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TRIS (DIPIVALOMETHANATO) EUROPIUM - INDUCED SHIFTS IN PMR OXIMES

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Proton magnetic resonance has revealed itself as a method of choice in the investigation of isomeric oximes, since the anisotropy of the hydroxyimino group determines large chemical shift differences between syn and anti protons (1). Positive results in assignment by PMR have also been obtained from benzene-induced shifts (2)(3), protonation of oxime in solution (4) or complex formation with trimethylaluminium (5). We wish to report a NMR technique which seems superior to hitherto used methods and consists in interaction with tris(dipivalomethanato)europium (6).

The results presented in Table 1 for some linear and cyclic oximes were obtained at 60 MHz for 10% CCl_4 solutions after extrapolation to an equimolar ratio of $Eu(DPM)_3$ to oxime, $\Delta Eu = (\delta - \delta_{CCl_4})$ ppm. Since the positions of the oxime group, responsible for the interaction are very different in the syn and anti forms, important shift differences between protons in both isomers could be anticipated (7). Syn protons are more strongly shifted than anti. The methyl resonances in acetoxime, which under standard conditions give a unique signal, become separated by almost 6 ppm (I), and the separation between syn and anti methyls in acetaldoxime (II) is 9.6 ppm. The aldehyde proton in acetaldoxime undergoes a shift increase of over 16 ppm between anti and syn positions, compared to only 0.6 ppm in absence of the chelate. The influence of increasing amounts of the shift reagent is apparent from the spectrum of diethylketoxime (III), where two distinct series of signals appear, with larger spacing between methylenes than methyls (Fig. 1). Line-broadening is more important than in alcohols and ketones (7)(8), so that even couplings across three bonds are rapidly lost. The hydroxyl proton is shifted by about 40 ppm.

The distance dependence of the paramagnetic shifts was first determined on the well-known example of isophorone oximeisomers (9) (IV). As a result, 3-methyl cyclopentenone oxime (V) can readily be classified as an anti-ethylenic isomer, by comparing shifts for protons α to the oxime group: methylene 4 (syn) even overtakes the ethylenic proton 2 (anti) (Fig. 2). Assignments can also be made for α,β unsaturated oximes with potential conformational mobility: the predominant isomer obtained by oximation of methyl vinyl ketone (3) (VI) is s- trans anti ethylenic, and the same form is assigned to the solid form of the oxime of mesityl oxide (VII) (melting point 49°C).(10) It appears therefore that the proton to oxygen distance is a predominant factor in the induced shifts, while the nitrogen lone pair plays an insignificant role (11). The distances measured on molecular models between oxygen and protons (hydroxyl excepted) were plotted against ΔEu, on logarithmic scales, for a series of oxime isomers (Fig.3)

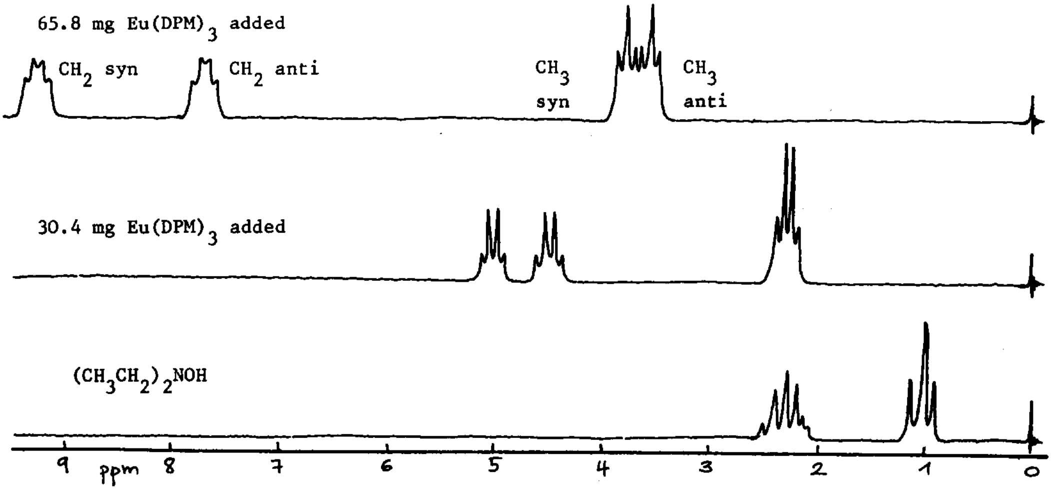


Fig. 1 Influence of increasing amounts of Eu(DPM)$_3$ on the spectrum of diethylketoxime (31.0 mg in CCl$_4$)

