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LANTHANIDE-INDUCED SHIFTS OF PYRIDINES, PYRIDINIUM AND PYRYLIUM SALTS

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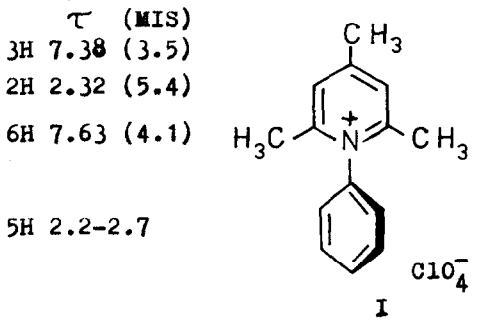
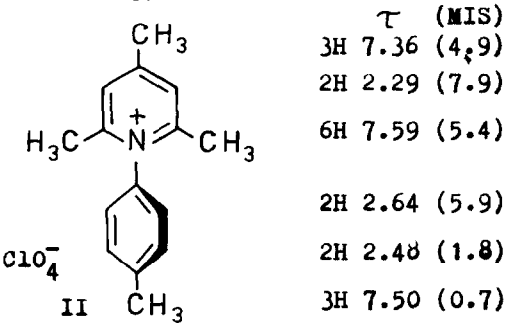
Though lanthanide-induced shifts (LIS) of pyridines have been intensely explored,[1] including the study of secondary isotope effects with deuteriated α-methyl substituents,[2] only one paper presented data on LIS of pyridinium salts,[3] and so far there are no reported investigations on LIS of pyrylium salts.

Pyridinium perchlorates were prepared from primary amines and substituted pyrylium perchlorates ;[4] when larger N-substituents are present, as in I or II, the solubility of these salts in $CDCl_3$ is satisfactory. All present results refer to ^{1}H-NMR spectra (τ values) using $CDCl_3$ as solvent (unless otherwise stated) and Eu(fod)$_3$ as lanthanide shift reagent. Chemical shifts and molar induced shifts (MIS, in brackets) are indicated on the formulas of pyridinium salts I and II.

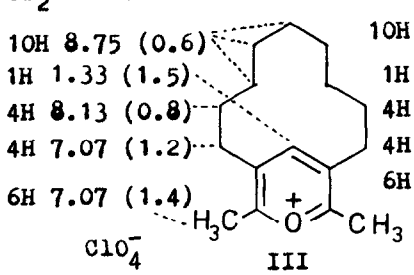


I

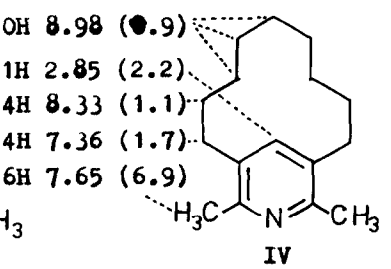


II

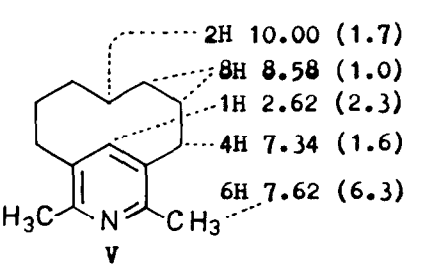
Pyrylium perchlorates are too little soluble in $CDCl_3$ unless they have large alkyl substituents, like III.[5] For comparison, chemical shifts and MIS values in CS_2 are indicated for the related pyridines IV,[5] and V.[6]



III



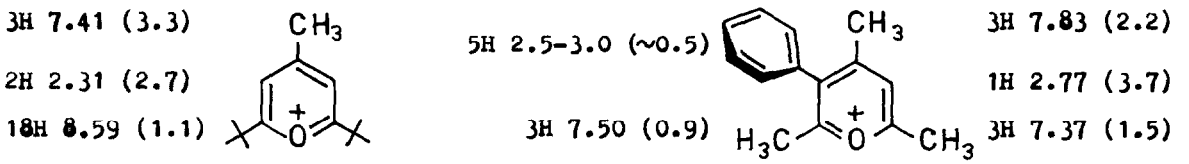
IV



V

In order to increase the solubility of pyrylium salts, organic anions were tested in the place of perchlorate anion. The easily formed pyrylium trifluoroacetates or trichloroacetates [7] which have satisfactory solubilities in $CDCl_3$ and even in benzene are, however, double salts including one mole of acid like the

pyrylium halides ;[8] hence they decompose the europium chelates and are unfit for LIS studies. We chose therefore pyrylium bis(pyrocatechol)borates VI and VII,[9] formed from pyrylium pseudobases and 2-alkoxy-1,3,2-benzodioxaboroles.[10]



VI VII

The results indicate that unlike pyridines which coordinate the europium atom through their nitrogen lone pairs (n-donors), the pyridinium salts (I, II) and the pyrylium salts (III, VI, VII) appear to be π-donors : the highest MIS values of I, II and VII are those of the heterocyclic β-standing protons (though in VII the π-electrons of the benzene rings are also available, the benzene protons have small MIS values) ; the highest MIS values of III and VI are those of the γ-protons, but in both these cases steric factors are important. The conclusion is that the europium seems to coordinate the π-electrons of the six-membered heterocyclic ring, above it and as far as possible from the electronegative heteroatom and from bulky groups like t-butyl in VI or the non-coplanar [9] phenyl in VII.

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