

The unambiguous assignment of ^1H and ^{13}C signals in the NMR spectrum of cacalone acetate

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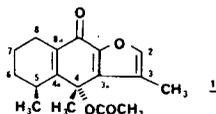
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1. Introduction

The proton and carbon NMR spectra of cacalone acetate (**1**) have been the object of some misinterpretations, (Joseph-Nathan *et al* 1966; Naya *et al* 1976; Casares and Maldonado 1976; Omura *et al* 1978; Chiasson *et al* 1983). Though the downfield signals assignment does not represent any particular controversy, the upfield proton (1–3 ppm) as well as the carbon (5–35 ppm) resonance signals for this compound have been of more speculative nature.

The shift reagent experiments (Yuste *et al* 1976) and their simulation (Chiasson *et al* 1983) particularly, cannot unambiguously prove all assignments.

We report here two experiments carried out on this intriguing molecule: The two-dimensional (2D) heteronuclear shift correlated ^1H , ^{13}C experiment and the INEPT (insensitive nuclei enhancement by polarization transfer) experiments (Morris 1980).



The 2D hetero shift correlated experiments are presented in figure 1. From four methyl groups, the methyl carbon CH_3 -3 signal at 8.5 ppm is correlated to the signal of proton at 2.1 ppm and the other methyl CH_3 -5 to the upfield doublet at 1.3 ppm in proton spectrum. The remaining methyl acetate at 20.75 ppm is correlated to 2.15 singlet. However, CH_3 -4 at 27.9 is correlated to a proton singlet signal at 1.65 ppm.

Methylenes at C-6, C-7 and C-8 are equally well correlated; as shown, the C-7 signal is in the most upfield area because of the CH_3 -5 carbon presence. The allylic methylene carbon at C-8 is correlated to the protons in the most upfield area from all three methyls (at 1.6 ppm).

Finally the C-5 methine at 28.3 ppm is correlated to the downfield proton multiplet at 2.6 ppm.

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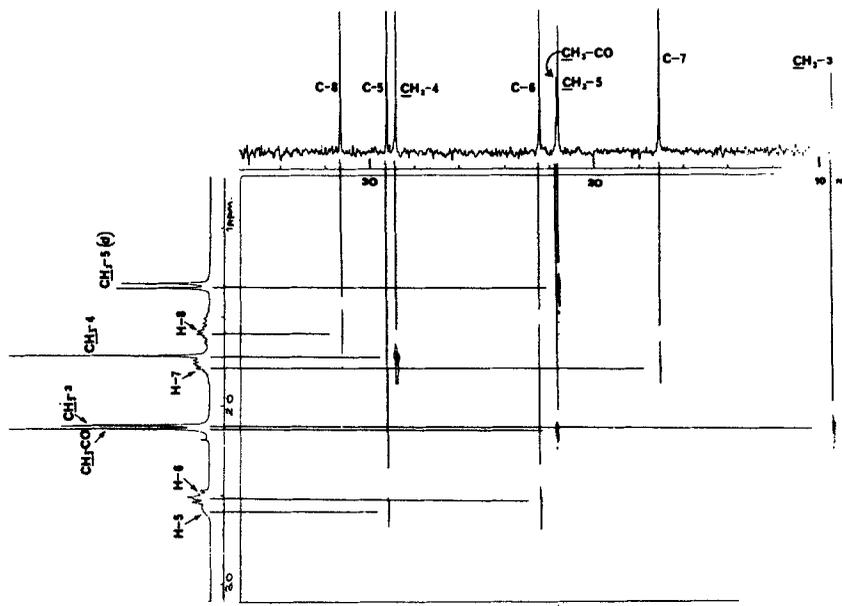


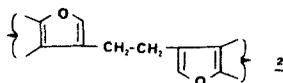
Figure 1. 2D ^1H , ^{13}C heteronuclear shift correlated experiments.

The results clearly show the utility of the 2D hetero nuclear shift correlated NMR experiments in the structural problems.

