

Article

Skeletal and Chlorine Effects on ^{13}C -NMR Chemical Shifts of Chlorinated Polycyclic Systems

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Com o objetivo de realizar uma análise comparativa do efeito de compressão anelar e do Cl no deslocamento químico dos carbonos clorados tencionados, foram analisados os deslocamentos químicos de 27 estruturas policíclicas cloradas e não cloradas derivadas dos inseticidas “aldrin” (5) e “isodrin” (14). Os compostos foram divididos em quatro grupos de acordo com a conformação e número de anéis: tetraciclododecanos *endo-exo*, tetraciclododecanos *endo-endo*, pentaciclododecanos e hexaciclododecanos. A comparação do deslocamento químico de carbono-13 entre compostos clorados e não-clorados mostrou que, quando C-9 e C-10 são carbonos olefínicos, ocorre um deslocamento para baixa frequência de 0.5-2.4 ppm para os tetraciclododecanos *endo-endo* e de 4.7-7.6 ppm para os tetraciclododecanos *endo-exo*. Para C-11, a variação do deslocamento químico atinge valores de 49-53 ppm para os tetracíclicos *endo-exo* e *endo-endo*, de 54 ppm para o pentacíclico e de 56-59 ppm para os hexacíclicos. A partir desses dados foi possível observar a influência da compressão anelar no deslocamento químico.

In order to establish a comparative analysis of chemical shifts caused by ring compression effects or by the presence of a chlorine atom on strained chlorinated carbons, a series of the chlorinated and dechlorinated polycyclic structures derived from “aldrin” (5) and “isodrin” (14) was studied. Compounds were classified in four different groups, according to their conformation and number of ring such as: *endo-exo* and *endo-endo* tetracyclics, pentacyclics and hexacyclics. The ^{13}C chemical shift comparison between the chlorinated and dechlorinated compounds showed that when C-9 and C-10 are olefinic carbons, it occurs a shielding of 0.5-2.4 ppm for *endo-endo* tetracyclics and of 4.7-7.6 ppm for *endo-exo* tetracyclic. The chemical shift variation for C-11 reaches 49-53 ppm for *endo-exo* and *endo-endo* tetracyclics, 54 ppm for pentacyclic and 56-59 ppm for hexacyclic compounds. From these data, it was possible to observe the influence of ring compression on the chemical shifts.

Keywords: chlorinated polycyclic compounds, ^{13}C -NMR, ring compression

Introduction

The synthesis of hexachlorinated polycyclic systems like insecticides 5, 14 and their derivatives was already reported thirty years ago¹. Cox and McKinney² observed that the degradation of chlorinated polycyclic systems in the environment usually involves hydrolytic, oxidative and intramolecular rearrangement reactions, and leaves the basic carbon skeleton intact. In their work, they assigned the chemical shift of thirty spectra of hexachlorinated polycyclic systems derived from 5 and 14 and concluded that the ^{13}C -NMR technique was efficient in the identification of the degradation products from these compounds.

Polycyclic compounds have been a central research object in a number of investigations focusing on aspects of theoretical chemistry as well as NMR spectroscopy³. Lipmaa and Pehk⁴, using the ^{13}C -NMR techniques, verified that it is very useful for the elucidation of polycyclic systems. Research on derivatives of bicyclo[2.2.1]heptane and bicyclo[2.2.2]octane showed a good correlation between chemical shifts and geometric effects⁵.

Several studies on rigid polycyclic systems, involving correlations between the stereochemistry of the substituent on the ring and ^{13}C -NMR chemical shifts were reported⁶. The investigation of rigid polycyclic systems with unique

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conformations has contributed to the understanding of several aspects of NMR spectroscopy in relation to geometry and steric parameters. Long-range steric effects of *endo-endo* and *endo-exo* tetracyclododecanes have been studied by our group using ^{13}C and ^1H -NMR⁷. In spite of the large amount of work available on this subject, some effects caused by the six chlorine atoms on the hexachlorinated polycyclic compounds, with respect to both electronic and ring compression, have not been studied properly.

