Tetrahedron Letters No. 39, pp 4033 - 4034, 1972. Pergamon Press. Printed in Great Britain.

^{13}C AND ^{1}H NUCLEAR MAGNETIC RESONANCE SPECTRA OF QUINOLINE IN THE PRESENCE OF LANTHANIDE SHIFT REAGENTS

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(Received in UK 18 August 1972; accepted for publication 24 August 1972)

For the use of lanthanide shift reagents Ln(β-diketonato)$_3$ in the assignment of nmr spectra, it is necessary that the isotropic shifts they produce be predominantly pseudocontact in origin. The pseudocontact nature of the isotropic shifts of ^{1}H lines in the presence of Ln(dpm)$_3$ complexes has been confirmed for numerous systems (*e.g*. reference 1) and specifically for quinoline[2]. Carbon nuclei are expected to be more sensitive to contact interaction[3] and although the isotropic shifts of borneol ^{13}C lines in the presence of Pr(dpm)$_3$ can be explained on a pseudocontact basis[4], more experimental results on ^{13}C shifts are required before the method can be applied with confidence.

The table shows the isotropic shifts of all the ^{1}H and ^{13}C resonances of quinoline[5,6] in the presence of the four most popular shift reagents Eu(dpm)$_3$, Eu(fod)$_3$, Pr(dpm)$_3$, and Pr(fod)$_3$; and also gives the expected pseudocontact ratios calculated from the previously proposed Eu-quinoline geometry[2]. It is clear from the ^{13}C data that a completely pseudocontact mechanism is inadequate for the shifts produced by the Eu(β-diketonato)$_3$ complexes: the shifts of C-3 and C-10 are small and negative, respectively, and there is a large difference between the shifts of C-2 and C-9. These deviations are greater in Eu(fod)$_3$ and with this complex the ^{1}H shifts show an anomaly in that H-3 shifts less than H-4. The shifts of the ^{13}C lines produced by Pr(β-diketonato)$_3$ complexes agree more closely with the expected geometric ratios even though the geometry was taken from Eu(dpm)$_3$ ^{1}H measurements, but the observed shifts attenuate too rapidly from C-2 to C-3 and the differences between C-2 and C-9, and C-3 and C-10 are too great. The differences between observed and calculated ^{13}C:^{1}H shift ratios at each ring position are small for the Pr complexes, but for the Eu complexes these

Nucleus	$Eu(dpm)_3^a$	$Eu(fod)_3^a$	$Pr(dpm)_3^a$	$Pr(fod)_3^a$	R^b
C-2	87.6	119.5	-99.5	-139.8	1.00
C-3	6.0	0.0	-27.5	- 37.1	0.47
C-4	21.9	29.0	-25.1	- 33.5	0.37
C-5	7.6	10.8	-15.5	- 21.5	0.26
C-6	7.2	12.0	-11.2	- 15.5	0.21
C-7	14.3	24.0	-18.7	- 26.3	0.25
C-8	46.2	69.3	-53.8	- 80.1	0.62
C-9	43.8	55.0	-71.7	- 87.3	0.88
C-10	-2.4	-9.6	-19.9	- 26.3	0.45
H-2	24.7	27.3	-53.7	- 74.1	0.87
H-3	7.9	10.1	-16.1	- 20.7	0.29
H-4	7.7	10.9	-13.8	- 17.0	0.23
H-5	5.2	7.9	- 9.7	- 13.3	0.18
H-6	4.2	7.4	- 7.5	- 10.4	0.12
H-7	3.7	7.1	- 7.5	- 11.9	0.12
H-8	21.2	39.0	-44.0	- 61.5	0.71

[a] Observed isotropic shifts in $CDCl_3$ solution in ppm, positive downfield.

[b] Ratios of $(3\cos^2\theta-1)/r^3$ calculatedfor geometry ref. 2.

differences are large and their signs alternate. Deviations of the observed ^{13}C shifts from the predicted are in the order $Eu(fod)_3 > Eu(dpm)_3 \gg Pr(fod)_3 > Pr(dpm)_3$.

The larger than expected difference between C-2 and C-3 in all cases suggests that both Eu and Pr complexes produce a contact shift of C-2 in the same direction as the pseudocontact shift, indicating that C-2 has gained positive spin density from Eu complexes and negative spin density from Pr complexes. This change of sign and also the magnitudes of the contact shifts are in agreement with observations on the isotropic shifts of the ^{17}O resonance of water in the presence of Ln^{3+} ions which are believed to be predominantly contact[7].

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