CHEMISTRY LETTERS, pp. 1073-1076, 1972. Published by the Chemical Society of Japan

STERIC EFFECTS IN COMPLEXATION OF N-ALKYLIDENEANILINES WITH TRIS(DIPIVALOMETHANATO)EUROPIUM [1)]

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The pmr paramagnetic shifts induced by Eu(DPM)$_3$ have been studied in a series of N-sec-alkylideneanilines and related to their structures around the C=N bond. Steric effects in complexation with Eu(DPM)$_3$ are discussed from the values of the intrinsic paramagnetic shifts, Δ_{max}, and the complexation equilibrium constants.

Studies of pmr paramagnetic shifts induced by lanthanide shift reagents are useful in structural assignment of the geometrical isomers pertaining to the C=N bond.[1~3)] We now present the results on a series of N-alkylideneanilines which indicate the importance of steric effects in the part of N-alkylidene groups to complexation with Eu(DPM)$_3$.

A typical paramagnetic shift of various proton signals induced by Eu(DPM)$_3$ is exemplified in Figure 1 by N-isopropylidene-p-toluidine (I). Identification of three singlet lines due to the methyl groups and multiplets due to the aromatic ring protons ortho and meta to the nitrogen atom is unequivocally made by a qualitative application of the McConnell-Robertson equation.[4)] Since the donor center for complexation with the lanthanide shift reagent is evidently the nitrogen lone pair of electrons in the N-alkylideneanilines, the methyl protons anti to the phenyl ring and the ring protons ortho to the nitrogen atom which are both more closely located to the lanthanide atom in the reagent-substrate complexes are considered to be subject to stronger paramagnetic shifts than the methyl protons syn to the aromatic ring and the meta ring protons, respectively. Thus, of the two methyl signals at δ 1.77 and 2.15 in CDCl$_3$ the lower field one is assigned to the methyl protons anti to the phenyl ring. This conclusion is in accord with that derived by considering the anisotropic effects of the lone pair of electrons[5)] and the benzene ring.[6)]

The methylene protons of N-3-pentylidene-p-toluidine (II) behave similarly on addition of Eu(DPM)$_3$, although the induced shifts are always about 20% smaller than the corresponding ones in I. The amount of the paramagnetic shifts is larger for the quartet signal originally at a lower field than for that at a higher field. It is also confirmed by a decoupling experiment that the triplet signal at the higher field corresponds to the methyl protons in the ethyl group syn to the phenyl ring. The assignments are again reasoned by considering the anisotropic effects of the nitrogen lone pair and the aromatic ring current. The same argument, however, fails to explain

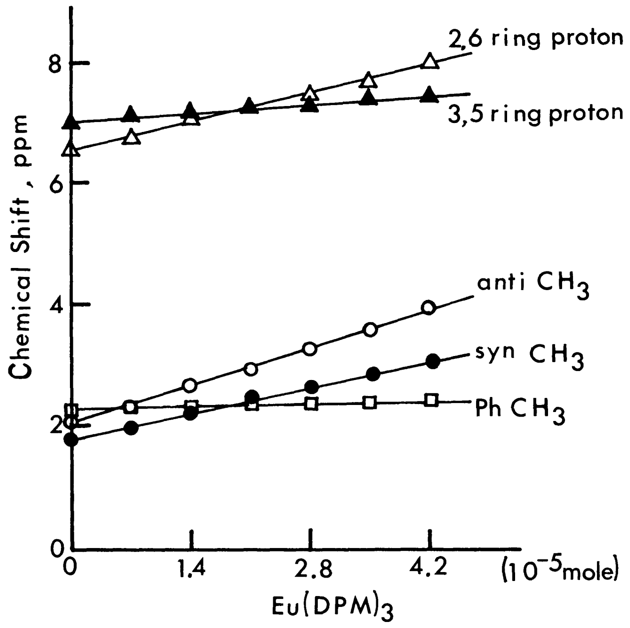


Fig. 1. Variation in observed chemical shifts with the amount of $Eu(DPM)_3$ for I in a $CDCl_3$ solution.

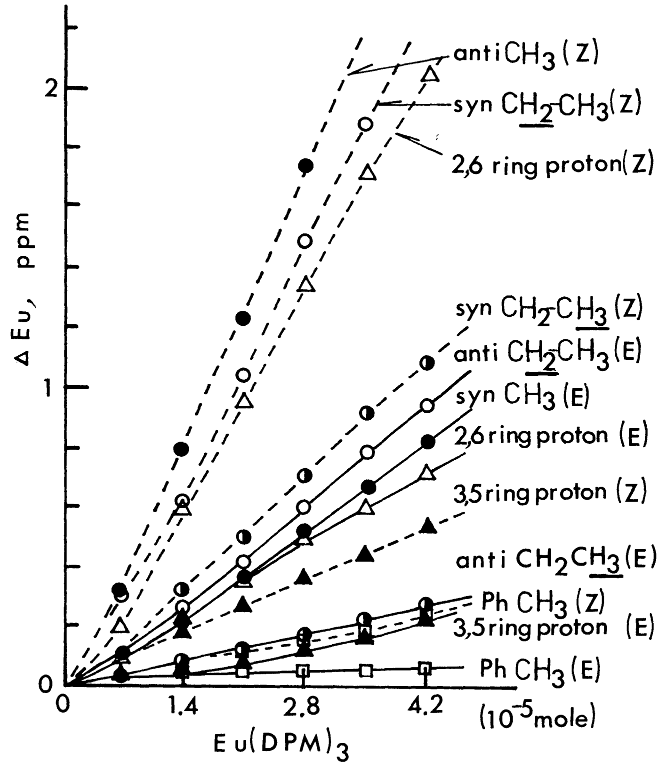
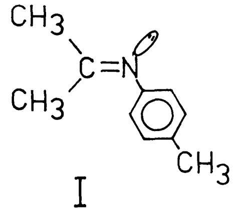
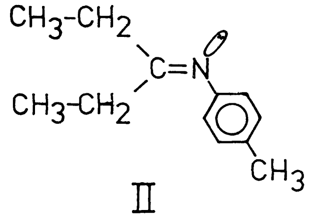


