Tetrahedron Letters No. 33, pp 2925 - 2928, 1975. Pergamon Press. Printed in Great Britain.

LANTHANIDE INDUCED SHIFTS ON THE CARBON-13 CHEMICAL SHIFTS OF 2-ADAMANTANOL AND 2-ADAMANTANETHIOL [1]

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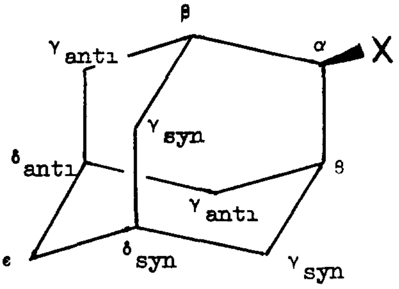
(Received in UK 23 June 1975; accepted for publication 7 July 1975)

Maciel and coworkers[2] recently reported different chemical shifts for the two δ carbons of 2-substituted adamantanes. They carried out a tentative assignment in analogy to the well known assignment of the two γ carbons. In this case the signals of the carbons in γ_{syn} position relative to the substituent are shifted significantly upfield compared with those of the γ_{anti} carbons which is due to a steric compression. Newly published findings[3] show that for δ carbons another interaction mechanism dominates, because δ_{syn} carbons can be more deshielded than δ_{anti} carbons.



1 : X = OH
2 : X = SH

Measurements of the longitudinal relaxation times T_1 of the carbons of 2-monosubstituted adamantanes[4] and the chemical shifts of 4-substituted adamantanones[5] clearly demonstrate that the δ_{anti} carbons of 2-substituted adamantanes are more shielded than the δ_{syn} carbons. The sequence of the two δ signals is reverse to the sequence of the γ signals. This assignment is now confirmed by the LIS data of the compounds 1 and 2 :
The substrates for the LIS measurements are 2-adamantanol (1) and 2-adamantanethiol (2)[6]. Though 2 is a weakly complexing reagent, it was chosen because relaxation measurements have shown that the T_1 values of the δ carbons differ significantly only if X is a relatively heavy substituent as SH, Cl, Br or I. For X = OH and NH_2 these two T_1 values are nearly identical, thus no assignment of the δ signals can be executed from such measurements.

The spectra were recorded with a Bruker WH 90 spectrometer. The chemical shifts are in ppm relative to TMS as internal standard, the solvent being $CDCl_3$.

Table 1 : Chemical Shifts of 2-Substituted Adamantanes[a]

	α	β	γ_{syn}	γ_{anti}	δ_{syn}	δ_{anti}	ϵ
X = OH	74.7	34.7	31.2	36.7	27.8	27.3	37.8
X = SH	46.5	35.7	31.0	38.9	27.9	27.1	37.9

[a] In ppm; TMS: 0 ppm; positive values correspond to deshielding.

From the measured LIS, $\Delta\delta$, the experimental b_i values were calculated using the following equation:

$$\Delta\delta = b_i \frac{n}{m} \qquad (1)$$

with n representing the molarity of the shift reagent and m the molarity of the substrate 1 or 2. The maximal n/m ratios are given in the last column of Table 2. The experimental b_i's are interpreted according to the McConnell equation:

$$b_i = c\,\frac{3\cos^2\alpha_i - 1}{r_i^3} \qquad (2)$$

and were approximated as far as possible by iterative determination of the position (x_o, y_o) of the lanthanide ion with a relative least square fit:

$$S = \sum_i \left[\frac{c\,\frac{3\cos^2\alpha_i - 1}{r_i^3} - b_i}{b_i} \right]^2 \qquad (3)$$

where S is the sum of the squared deviations. The position of the lanthanide ion was assumed to be in the symmetry plane of the molecule ($z_o = 0$). Therefore an iteration only for x_o, y_o and c was performed. The experimental and the calculated b_i values are listed in Table 2, the calculated values in parentheses.

Results

2-Adamantanol + $Eu(dpm)_3$:

Recently it was reported[7] that contact interaction for LSR complexes with alcohols is restricted essentially to the nearest carbon. Therefore the iteration of the LIS was carried out excluding the α carbon. The calculations provided a distance Eu - O of 4.9 Å and the angle C_α - O - Eu = 177.1°. A contact term of about 39 ppm for the α carbon could be derived from the difference between the experimental and the calculated b_α. The b_i's were calculated with both alternative assignments of the two δ signals. A remarkably smaller divergence between the experimental and the calculated b_i's resulted, if the assignment is that given in Table 1. That means, the δ_{anti} carbon is more shielded than the δ_{syn} carbon.

Table 2 : Experimental b_i values from equation (1) and error limits (95%), and calculated b_i values using equations (2) and (3) in parentheses.

	α	β	γ_{syn}	γ_{anti}	δ_{syn}	δ_{anti}	ϵ	n/m_{max}
X = OH (1) + $\mathrm{Eu(dpm)_3}$	61.85 ± 10%	16.43 ± 11%	16.96 ± 14%	8.25 ± 11%	11.17 ± 14%	8.14 ± 14%	6.99 ± 10%	0.2
	(22.70)	(16.13)	(16.81)	(8.96)	(11.35)	(7,56)	(6.86)	
X = SH (2) + $\mathrm{Eu(fod)_3}$	0.3916 ± 6%	0.1692 ± 19%	0.2098 ± 16%	0.1388 ± 16%	0.1969 ± 19%	0.1564 ± 25%	0.1255 ± 26%	0.5
	(0.3750)	(0.2006)	(0.2056)	(0.1486)	(0.1709)	(0.1321)	(0.1293)	
X = SH (2) + $\mathrm{Yb(dpm)_3}$	-0.1437 ± 23%	-0.3224 ± 8%	-0.3996 ± 6%	-0.3177 ± 5%	-0.3960 ± 7%	-0.3557 ± 11%	-0.3285 ± 9%	0.5

2-Adamantanethiol + $Eu(fod)_3$:
An analogous result for the two δ carbons and therefore the same assignment was obtained with the same least square fit. The distance Eu - S was 10.3 Å and the angle C_α - S - Eu was 170.0°. The relatively large distance between Eu and sulphur is understandable, if we consider that a mercapto group complexes rather weakly. Here the lanthanide position was also iterated including the C_α signal, too. No significant contact interaction could be detected.

2-Adamantanethiol + $Yb(dpm)_3$:
Surprisingly, in this experiment all carbon chemical shifts are shifted upfield by the LSR. With the exception of the C_α signal the b_i values of all signals are very similar. Therefore we assume that an upfield shift of the entire spectrum has occurred, caused by a change of the susceptibility in solution. Relative to that general upfield shift the signal of the α carbon is shifted downfield. No calculation was carried out in this case, of course.

REFERENCES AND FOOTNOTES

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