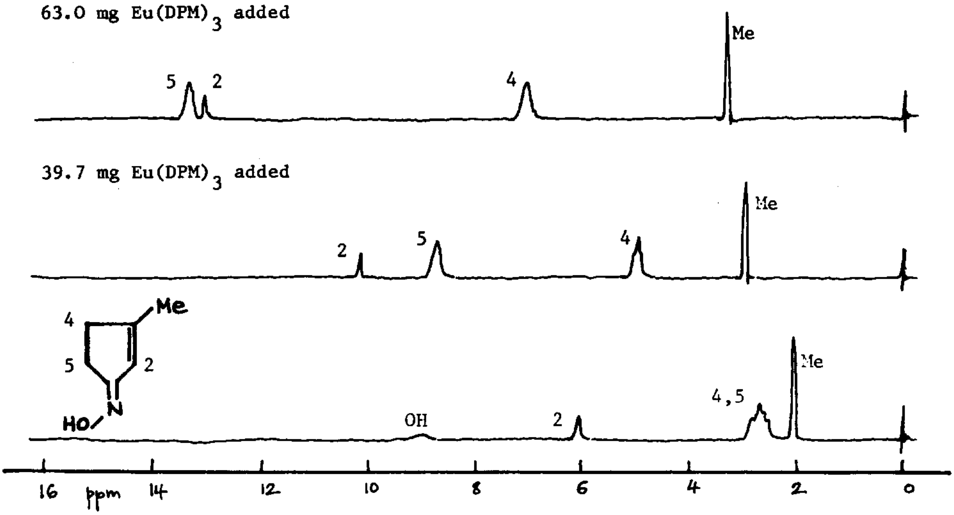
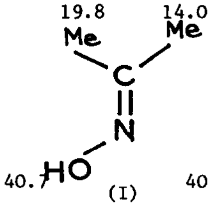
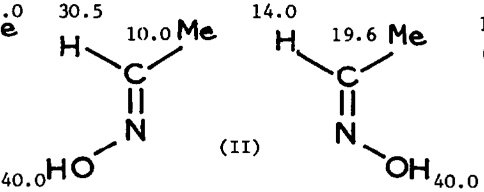


Fig.2 Influence of increasing amounts of Eu(DPM)$_3$ on the spectrum of 3-methyl cyclopentenone oxime (20.5 mg in CCl$_4$)

Table 1. Eu (Eu(DPM)$_3$-induced shifts) ppm



(I)



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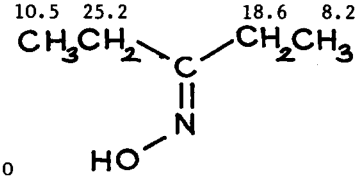
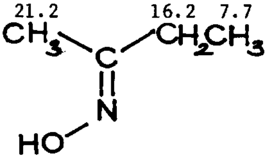
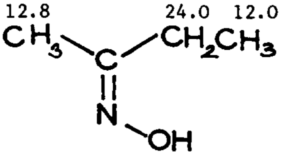
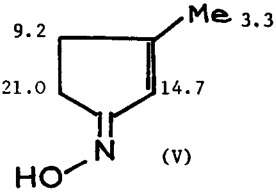


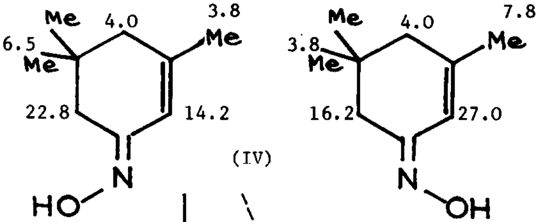
(III)



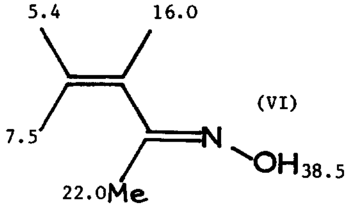




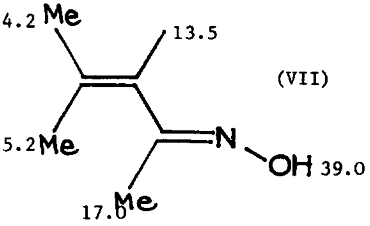
(V)



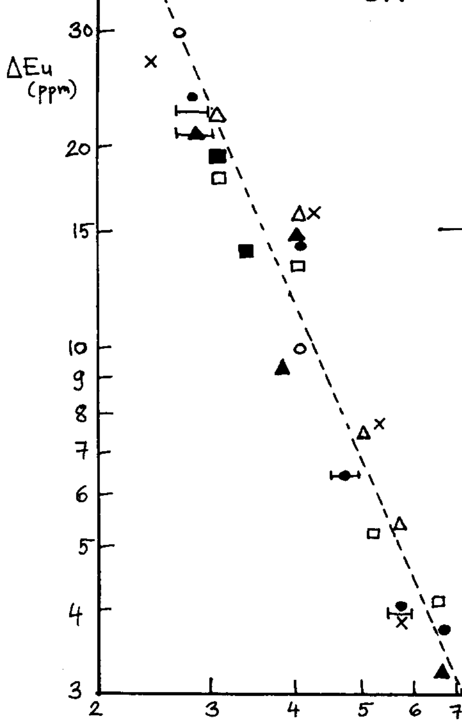
(IV)



(VI)



(VII)



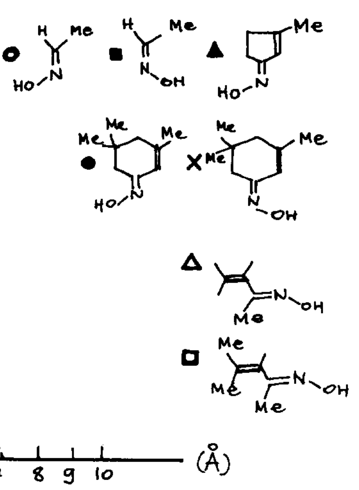


FIG. 3

and an overall agreement suggests a rather linear variation with a slope of about -2.3. The expected pseudocontact influence with predominant distance factor (8)(12) is described by relating ΔEu to $1/R^3$ (R- europium to proton distance), which in logarithmic scales becomes a straight line with a slope of -3.

Although it is not possible at this point to give a more precise geometrical model for the interactions between oxime and $Eu(DPM)_3$ in solution because of oxime autoassociation and necessity of further information on the role of the available lone pairs in the interaction, we believe the general trend of variations given in Fig. 3 may be applied to stereochemical studies in oximes by PMR.

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