Fig. 2. Variation in induced shifts for various proton signals of III.

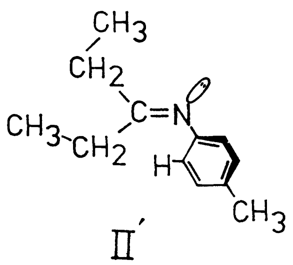
the relative amounts of the induced shift of the methyl signals. Unexpectedly, it is the triplet methyl signal at the higher field which moves faster to lower fields by addition of $Eu(DPM)_3$. The two curves obtained by plotting observed chemical shift of the two methyl triplets vs. the amount of $Eu(DPM)_3$ cross at 0.028 mmole of the latter added to a 0.5 mmole/ml solution of II in $CDCl_3$. One of the possible explanations which might account for the reversal of the induced shifts is that conformation II' is preferred by the buttressing effect of the phenyl group. The methyl protons syn to the lone pair of electrons are more closely located to the lanthanide atom in the complexed species but unfavorably situated in terms of the angular dependence of the McConnell-Robertson equation.[4,7]



I

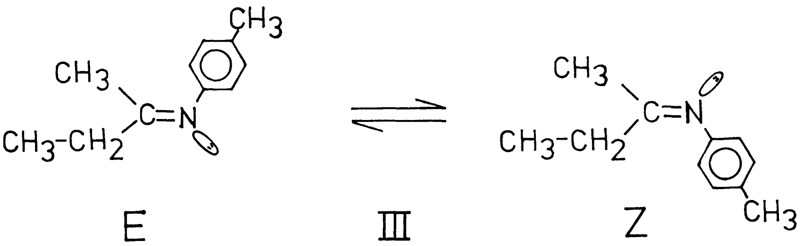


II



II'

The pmr spectra of N-sec-butylideneanilines are composed of two sets of the peaks, one of which are always about 4 times stronger than the other. By numerical comparison of the chemical shifts with those of I and II, it is concluded that geometrical isomers are present and that the E isomer is more abundant than the Z isomer. The isomer ratio is rather indifferent to the nature of ring substituents and seems to be governed primarily by the steric requirement of the ethyl relative to the methyl group. In this connection, it is interesting to note that, in the anils of t-butyl methyl ketone, only one singlet methyl signal is reported to appesr at δ 1.5 which corresponds in chemical shift to the methyl group of the E form.8) The shift reagent study of N-sec-butylidene-p-toluidine (III) summarized in Figure 2 reveals that the induced shifts are always larger for the less populated Z isomer than for the more abundant E isomer. The difference indicates that the Z isomer is more effectively complexed with Eu(DPM)$_3$ than the E isomer due to the larger steric requirement of the ethyl group for complexation at the nitrogen lone pair in the latter isomer.



III

A couple of precedents appeared recently for the role of steric hindrance to complexation of aniline substrates with the lanthanide shift reagents.9,10) It therefore seemed of interest to examine further the nature of the steric effect by comparing the complexation equilibrium constants of I and II. These are measured by a plot of an inverse of the observed downfield shifts vs. the total concentration of the substrate in large excess at a fixed amount of Eu(DPM)$_3$.11,12) The results are given in Table I. We note that the apparent steric hindrance to the observed down-

Table I. Complexation Equilibrium Constants and Intrinsic Paramagnetic Shifts of I- and II-Eu(DPM)$_3$

I			II		
Protons	Δ_{max} (ppm)	K (mole^{-1} l)	Protons	Δ_{max} (ppm)	K (mole^{-1} l)
syn-CH$_3$	8.03	22.6	syn-CH$_2$	5.46	20.9
anti-CH$_3$	9.29	22.2	anti-CH$_2$	6.18	21.1
ϕ-CH$_3$	0.89		syn-CH$_3$	2.67	21.3
o-H	7.52		anti-CH$_3$	1.75	21.0
m-H	2.18		ϕ-CH$_3$	0.56	
			o-H	5.05	
			m-H	1.46	

field shifts of II is better reflected in the intrinsic paramagnetic shift of the pure complex Δ_{max} than in the complexation equilibrium constant K. In other words, both I and II form the substrate-Eu(DPM)$_3$ complexes almost to the same extent, but their characteristic shift values are larger for the protons of I than for those of II. Thus the larger steric effect of the ethyl group compared to the methyl group appears to result in deformation, most probably separation of the distance between the nitrogen and the lanthanide atoms of the substrate-Eu(DPM)$_3$ complex to induce a poorer shift at the expense of only slight decrease in the complexation constant.

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(Received August 31, 1972)