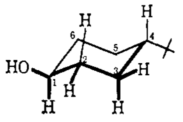
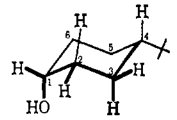
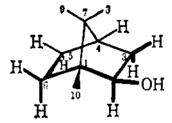
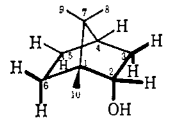
Table I. Δ_{Eu}[a] Values (ppm) Recorded for the Different Protons and Methyl Groups in Compounds **1–4**

Compd		OH	H_1	H_{2eq} (H_{6eq})	H_{2ax} (H_{6ax})	H_{3eq} (H_{5eq})	H_{3ax} (H_{5ax})	H_4	*tert*-Butyl
 **1**	Δ_{Eu}	−78.7	−21.7	−13.6	−14.7	−4.4	−5.4	−5.4	−1.8
	R[b]	0.97	2.09	2.65	2.62	4.52	4.05	4.48	6.73
 **2**	Δ_{Eu}	−81.7	−24.7	−14.9	−8.2	−6.7	−13.6	−6.5	−2.8
	R	0.97	2.08	2.65	3.33	3.92	2.65	4.25	5.60

Compd		OH	H_2	H_{3exo}	H_{3endo}	H_4	H_{5exo}	H_{6exo}	H_{6endo}	8-CH_3	9-CH_3	10-CH_3
 **3**	Δ_{Eu}	−78.4	−26.7	−19.2	−9.3	−6.7		−5.1	−7.2	−11.0	−4.7	−10.5
	R	0.97	2.08	2.52	3.16	4.24		4.54	3.88	3.0	4.9	3.1
 **4**	Δ_{Eu}	−81.2	−25.5	−8.8	−16.7	−5.1	−5.1		−17.5	−4.4	−4.0	−8.6
	R	0.97	2.07	3.16	2.49	4.39	4.50		2.43	4.5	5.2	3.4

[a] $\Delta_{Eu} = \delta_{CDCl_3} - \delta^{n=1}_{Eu(DPM)_3}$, *i.e.*, the difference in resonance position for a given solute proton when dissolved in inert $CDCl_3$ from that when an equimolar amount of $Eu(DPM)_3$ is present in the same solvent. Δ_{Eu} values reported in the table are valid only for $CDCl_3$ solutions of the complex and are expected to be accurate to within ±2%. [b] For a methyl group R is taken as the distance from the center of the circle of rotation of the methyl protons to the hydroxyl oxygen atom. Values reported for R were determined from the Westheimer method for calculating nonbonded atomic distances (for a discussion of the method, see N. L. Allinger, *et al., J. Amer. Chem. Soc.*, **91**, 337 (1969)).

sociated with europium,[14] this empirically derived slope value is unexpected since a $1/R^3$ dependency for the pseudocontact shift is well established.[12,13] We believe this discrepancy to be a consequence of either error involved in the measurement[10] of R and/or in the neglect of angular variables manifest in the pseudocontact term.[11] Thus, contrary to the cholesterol system studied by Hinckley,[1] where angular variables do not vary significantly from one proton to the next, compounds **1–4** present a variety of different angular situations between the coordinated metal ion and various solute protons. These points are presently being investigated and will be reported in a future paper. The fact that points for the carbinol methine and OH protons do not fall within the normal range of scatter (see Figure 3) suggests sizable contact contributions to the shifts of these protons. Extrapolation of the least-squares line to the origin reveals that even for distances of up to 26.7 Å from the site of coordination a sizable paramagnetic shift (*ca.* 0.1 ppm) is to be expected. It is important to emphasize that the distance–shift relationship shown in Figure 3 is valid only for deuteriochloroform solutions in which the molar ratio of solute–metal complex is one and for solutes containing only one function, *i.e.*, a hydroxyl function.

Acknowledgments. The authors are indebted to Professor N. L. Allinger for furnishing the Westheimer calculated internuclear distances used in this study.

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Received May 27, 1970

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[14] D. R. Eaton, *J. Amer. Chem. Soc.*, **87**, 3097 (1965); F. A. Hart, J. E. Newberry, and D. Shaw, *Nature* (*London*), **216**, 261 (1967); J. Reuben and D. Fiat, *Chem. Commun.*, 729 (1967).

