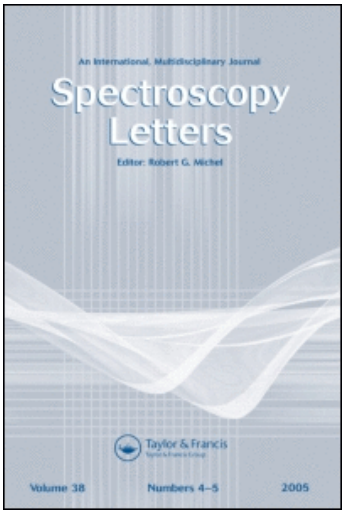

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Long Range Proton Couplings in Estrones

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LONG RANGE PROTON COUPLINGS IN ESTRONES

Key Words: ^{1}H-NMR,long-range couplings, estrones

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Abstract: $^{4,6}J_{HH}$-long range couplings in an estrone-type molecule are observed and demonstrated to be helpful for the complete proton chemical shift assignment.

RESULTS

Recent papers [1-7] demonstrate the power of modern ^{1}H-NMR-spectroscopy for structural investigations of steroids. Nevertheless, even with the application of high magnetic fields and correlation spectroscopy [1-8] there still remain regions with severe signal overlap. Thus, unequivocal assignment aids are desirable to exclude alternate pathways of interpretation.
One possibility is given by long-range couplings to

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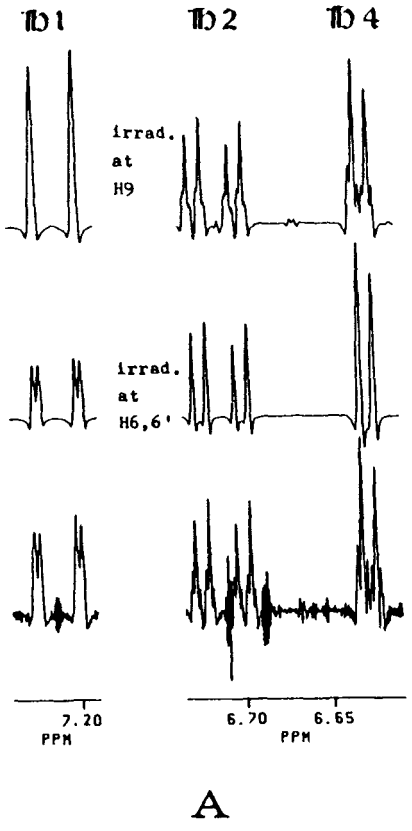
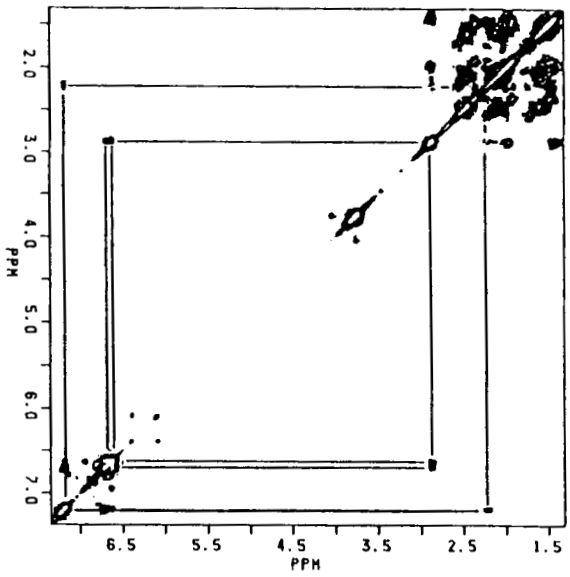


FIG. 1: A) Normal spectrum of I, aromatic region ($CDCl_3$,degassed,Bruker AM-360) and homodecoupling experiments using the correlations obtained from B) H,H-COSY-spectrum of I, long-range couplings emphasized [9] (D2 = 0.08 sec)



B

(Fig. 1 Continued)

protons with remarkably different chemical shifts. They exhibit cross-peaks in H,H-COSY-spectra [8] far away from the diagonal and simplify the assignments. This is now observed in an estrone-type molecule I (scheme 1), which shows $^{4}J_{HH}$- and $^{6}J_{HH}$-couplings from H6,6' and H9 to the aromatic protons (fig. 1 and table 1), which are identified easily.