This paper, describes a systematic and comparative study about the chlorinated polycyclic compounds and their dechlorinated derivatives, in order to verify the effects of the chlorine atoms on the chemical shifts of the carbons on chlorinated rings. Thus, 27 tetra, penta and hexacyclic structures were analyzed.

Results and Discussion

In order to carry out this work, carbons C-1, C-8, C-9, C-10 and C-11 of the polycyclic compounds were studied. Chlorinated and dechlorinated compounds were prepared according to procedures reported in the literature^{1,8}. Carbon-13 spectra of the dechlorinated polycyclic systems **2**, **4**, **6**, **8**, **17** and **19** as well as the chlorinated polycyclic systems **7** and **18** were assigned by the combination of Lanthanide Induced Shift (*LIS*) methodology with pulse techniques like APT, COSY, and HETCOR⁹. The assignments of the ^{13}C chemical shift of the molecules **1**, **5**, **14**, and **26** were the same as those reported by Cox and McKinney² but, relatively to these data, we observed a different assignment for C-1, C-8, C-9 and C-10 of compounds **18** and an inversion of the assignment of C-8 and C-9 for compounds **23** and **27**.

The assignment differences between our data and those reported by Cox and McKinney can be attributed to the different techniques used. What they did was to correlate the slopes of *LIS* curves of each carbon with the effect of the induced shift on distance, assuming that the lanthanide oxygen shift reagent was complexing with the carbonyl of **18**. This methodology does not provide good results because it does not foresee the effects of contact and pseudo-contact in the induction shift. As it has been reported, ^{13}C resonances happen to be more sensitive to contact contributions than proton resonances involving the same number of intervening bonds at the site of metal-atom coordination, so that the induced chemical shift, especially for the nuclei distant from the complexation center, should be negligible for ^{13}C in comparison to ^1H ¹⁰.

Table 1 shows the chemical shift variation ($\Delta\delta$) for the carbons C-1, C-8, C-9, C-10 and C-11 of chlorinated and dechlorinated *endo-exo* (**1-6**), *endo-endo* (**7-15**) tetracyclic, pentacyclic (**16**, **17**) and hexacyclic compounds (**18-21**). In this Table it is possible to observe that, for the analogous series of compounds **7** (trichlorinated), **8** (dechlorinated)

and **9** (hexachlorinated), the olefinic carbons C-9 and C-10 present small chemical shift variations, while C-1 and C-8 are strongly deshielded (33.7-35.0 ppm). In general, C-9 and C-10 show a similar behavior to C-1 and C-8 when C-9 and C-10 are saturated carbons. The average deshielding for these carbons is in the order of 35.0 ppm. This is in accordance with the data already described for cyclohexane¹¹. But, when C-9 and C-10 are olefinic carbons, a shielding of 0.5-2.4 ppm occurs for the tetracyclic *endo-endo* compounds and of 4.7-7.6 ppm for the tetracyclic *endo-exo* isomers. On the other hand, when C-11 possesses two bonded chlorine atoms, its chemical shift is more strongly deshielded. This carbon displays an interesting behavior, because the chemical shift variation increases with the number of rings: 49-53 ppm for *endo-exo* and *endo-endo* tetracyclic, 54 ppm for pentacyclic, and 56-59 ppm for hexacyclic compounds, indicating the existence of a ring compression effect on the chemical shift.

Table 2 shows the chemical shifts for C-11 of hexachlorinated *endo-endo* and *endo-exo* tetracyclic compounds and hexachlorinated pentacyclic compounds. In this Table it is interesting to observe that chemical shift variations between *endo-endo* and *endo-exo* tetracyclic as well as *endo-exo* tetracyclic and pentacyclic compounds are of the order of 5 ppm. Another possible conclusion from Table 2 is that each type of chlorinated compound possesses a characteristic chemical shift for C-11. This effect is better observed when the chemical shift of C-11 for all chlorinated compounds is examined: ~109 ppm for tetracyclic *endo-endo*, ~104 ppm for tetracyclic *endo-exo* and ~99 ppm for pentacyclic compounds, indicating the influence of ring compression effects on the chemical shift of C-11.

