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Preliminary communication

The non-equivalence of chemical shifts of the diastereotopic carbons in the cyclopentadienyl ring of chiral monosubstituted cymantrene derivatives

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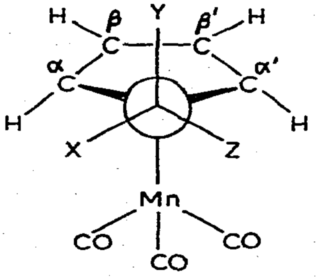
A consideration of steric relations of the atom groups in the cyclopentadienyl ring of the monosubstituted chiral compounds of cymantrene, (I), shows that both the C–H groups at the α and α' positions and those at the β and β' positions are diastereotopic. Therefore, the physico-chemical properties of such groups and of their constituent atoms should be different. Actually, we found[1] earlier that the non-equivalence of the hydrogen atoms at the α and α' positions in the cyclopentadienyl ring of 1,1,1-trifluoro-2-hydroxyethylcymantrene, (Ia), and diethyl ester of 1-cymantryl-1-hydroxyethylphosphonic acid, (Ib), could be detected by PMR techniques. In the PMR spectra of compounds (Ia) and (Ib), the α and α' protons have different chemical shifts, *i.e.* they are anisochronic. In the carbinol (Ib) it is also possible to observe the non-equivalence of the chemical shifts of the β and β' ring protons.

The present paper is concerned with the magnetic non-equivalence of the diastereotopic carbon atoms in the cyclopentadienyl ring of chiral monosubstituted cymantrenes as shown in the NMR spectrum.



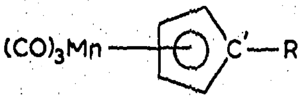
(I)

(Ia : X = OH , Y = CF_3 , Z = H ;
Ib : X = OH , Y = CH_3 , Z = $PO(OC_2H_5)_2$;
Ic : X = OH , Y = CH_3 , Z = H)

The ^{13}C NMR spectrum of the ring carbons of the achiral monosubstituted cymantrenes shows three signals: from the carbon atom bonded to the substituent, and from carbon atoms at α and β positions. However in the chiral compounds (Ia) and (Ib) all five carbons are anisochronic (Fig.1 and Table 1). The presence of five signals in the region of the cyclopentadienyl ring carbon resonances can be explained by a diastereotopy of the α and α' as well as the β and β' carbons.

TABLE 1

^{13}C NMR SPECTRAL PARAMETERS OF CHIRAL CARBINOLS [δ(CHCl$_3$) 0 ppm]

I		α, α'	β, β'	$\underline{C}$–OH	$\underline{CH}_3(\underline{C}F_3)$	$\underline{C}'$	$\underline{CH}_2CH_3$	$CH_2\underline{CH}_3$	$(\underline{C}O)_3$
a	$-CH-CF_3$ | OH	6.89 5.98	4.81 4.42	−9.41 (quartet) *J*(CF) 32.36 Hz	46.4 (quartet) *J*(CF) 282.4 Hz	19.9			146.9
b	CH_3 | $-C-PO(OCH_2CH_3)_2$ | OH	8.65 6.65	4.80 0.80	−11.3	−51.9	29.53	−13.8	−61.2	147.1
c	$-CH-CH_3$ | OH	4.94 4.42	4.16 3.64	−13.13	−52.77	33.2			147.5

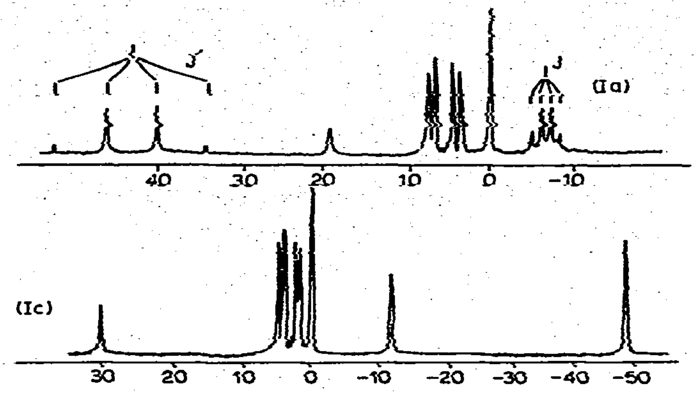


Fig. 1. The ^{13}C NMR spectra of (Ia) and (Ic).

We failed to detect the non-equivalence of diastereotopic ring hydrogens in the chiral methylcymantrylcarbinol (Ic) unlike compounds (Ia) and (Ib), by means of proton magnetic resonance spectroscopy. The PMR spectrum of (Ic) is characteristic of achiral monosubstituted cymantrenes and it contains two pseudotriplets at δ 4.61 and 4.78 ppm from the α and β protons respectively. However in the ^{13}C NMR spectrum of (Ic) non-equivalence of the carbons in the C—H groups is observed distinctly (Fig. 1). Thus, while the difference in the degree of shielding of the protons of these groups is rather small and does not show up in the PMR spectrum, the non-equivalent shielding of the diastereotopic carbons in compound (Ic) is apparent in the ^{13}C NMR spectrum.

This is further evidence that diastereotopic relations are a necessary, but not sufficient, condition for revealing differences in the properties of symmetrically non-equivalent groups.

Table 1 lists the ^{13}C NMR spectral parameters of compounds (Ia—c) obtained in chloroform on a HX-90-Brucker spectrometer at 22.63 MHz with double ^{1}H—^{13}C-resonance. Chemical shifts are given in ppm using chloroform as the internal standard. The assignment of the resonance frequencies to the cyclopentadienyl ring carbons is as usual (apart from the atom bound to the substituent). An accurate signals assignment will be reported in a later communication.

Thus in the present paper we have initially demonstrated the non-equivalence of chemical shifts of diastereotopic carbon atoms, the chiral monosubstituted cymantrene derivatives having been chosen as examples.

REFERENCES

1 D.N. Kursanov, Z.N. Parnes, N.M. Loim, N.E. Kolobova, I.B. Zlotina, P.V. Petrovskii and E.I. Fedin, *J. Organometal. Chem.*, 44 (1972) C15.