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TEMPERATURE DEPENDENCE OF NMR SHIFTS INDUCED BY TRIS(DIPIVALOMETHANATO) YTTERBIUM

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Numerous structural problems in organic chemistry have been successfully resolved (1) with the help of NMR shifts induced by rare earth chelates and use of the simplified McCONNELL and BLOEMBERGER equation (2). According to this equation, the magnitude of induced shifts varies as an inverse function of temperature. However, the temperature dependence of these shifts has hardly been investigated (3)(4)(5).

Although no effect is observed at normal insert temperature for methyl vinyl ketone, a shift is apparent with $Yb(DPM)_3$ at -10°C. This study was undertaken with three types of molecules: alkyl vinyl ketones, furfural and octalone. Neither the observed chemical shifts nor their logarithms are linear variations of 1/T. Although the exact temperature dependence is probably much more complex, a linear variation is observed over a large temperature range when the shifts are plotted against $1/\sqrt{T}$ (Table 1-3). Such a representation has the advantage of incorporating both a 1/T factor for the pseudocontact effect, and a $\sqrt{T}$ factor for a collision phenomenon between the rare earth chelate and the complexed organic molecule (4). The slope of the straight line related to a given proton increases with reagent concentration. For each alkyl vinyl ketone there is a temperature at which the induced shift is nearly zero for all protons (Table 3).

The deviation from the 1/T relationship of McCONNELL could be explained by the following hypothesis: formation of a definite complex of the AB_n type between reagent A and ligand B

$$A + nB \rightleftarrows AB_n \;;\quad K = \frac{\alpha}{(1-n\alpha)^n (A_o - \alpha)} \;;\quad \alpha = (AB_n) \qquad \text{(I)}$$

The shift is a statistical time-averaged value between that observed for the free and complexed site.

$$\Delta\delta = \delta_{obs} - \delta_B = \frac{\alpha}{1 - \alpha(n-1)} \left(\delta_{AB_n} - \delta_B \right) \qquad \text{(II)}$$

with δ_i = chemical shift of the $_i$ species. The proportionality between $\Delta\delta$ and the amount of added reagent

$$\Delta\delta = k'(A_o) \qquad \text{(III)},$$

which is always observed experimentally, cannot be reconciled with equation (II). Therefore there would be no definite complex. On the otherhand, a hypothesis based on a collision-type complex is in agreement with equation (III).

A conclusion of the present work seems to be that although the use of the geometric factor $\left(\frac{3\cos^2\theta - 1}{r^3}\right)$ in structural studies with rare earth chelates has proved to be most fruitful, it should be applied with caution. In fact, the induced shifts are subject to a strong temperature dependence which does not follow 1/T but appears to obey $1/\sqrt{T}$ which may be explained by the existence of a collision-type complex.

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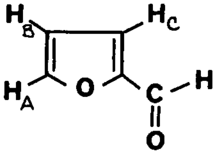
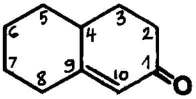
TABLE 1. Induced shifts observed for furfural (41 mg for 13.5 mg of Yb(DPM)$_3$ added) in CDCl$_3$ at 60 MHz (VARIAN HA60).



T°K	333	323	313	293	265	253	243
H_A (Hz)	27	32	38	52	72	86	94
H_B	26	31	35	48	65	76	83
H_C	28	36	48	74	106	126	141
H	130	150	185	270	365	430	-

TABLE 2. Induced shifts observed for octalone (31.6 mg in CCl$_4$)



	Yb(DPM)$_3$ added	313°K	283°K	253°K
Δδ(Hz) H_{10}	10.0 mg	11	14	20
	23.8	29	44	63
	36.3	48	73	102
H_{ax2}	10.0 mg	9	13	18
	23.8	26	40	58
	36.3	45	73	102
H_{eq2}	10.0 mg	11	15	21
	23.8	31	47	63
	36.3	51	77	107
H_4	10.0 mg	2	3	5
	23.8	8	14	20
	36.3	15	25	34

TABLE 3. Induced shifts in alkyl vinyl ketones. R=CH$_3$ (30.2 mg of methyl vinyl ketone in CDCl$_3$ for 9.4 mg Yb(DPM)$_3$ added).

T°K	263	253	243	233	219
Δδ H_A (Hz)	10	12	13	15	17
H_B	14	16	19	21	25
H_C	20	24	27	31	36

R	No shift observed at:
CH$_3$	0°C
C$_2$H$_5$	+ 10°C
n-C$_3$H$_7$	+ 15°C
n-C$_4$H$_9$	+ 20°C
n-C$_7$H$_{15}$	+ 30°C
C$_6$H$_5$	+ 35°C