Experimental

The studied compounds were synthesized in our laboratory following procedures reported in the literature⁹ with exception of the start products isodrin (**14**) and aldrin (**5**). Analytical data of these compounds were collected with an Electrothermal IA 9100 digital melting point apparatus and a Perkin-Elmer 2400 CHN elemental analyzer apparatus. The measurement results are in agreement with the literature^{1,8}.

Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadionate)europium(III), $\text{Eu}(\text{fod})_3$, Chloroform-*d*₁, 99.8% atom D, and Isodrin 98% were purchased from Aldrich Chemical Co. as pure materials. Nuclear magnetic resonance spectra were obtained in Varian VXR-200 and Varian Inova-300 spectrometers, respectively with magnetic fields of 4.7 T and 7.0 T and at a temperature of 22 °C. Chemical shift values are expressed as δ (parts per million) relative to TMS as an internal standard. Standard Varian software was used to acquire and process the ^{13}C APT, HETCOR and COSY spectra¹².

Table 1. Chemical shift variation ($\Delta\delta^{13}\text{C}$) in ppm for chlorinated and dechlorinated *endo-exo*, *endo-endo* tetracyclic, pentacyclic and hexacyclic compounds.

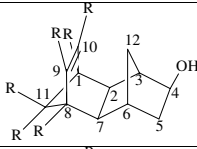
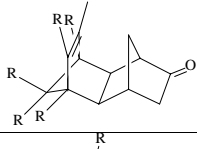
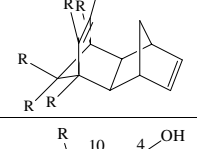
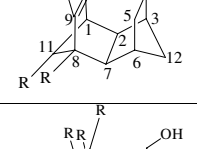
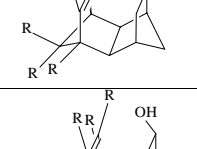
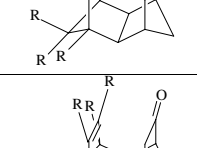
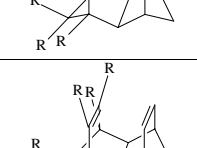
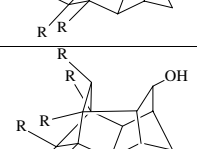
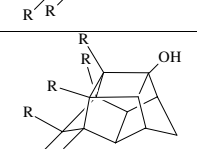
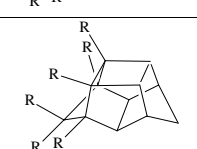