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Tris(dipivalomethanato)europium(III). A Shift Reagent for Use in the Proton Magnetic Resonance Analysis of Steroids and Terpenoids

Sir:

The usefulness of nuclear magnetic resonance in the study of hydrocarbon-like compounds has been severely limited by insufficient resolution. Although this deficiency has been partially overcome by the development of higher frequency spectrometers (220 MHz), the situation still remains unsatisfactory since considerable structural information usually remains buried in a featureless methylene–methine envelope common to such systems. The discovery by Hinckley[1]

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[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

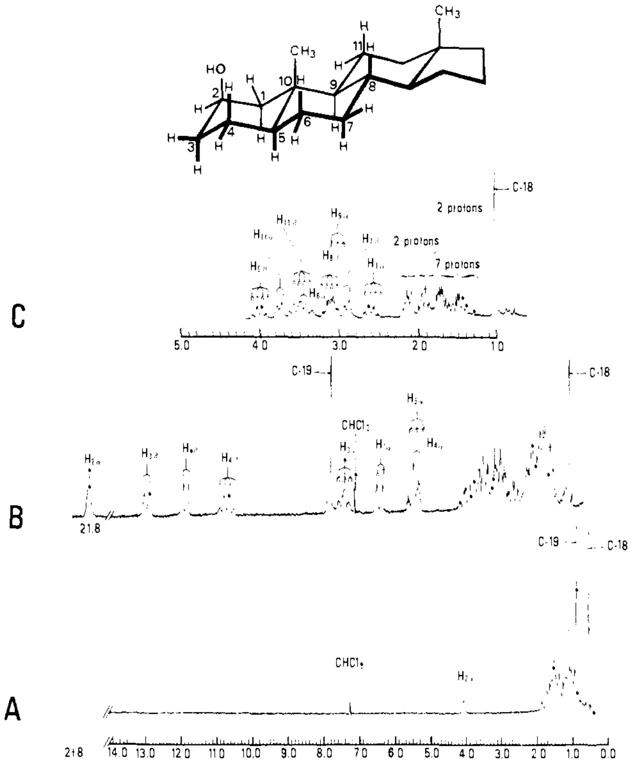

Figure 1. Pmr spectra of androstan-2β-ol (**1**) (20 mg, 0.73 × 10^{-4} mol in 0.4 ml of $CDCl_3$): A, normal spectrum at 100 MHz; B, 100-MHz spectrum of solution of **1** containing 40 mg of $Eu(DPM)_3$; C, 220-MHz spectrum of the δ 1.0–5.0 region of spectrum B.