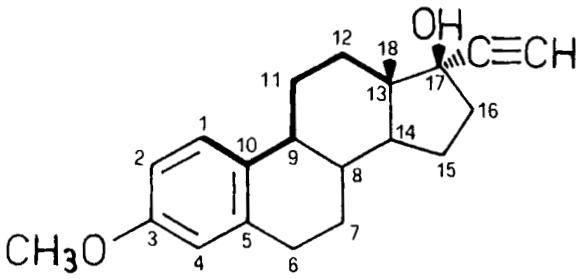
TABLE 1

Selected Chemical Shifts and Couplings of I

Proton	δ (ppm)	J(Hz)
1	7.21	J_{12} = 8.59
		J_{19} = 1.10
2	6.71	J_{24} = 2.82
		$J_{26/6'}$ = 0.78
4	6.63	$J_{46/6'}$ = 0.95
6,6'	2.87	
9	2.24	

Together with the $^4J_{H12H18}$ established earlier (4), the analysis of H11 is attacked from both ends of the carbon chain (fat in scheme 1) and should therefore be identified. Additionally, the entrance to the second chain is given via H6,6'. Furthermore, this observation allows the undoubtful differentiation in the chain H9, H8, H14, which, if possible, may be compared with the results of a H,C-COSY (8) experiment. Thus, a complete ^{1}H-chemical shift analysis of 8β,9α-estrone-type molecules should always be successful, even when no C,H-correlation data are available because lack of substance.

In order to avoid deceptive simplicity in the analysis of the spectrum, because of the close lying chemical shifts of H6/6', the measurement was repeated in C_6D_6.



(I)

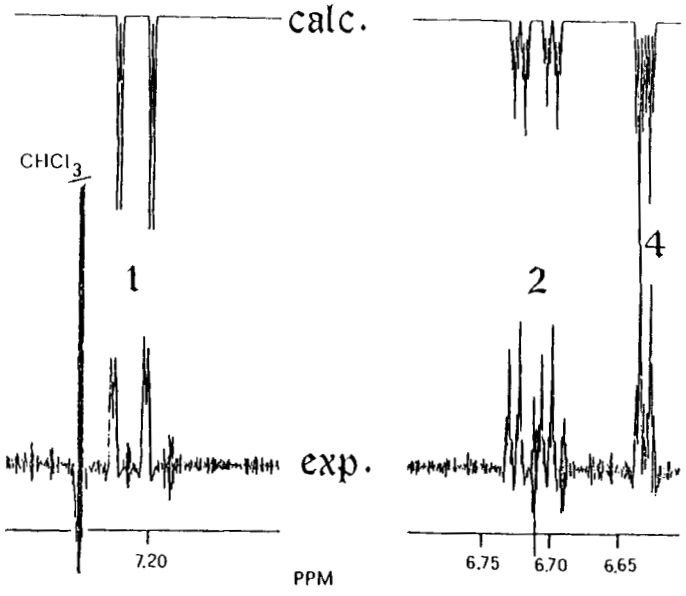


FIG. 2: Observed and calculated (parameters see tab.1) aromatic spectrum of I

Except differences in chemical shifts for all the protons mentioned, there was no characteristic effect on the appearance of the multipletts in the aromatic part. Even the calculation of the spectrum with the data of tab. 1 [10] shows good accordance with the experiment (fig.2).

Thus, we must conclude that the similarity of the coupling constants $J_{26}/J_{26'}$ and $J_{46}/J_{46'}$ is due to molecular geometry, e.g. assuming a Karplus-type relationship the plane of the aromatic ring bisects the H-C6-H moiety almost ideally [4].

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