# SHIFTS INDUCED BY TRIS(DIPIVALOYLMETHANATO)EUROPIUM IN THE PMR SPECTRA OF ACETYLINDOLES

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It is known that the lanthanide complexes of β-diketones ("shift reagents") cause shifts of the signals in the PMR spectra of π-deficient heterocycles [1, 3] due to the formation of secondary complexes with the participation of the unshared electron pair of the heteroatom. At the same time, there are indications that π-surplus heterocycles, particularly indole, in which this unshared electron pair participates in the aromatic sextet, are inert with respect to shift reagents [3].

We have found that tris(dipivaloylmethanato)europium [$Eu(DPM)_3$] induces shifts in the PMR spectra of 2- and 3-acetylindoles, as in the case of other carbonyl compounds [3, 4], and complexing proceeds only at the carbonyl group. The magnitude of the shifts are linearly dependent on the [$Eu(DPM)_3$] : [acetylindole] ratio up to 0.89:1; this made it possible to find the chemical shifts of the signals of the aromatic protons by extrapolating the spectra to zero $Eu(DPM)_3$ concentration. The observed induced shifts of the protons of the acetyl group are 14.9 and 15.3 ppm (relative to the signals of the free 2- and 3-acetylindoles, respectively) for an [$Eu(DPM)_3$] : [acetylindole] ratio of 1:1. The induced shifts ($\Delta H_{obs}$) of the remaining protons, which are presented in Table 1, are expressed in relative values, the unit of which was taken as the $Eu(DPM)_3$-induced shift of the signal of the protons of the $CH_3CO$ group.

A comparison of the data obtained with the calculated values for possible models of the complexes of acetyindoles with $Eu(DPM)_3$ demonstrates that planar conformations in which the methyl of the acetyl group is directed toward the hydrogen atom of the pyrrole ring (Figs. 1 and 2) are preferred. The europium atom

TABLE 1. Data from the PMR Spectra of 2- and 3-Acetylindoles and Shifts Induced in Them by Tris(dipivaloylmethanato)europium

| 2-Acetylindole | | | | | | | |
|---|---|---|---|---|---|---|---|
| | $1\text{-}CH_3$ | $2\text{-}COCH_3$ | 3-H | 4-H | 5-H | 6-H | 7-H |
| Free 2-acetylindole | 4,10 | 2,57 | 7,19 | 7,65 | 7,26—7,29 | | |
| $\Delta H_{obs}$ | 0,815 | 1,000 | 0,527 | 0,214 | 0,125 | 0,125 | 0,232 |
| r, Å | 4,75 | 4,75 | 7,08 | 9,70 | 10,85 | 9,90 | 7,57 |
| θ, ° | 37,8 | 33,0 | 8,3 | 4,7 | 17,0 | 29,5 | 34,0 |
| $\Delta H_{calc}$ | 0,815 | 1,000 | 0,525 | 0,209 | 0,131 | 0,125 | 0,236 |
| 3-Acetylindole | | | | | | | |
| | $1\text{-}CH_3$ | 2-H | $3\text{-}COCH_3$ | 4-H | 5-H | 6-H | 7-H |
| Free 3-acetylindole | 3,78 | 7,40 | 2,33 | 8,28 | 7,20—7,23 | | |
| $\Delta H_{obs}$ | 0,279 | 0,645 | 1,000 | 0,937 | 0,134 | 0,158 | 0,244 |
| r, Å | 9,50 | 7,00 | 5,25 | 4,95 | 7,25 | 9,23 | 9,25 |
| θ, ° | 1,0 | 12,0 | 31,0 | 36,5 | 46,0 | 35,0 | 19,0 |
| $\Delta H_{calc}$ | 0,280 | 0,655 | 1,000 | 0,930 | 0,141 | 0,155 | 0,255 |

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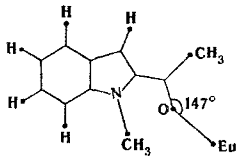

Fig. 1

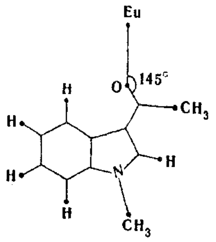

Fig. 2

Fig. 1. Scale diagram of the complex of 1-methyl-2-acetylindole with tris(dipivaloylmethanato)europium.

Fig. 2. Scale diagram of the complex of 1-methyl-3-acetylindole with tris(dipivaloylmethanato)europium.

in the complexes lies in the plane of the heteroring, and the O−Eu distance is 3.1 Å and angle C−O−Eu is 145-147°; these differ somewhat from the parameters of complexes of $Eu(DPM)_3$ with aliphatic ketones [3]. The $\Delta H_{calc}$ shifts calculated for the proposed models are presented in Table 1. The induced shifts were calculated from the formula for a pseudocontact interaction [3]:

$$\Delta H = \text{const}\,\frac{3\cos^2\theta - 1}{r^3},$$

where r is the H−Eu distance, and $\theta$ is the H−Eu−O angle. In the calculation of ΔH of the methyl group, the distance from Eu to the center of rotation of the hydrogen atoms was taken as r.

Precisely the same shifts of the signals as in the undeuterated products are observed in the PMR spectrum of 3-deutero-2-acetylindole, and the 3-H signal is, of course, absent.

The chemical shifts of the protons of the free acetylindoles are given for 0.2 mole solutions in $CCl_4$ in parts per million from tetramethylsilane (the internal standard). The PMR spectra were recorded with a ZKR-60 spectrometer with an operating frequency of 60 MHz at 25°.

## LITERATURE CITED

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