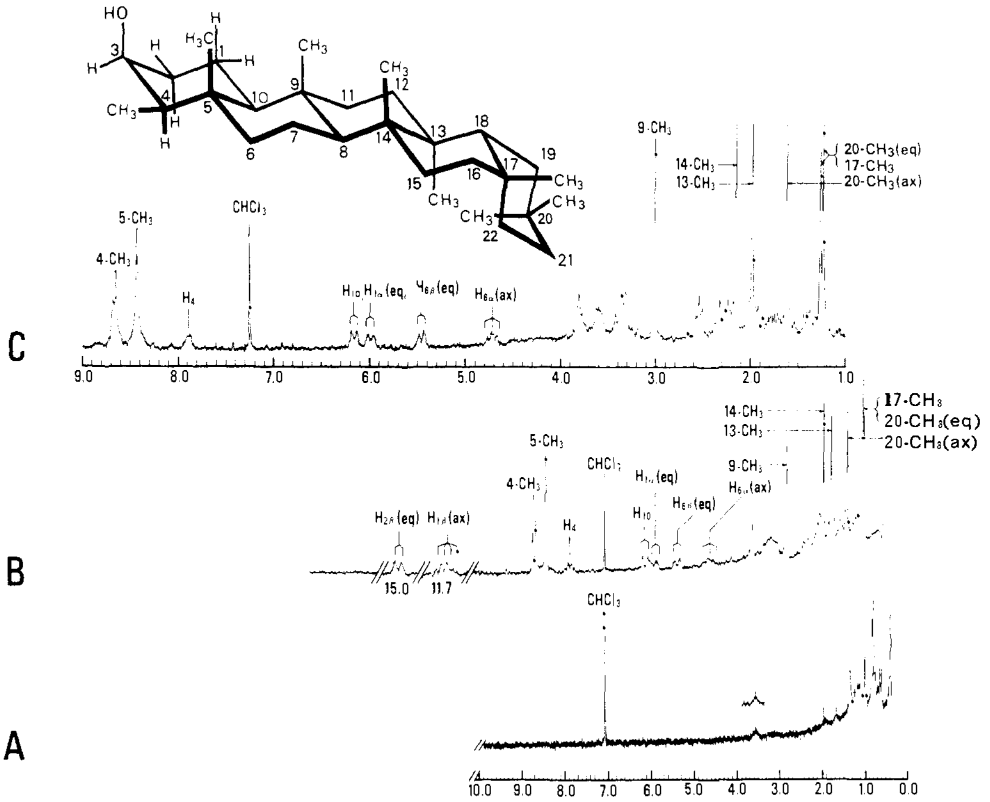

Figure 2. Pmr spectrum of friedelan-3β-ol (**2**) (10 mg, 0.24 × 10^{-4} mol in 0.4 ml of $CDCl_3$): A, normal spectrum at 100 MHz; B, 100-MHz spectrum of solution of **2** containing 1 mol equiv of $Eu(DPM)_3$ (17 mg); C, partial 200-MHz spectrum of same solution as in B.

that the dipyridine adduct of the rare earth complex tris(dipivalomethanato)europium(III) [$Eu(DPM)_3 \cdot 2py$] induces large paramagnetic shifts in the pmr spectra of molecules bearing lone-pair functionalities suggests considerable potential for paramagnetic materials in alleviating this deficiency. Although paramagnetic shifts induced by $Eu(DPM)_3 \cdot 2py$ in the spectrum of a steroid[1] (cholesterol) and, more recently, by the corresponding pyridine-free complex, $Eu(DPM)_3$, in the spectrum of a triterpene[2] (lupeol) have been reported, few details regarding the extent and potential of such shifts in the study of naturally occurring fused ring systems have been advanced. We therefore wish to report our observations on the use of $Eu(DPM)_3$ in the pmr analysis of a steroid and a triterpene.

Figure 1A shows the normal 100-MHz spectrum of 5α-androstan-2β-ol (**1**) (20 mg/0.5 ml of $CDCl_3$). As is observed, only $H_{2\alpha}$ and the C-18 and C-19 methyl signals can be readily assigned, while resonances arising from the remaining 25 skeleton protons give a broad envelope devoid of information ranging from δ 0.5 to 2.0. Upon addition of 40 mg (0.57 × 10^{-4} mol) of $Eu(DPM)_3$ to the solution dramatic changes occur in the spectrum of **1**, which are illustrated in Figure 1B. Most obvious of these changes is the shift, from under the methylene–methine envelope, of seven well-resolved signals to the lower field regions of the spectrum. From both an analysis of their signal multiplicities and spin-decoupling experiments at 100 MHz, these signals were assigned unambiguously to various protons in ring A of **1**, as is shown in Figure 1B. It is of interest to note that the order in which ring A protons appear, from low to high field, is in direct proportion to the magnitude of their distances from the site of coordina-

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(2) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

tion,[1-3] *i.e.*, the 2β-OH group. The enormous shift for the quaternary C-19 methyl group, which shifts from δ 1.03 to 7.85, is in accord with its spatial proximity, *i.e.*, 1,3 diaxial to the 2β-hydroxyl function.[3] Of further interest is the increased resolution of the methylene–methine envelope which is now spread over an area more than twice as wide as that in the normal spectrum, *i.e.*, from δ 1.25 to 4.20. The observed shift of this whole region to lower field indicates that *every* proton in **1** is significantly shifted, even ring D protons, the furthest of which is greater than 10 Å removed from the 2β-OH function. These observations are not unexpected since sizable paramagnetic shifts are expected for protons as far away as 27 Å from the site of coordination.[3]

Information regarding assignments for ring B and C protons can be obtained from closer scrutiny of the methylene–methine envelope (δ 1.0–5.0) at 220 MHz. The 220-MHz spectrum of this region together with proton assignments, most of which are tentative, are shown in Figure 1C. Irradiation of $H_{5\alpha}$ (δ 5.63) in the 100-MHz spectrum of **1** (see Figure 1B) causes the quartet of doublets on the low-field side of the methylene envelope (δ 4.00) to collapse to a triplet of doublets. This signal was assigned accordingly to $H_{6\beta}$. Saturation of $H_{6\beta}$ causes a collapse in what appeared to be a triplet of doublets centered at δ 2.60 at 100 MHz (see Figure 1B), but which, from the 220-MHz spectrum, is shown to be a quartet of doublets (see Figure 1C) and is thus assigned to $H_{7\alpha}$ axial. The remaining signals in the δ 2.5–4.5 region of the 220-MHz spectrum of **1** were tentatively assigned on the basis of their observed signal multiplicities and the expected dependence of their chemical shift on the distance of their location from the site of coordination. Thus, since $H_{11\alpha}$, $H_{6\alpha}$, and $H_{7\beta}$ are the only three protons (except for ring A protons) in the approximate vicinity of the 2β-hydroxyl function that can give rise to a doublet of quartet signal, the lowest field doublet of quartets (δ 3.75) is assigned to $H_{11\alpha}$, since[4] $R \simeq$ 4.4 Å, the highest field doublet of quartets (δ 2.90) is assigned to $H_{7\beta}$, since $R \simeq$ 6.3 Å, and the intermediately situated quartet of doublets (δ 3.50), partially overlapped by the tentatively assigned $H_{11\beta}$ signal, is assigned to $H_{6\alpha}$, since $R \simeq$ 5.3 Å. The remaining protons in this region were assigned in similar fashion.