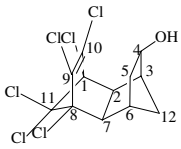
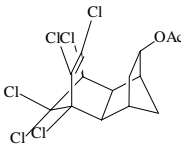
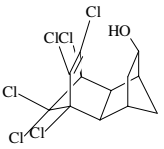
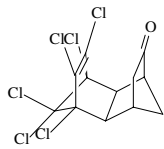
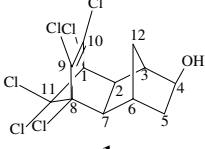
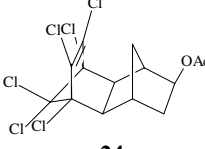
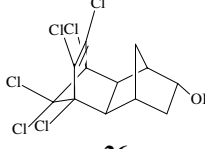
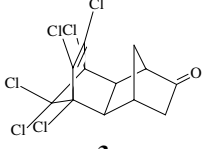
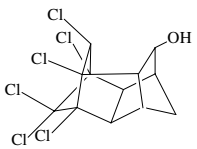
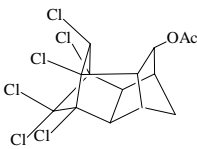
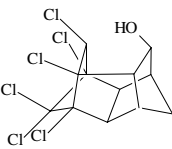
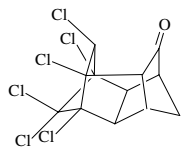
Compounds		C-1	C-8	C-9	C-10	C-11
	R Cl (1)	80.6	80.3	130.4	130.3	104.3
	R = H (2)	46.4	46.2	135.4	135.3	53.1
	$\Delta\delta^{13}\text{C}$	34.2	34.1	-5.0	-5.0	51.2
	R Cl (3)	80.3	79.9	130.7	130.4	104.0
	R = H (4)	46.6	46.6	135.4	136.6	53.6
	$\Delta\delta^{13}\text{C}$	33.7	33.3	-4.7	-6.2	50.4
	R Cl (5)	79.9	79.9	130.6	130.6	105.3
	R = H (6)	42.7	42.7	138.2	138.2	55.7
	$\Delta\delta^{13}\text{C}$	37.2	37.2	-7.6	-7.6	49.6
	R Cl (7)	48.9	79.5	133.3	126.6	83.6
	R = H (8)	44.3	44.5	132.7	132.0	58.9
	$\Delta\delta^{13}\text{C}$	4.6	35.0	0.6	-5.4	24.7
	R Cl (9)	78.0	79.5	132.0	131.5	109.4
	R = H (8)	44.3	44.5	132.7	132.0	58.9
	$\Delta\delta^{13}\text{C}$	33.7	35.0	-0.7	-0.5	50.5
	R Cl (10)	79.6	80.2	129.0	137.0	110.4
	R = H (11)	43.8	41.0	136.6	137.6	60.2
	$\Delta\delta^{13}\text{C}$	35.8	39.2	-7.6	-0.6	50.2
	R Cl (12)	77.2	77.9	134.0	133.7	108.7
	R = H (13)	43.6	44.6	136.4	134.2	57.3
	$\Delta\delta^{13}\text{C}$	33.6	33.3	-2.4	-0.5	51.4
	R Cl (14)	80.2	80.2	129.0	129.0	108.7
	R = H (15)	44.5	44.5	131.4	131.4	55.5
	$\Delta\delta^{13}\text{C}$	35.7	35.7	-2.4	-2.4	53.2
	R Cl (16)	85.0	79.6	74.3	64.5	98.6
	R = H (17)	45.4	39.0	37.9	35.3	44.8
	$\Delta\delta^{13}\text{C}$	39.6	40.6	36.4	29.2	53.8
	R Cl (18)	82.1	81.2	75.6	83.7	98.1
	R = H (19)	43.0	46.4	39.3	50.8	39.0
	$\Delta\delta^{13}\text{C}$	39.1	34.8	36.3	32.9	59.1
	R Cl (20)	83.5	83.5	78.2	78.2	97.5
	R = H (21)	46.1	46.1	43.8	43.8	41.2
	$\Delta\delta^{13}\text{C}$	37.4	37.4	34.4	34.4	56.3

Table 2. Chemical shift ($\delta^{13}\text{C}$) in ppm for C-11 of chlorinated *endo-endo*, *endo-exo* tetracyclic, and pentacyclic compounds.

				
	9	22	10	12
C-11	109.4	109.4	110.4	108.7
				
	1	24	26	3
C-11	104.3	104.3	104.3	104.0
				
	16	23	25	27
C-11	98.8	99.5	99.3	98.8

Conclusion

The outcomes suggest that the saturated carbons bonded with only one chlorine atom possess an average chemical shift variation of the order of 35 ppm. The effect of two chlorine atoms bonded in the same C-11 carbon atom is approximately 50 ppm, whereas the expected result would be of approximately 70 ppm. This seems to indicate that the shielding effect of chlorine atoms is not equivalent to that caused in the linear chain compounds.

Moreover, each kind of polycyclic hexachlorinated compound possesses a characteristic chemical shift for C-11. In fact, the number of rings induces a ring compression effect that produces an increase of C-11 chemical shift. This compression effect is also observed when *endo-endo* and *endo-exo* tetracyclic, and when *endo-exo* tetracyclic and pentacyclic compounds are compared.

The shielding effect that chlorine atoms cause on olefinic carbons can be attributed to the steric-electronic effect due to the interaction between non-bonded electrons of chlorine atoms with π -orbitals of olefinic carbons.

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