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Note**Tris(dipivalomethanato)holmium Induced NMR Shifts**

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Paramagnetic complexes of praseodymium and europium with 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione [Pr(fod)₃ and Eu(fod)₃]¹ and with 2,2,6,6-tetramethyl-3,5-heptanedione [Pr(DPM)₃ and Eu(DPM)₃] or sometimes abbreviated as [Pr(tmhd)₃ and Eu(tmhd)₃]²⁻⁵ have shown to be very useful NMR shift reagents which can greatly simplify spectra of compounds having functional groups with lone pair electrons. The only other lanthanide complex used for this purpose was Yb(DPM)₃^{6,7}. However, Yb(DPM)₃ exhibited a shift power between that of Pr(DPM)₃ and Eu(DPM)₃ and also strong line broadening⁸ and therefore did not offer any substantial advantage.

Initial studies of the chemical shifts of acetonitrile⁹ and *t*-butyl derivatives³ induced by different rare earth complexes indicated a great power of holmium. This prompted us to study shifts induced by tris(dipivalomethanato)holmium [Ho(DPM)₃]¹⁰. This reagent shifted the proton signals upfield, like Pr(DPM)₃, but was considerably more effective, being able to separate *all* different protons in 1-octanol (Fig. 1) and 1-methylcyclobutanol (Fig. 2A)*. For com-

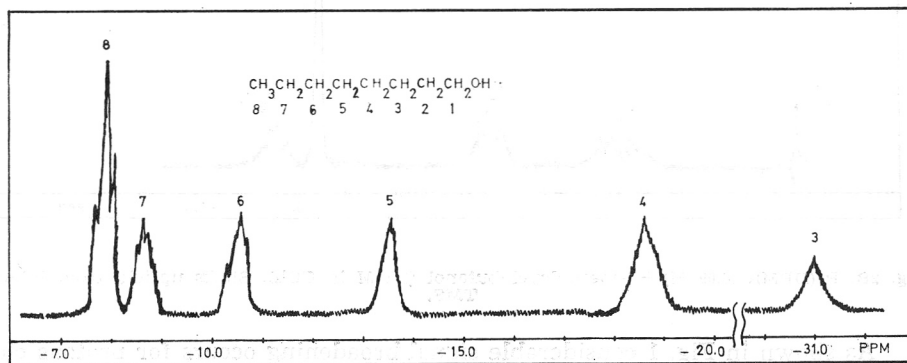


Fig. 1. Ho(DPM)₃ (0.1 M) induced NMR spectrum of 1-octanol (0.2 M) in CCl₄ (upfield from external TMS). The first two CH₂ groups (C₁ and C₂) are beyond the upfield sweep offset of the instrument.

*All spectra were recorded on a Varian A-60A instrument. At higher concentrations of Ho(DPM)₃ (0.16 M) all different protons even in 1-nonanol can be separated, but because of heavy signal broadening the integration becomes inaccurate. The spectra were assigned by inspection of the corresponding Dreiding models taking into account probable coupling constants and the mathematic expression for the pseudocontact shifts⁵.

parison, $\text{Pr}(\text{DPM})_3$ even at the highest possible concentrations failed to separate the protons of the terminal ethyl group in 1-octanol and the γ -protons in 1-methylcyclobutanol (Fig. 2B). (The accuracy of the integrals which are not shown in Figs. 1 and 2 was satisfactory).

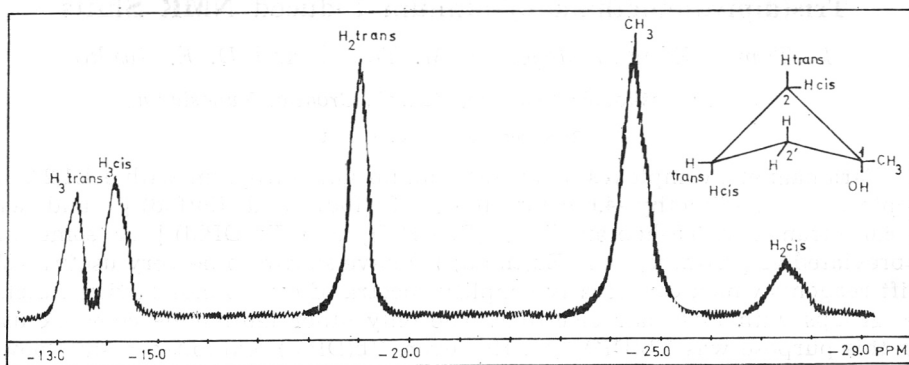


Fig. 2A. $\text{Ho}(\text{DPM})_3$ (0.05 M) + 1-methylcyclobutanol (0.2 M in CCl_4). Shifts upfield from external TMS.