It is apparent that shifts induced by Eu(DPM)$_3$ can give valuable insight not only into the structure of ring A, but also rings B and C even though only one OH function is present in the compound. We have also investigated the effects of Eu(DPM)$_3$ on a number of ring D hydroxy steroids and have found that all protons in both the C and D rings can be unambiguously assigned in a majority of cases. This method therefore offers a new and simple approach to ring D conformational analysis in steroids, since the magnitude of vicinal couplings between various D-ring protons can be simply related to dihedral angles through the Karplus relationship.[5]

The potential of shifts induced by Eu(DPM)$_3$ for the study of structurally complex triterpenes is illustrated by the spectra of friedelan-3β-ol (**2**) (10 mg, 0.23×10^{-4} mol). The normal spectrum of **2** ($CDCl_3$), shown in Figure 2A, is practically devoid of information with all eight methyl signals residing in a very narrow region to high field (δ 0.4–1.2). The addition of Eu(DPM)$_3$ (17 mg, 0.24×10^{-4} mol) results in a spectrum spread over more than 20 ppm and reveals a multitude of signals which are assigned, as shown in Figures 2B and 2C, by methods similar to those described for 1. In these spectra, all ring A protons (except $H_{3\alpha}$ which is farther than 20 ppm distant from TMS) and two ring B protons ($H_{6\alpha}$ and $H_{6\beta}$) are clearly in evidence. Further, all methyl signals are now separated distinctly from each other, with two, namely the tertiary 4-CH_3 (δ 8.67) and the quaternary 5-CH_3 (δ 8.42), suffering the most significant shifts to lower field in accordance with their spatial proximity to the site of coordination.[1-3] The remaining methyl singlets were assigned such that the order of their appearance from low to high field corresponds to the magnitude of their separation from the 3β-OH function.

In the large variety of hydroxy steroids we have studied to date, the most significant, although not serious, broadening effects have been recorded for protons close to the site of coordination. We interpret this broadening to originate from a direct electron–proton dipole–dipole interaction[6,7] between unpaired metal electrons and nearby protons.

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[3] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

[4] As in the accompanying communication, *R* represents the vector distance from the proton(s) in question to the hydroxyl oxygen atom. Values for *R* were measured from Dreiding models.

[5] M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963); M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).

[6] The contribution to T_1 resulting from the dipole–dipole interaction of an unpaired electron and a proton is given by[7] $1/T_1 = h^2\gamma_e^2\gamma_p^2\tau/r^6$, where τ is the correlation time for random molecular rotation, r is the distance between the nuclear and electron dipoles, and other signals have their usual significance.

[7] A. Abragam, "The Principle of Nuclear Magnetism," Oxford University Press, London, 1961, p 264; N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 73, 679 (1948).

[8] (a) Address correspondence to this author. (b) Public Health Service Predoctoral Fellow, 1969.

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Received May 27, 1970

Preparation and Properties of $H_4Re_4(CO)_{12}$, an Unsaturated Polynuclear Carbonyl Hydride Cluster[1]

Sir:

During a study of the thermal cleavage of metal cluster compounds we have observed, while heating $H_3Re_3(CO)_{12}$ to 190° in hydrocarbon solution, a deep red coloration through which we have identified a new polynuclear tricarbonyl hydride of rhenium.

Decalin (60 ml, cis–trans, degassed and dried over Na) containing $H_3Re_3(CO)_{12}$[2] (0.51 g, 0.57 mmol) is heated under nitrogen at reflux for 0.5 hr. Uncon-

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[1] Work supported by NSF Grant No. GP6720. Departmental instruments used in this work were supported as follows: Varian A 60 nmr spectrometer, E. I. duPont de Nemours & Co. and NSF Grant No. G 20207; Beckman IR 4, E. I. duPont de Nemours & Co.; A.E.I. MS9 Mass Spectrometer, NSF Grant No. GP 3672.

[2] D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **86**, 4841 (1964).