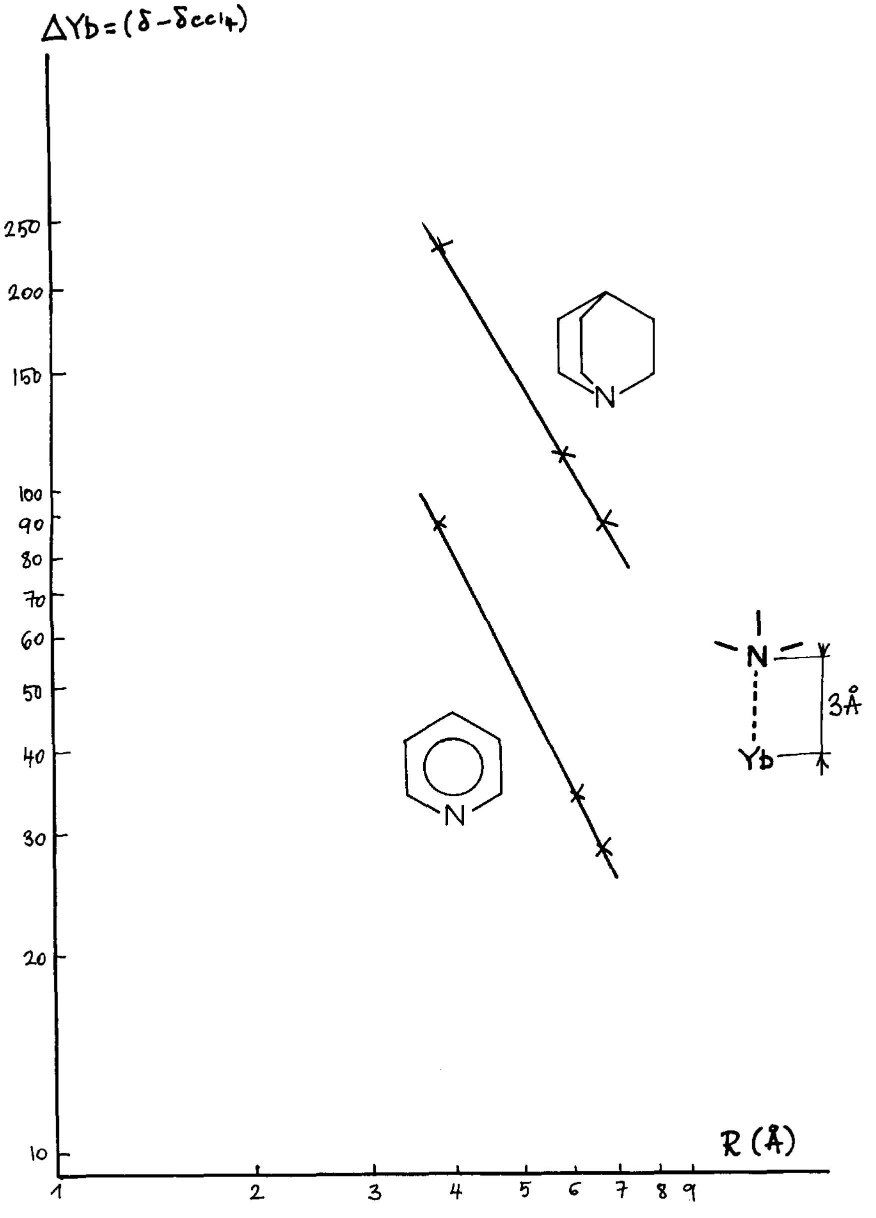


Fig. 1

The relative positions of the lines in Fig. 1 for pyridine and quinuclidine, with well-exposed lone pairs, may be explained by the increase in basicity. It should be noted that trace amounts of water are primarily responsible for irreproducible results (the molecular weight of $Yb(DPM)_3$ is 40 times that of water). Shifts reported for cholesterol hydrate are only half those measured for the anhydrous steroid (9). These difficulties are particularly apparent in work with amines and other moisture-absorbing organic compounds; this, of course, will alter equation (I) by lowering the parameter k.

Although this relationship cannot be extended to amines for which approach to the lone pair is sterically impeded, nor to conformationally mobile molecules, it is quite apparent for the other amines listed that shifts are *R*-dependent in some manner, as can be seen from first-order separations between ring protons in benzylamine, protons 3 and 4 in cyclohexylamine or β and γ in piperidine.

We wish to conclude by noting that since this method supplies a quantity of chemical information, it may, after additional refinements, be applied successfully to such problems as structural assignments, nitrogen inversion or study of lone pair character in heteroatoms by PMR. Further work will be carried on in these directions (10).

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(1) Author to whom inquiries should be sent

(2) We find $Yb(DPM)_3$ to be a +2.0±0.1 times stronger shift reagent than $Eu(DPM)_3$, with fivefold line broadening (7). This conversion factor remained constant for different functional groups. For $Nd(DPM)_3$ it is equal to -0.4, while $La(DPM)_3$ and $Ce(DPM)_3$ (3) are inactive

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(10) Results concerning application of $M(DPM)_3$ - induced shifts in ^{14}N NMR of organic compounds will be reported elsewhere