Tris(dipivaloylmethanato)ytterbium-induced Shifts in the ^{1}H Nuclear Magnetic Resonance Spectra of Some Nitrogen Compounds

By C. BEAUTÉ, Z. W. WOLKOWSKI,* and N. THOAI

(*Laboratoire de Chimie Organique Structurale*, 8 *Rue Cuvier, Paris* 5, *France*)

Summary Yb(dpm)$_3$ has been used to obtain the n.m.r. spectra of imines, azo- and nitro-compounds, nitriles, and amides; the shifts obtained have been related to structure.

THE investigation of Yb(dpm)$_3$-induced shifts[1,2][†] in amines and oximes[3] has been extended to other nitrogen functional groups. We find that the ^{1}H spectra of mono- and di-imines as well as those of azobenzenes remain unperturbed. We therefore conclude that the nitrogen lone pair at the imino- and azo-double bonds has no affinity towards Yb(dpm)$_3$. The important shifts reported for oximes[3] must be attributed totally to interaction with the oxygen atom of the hydroxy-group.[4]

Results obtained at 38 °C and 60 MHz for 10% CCl_4 solutions, after extrapolation to an equimolar ratio of ytterbium complex to substrate $\Delta\text{Yb} = [\delta - \delta(CCl_4)]$ p.p.m., are given for other functional groups (Figure 1). Nitro-compounds have practically no affinity, while nitriles exhibit relatively small shifts. Large shifts, comparable with those obtained for ketones,[5] are recorded for amides. The basic lone pair on oxygen is responsible for this interaction, and the induced shifts can be associated with the distance of the proton concerned from oxygen, in agreement with a pseudo-contact interaction.[6]

Therefore, rotation around the single C–C bond is apparent in acrylamide (I), since similar shifts are experienced by protons B and C: their distances from oxygen in the *s-cis* and *s-trans* forms are, respectively, 2·5—3·9 (B),

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[†] As a standard M(dpm)$_3$ we prefer the ytterbium complex to that of europium and those of the other rare earths because of the greater solubility of the chelate and because it gives stronger shifts and comparable or less line-broadening. The use of upfield shift reagents such as Pr(dpm)$_3$, Dy(dpm)$_3$, or Ho(dpm)$_3$ is not practicable with the Varian A60 instrument with little available upfield offset.

TABLE

	Amide	Concentration (% in $CHCl_2 \cdot CHCl_2$)	Molar ratio of $Yb(dpm)_3$ to amide	G_c‡ (kcal mol^{-1})		T_c (°C)	
(1)	$HCONMe_2$	5	0	20·9	21·7[7]	113	116[7]
(2)		5	0·06	20·4		127	
(3)	$AcNMe_2$	4	0	18·5	18·9[8]	73	87[8]
(4)		4	0·05	17·9		84	

T_c: coalescence temperature; G_c: free enthalpy of activation from coalescence temperature, calculated with the Eyring equation and rate constant $k_c = \pi\Delta\nu/\sqrt{2}$.

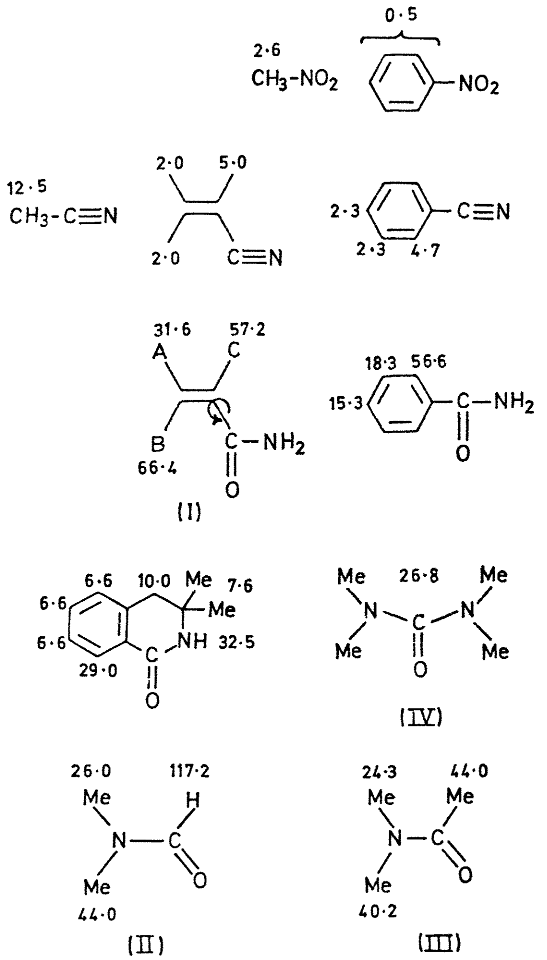

FIGURE 1

3·3—2·5 (C), and 3·9—4·5 (A)Å. When studied below the coalescence temperature, the methyl resonances in dimethylformamide (II) and dimethylacetamide (III) are strongly differentiated, the group *cis* to the carbonyl group being more shifted. For the four equivalent methyls in tetramethylurea (IV) a single shift value is observed after coalescence, equal to the one experienced by a *trans* methyl under conditions of hindered rotation. A variable temperature study on dimethylformamide and dimethylacetamide gives the values shown in the Table.

It seems that the presence of $Yb(dpm)_3$ introduces additional steric hindrance and therefore retards the coalescence. Figure 2 represents the variation of Δν (line separation between methyls) in Hz with temperature for the examples reported.

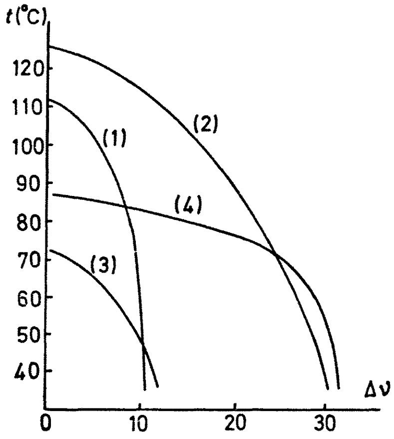

FIGURE 2

As for other functional groups, the induced paramagnetic shifts can be applied to structural problems in amides. The investigation and assignments in polyfunctional compounds become simplified when only one function is capable of complex formation, and the other groups have no affinity towards $M(dpm)_3$.

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