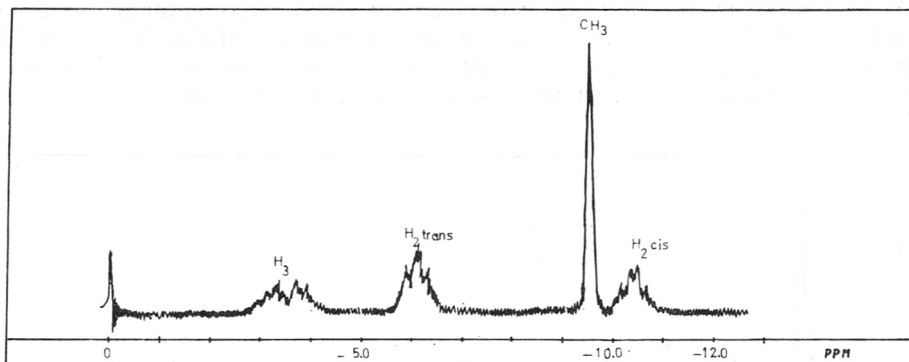


Fig. 2B. $\text{Pr}(\text{DPM})_3$ (0.09 M) + 1-methylcyclobutanol (0.2 M in CCl_4). Shifts upfield from internal TMS.

As shown in Fig. 1 considerable signal broadening occurs for protons close to the coordination site and spin-spin splittings are observable only for the most distant protons. However, just these protons cannot be separated by $\text{Pr}(\text{DPM})_3$ and, therefore, $\text{Pr}(\text{DPM})_3$ and $\text{Ho}(\text{DPM})_3$ efficiently complete each other*.

A direct comparison of $\text{Ho}(\text{DPM})_3$ and $\text{Pr}(\text{DPM})_3$ was made by recording NMR spectra of (1-methylcyclopropyl)methanol in CCl_4 . With both reagents

* Because of better complexing properties $\text{Ho}(\text{DPM})_3$ is in the presence of alcohols about seven times more soluble in CCl_4 than $\text{Pr}(\text{DPM})_3$. This may be of convenience in separation of protons very distant from the coordination site.

all the different protons could be separated but the chemical shifts and signal widths at half heights were quite different (see Table I).

TABLE I
*¹H NMR Spectra of (1-Methylcyclopropyl)methanol in the Presence of Pr(DPM)₃ and Ho(DPM)₃**

Protons	Pr(DPM) ₃			Ho(DPM) ₃		
	Chem. shift (ppm)	Half-width (Hz)	Broadening (Hz/Hz of shift)	Chem. shift (ppm)	Half-width (Hz)	Broadening (Hz/Hz of shift)
H ₃ <i>trans</i>	-2.2	—	—	-8.2	—	—
CH ₃	-2.6	2	—	-10.9	11	0.017
H ₃ <i>cis</i>	-3.1	—	0.013	-11.4	—	—
H ₁	-5.5	4.3	0.013	-27.6	37	0.022

* 0.2 M in CCl₄ containing 0.04 M of Pr(DPM)₃ and Ho(DPM)₃, respectively; internal TMS; the Pr(DPM)₃ induced spectrum of (1-methylcyclopropyl)methanol has been published (see ref. 2).

These results show that Ho(DPM)₃ is a 3.7—5 times more powerful shift reagent than Pr(DPM)₃ and introduces 1.3 and 1.7 larger line broadenings. The half-widths were 5.5 and 8.6 times larger with Ho(DPM)₃ indicating that the advantage of this reagent lies in its ability to separate signals of protons which are more distant from the coordination site.

REFERENCES

1. R. E. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.* **93** (1971) 1522.
2. L. Tomić, Zdenko Majerski, M. Tomić, and D. E. Sunko, *Chem. Commun.* **1971**, 719, and references therein.
3. D. R. Crump, J. K. M. Sanders, and D. H. Williams, *Tetrahedron Letters* **1970**, 4419.
4. J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *Chem. Commun.* **1971**, 364.
5. J. K. M. Sanders and D. H. Williams, *J. Am. Chem. Soc.* **93** (1971) 641, and references therein.
6. C. Beauté, Z. W. Wolkowski, and N. Thoai, *Tetrahedron Letters* **1971**, 817.
7. Z. W. Wolkowski, *Tetrahedron Letters* **1971**, 821.
8. Approximately fivefold to that of Eu(DPM)₃ (see ref. 6).
9. J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *Chem. Commun.* **1970**, 749.
10. K. J. Eisentraut and R. E. Sievers, *J. Am. Chem. Soc.* **87** (1965) 5254.

IZVOD

NMR pomaci uzrokovani tris(dipivalometanato)holmijem

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Tris(dipivalometanato)holmij uzrokuje veće kemijske pomake protonskih NMR signala od tris(dipivalometanato)kompleksa praseodija i europija, ali su linije znatno šire; spin-spin cijepanje može se primijetiti jedino kod signala onih protona koji su suviše udaljeni od mjesta koordinacije da bi ih Pr(DPM)₃ mogao razlučiti.