Figure 2 shows the cross-section through each C-13 chemical shift confirming our final assignment.

The INEPT experiment (figure 3) was run on the cacalone sample for a long time.

After 72 hr, the upfield CH_3 signal (upper run) shows a negative sign when the quaternary carbons have been suppressed and methine and methyl remain positive. The possible explanation for this signal sign inversion is that the compound 1 under these conditions dimerises, *via* methyl-3, giving $\text{CH}_2\text{-CH}_2$ dimer 2 in the oxygen assisted reaction.



In contradistinction of this result, the short time INEPT experiment (6 hr) on 1 in a chloroformic solution (figure 4) gives the same signal as the methyl (positive one, upper run).

2. Experimental

The spectrum of cacalone acetate (1) (12 mg) was recorded in CDCl_3 solution. The 2D ^{13}C , ^1H correlation was determined on a Bruker 250 MHz instrument using 5 mm dual ^{13}C , ^1H probe with acquisition time of 7 hr and processing time of 20 min. A ^{13}C INEPT experiment was recorded with refocusing and decoupling.

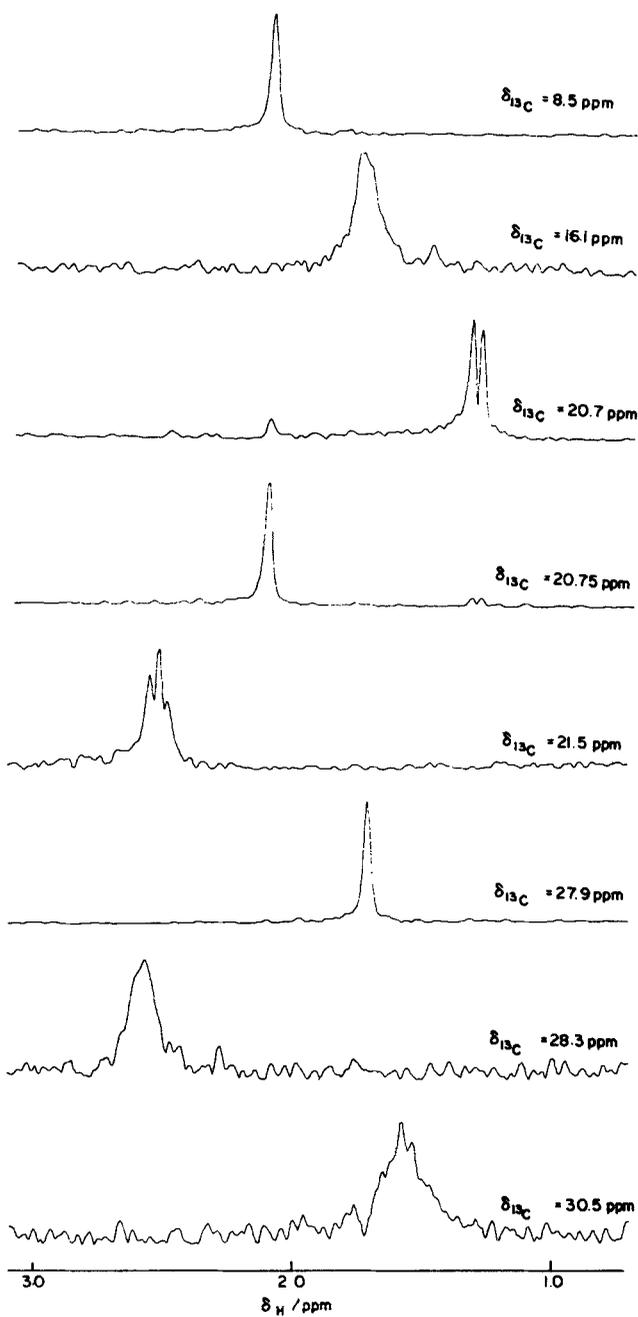


Figure 2. Cross-sections through each C chemical shift.

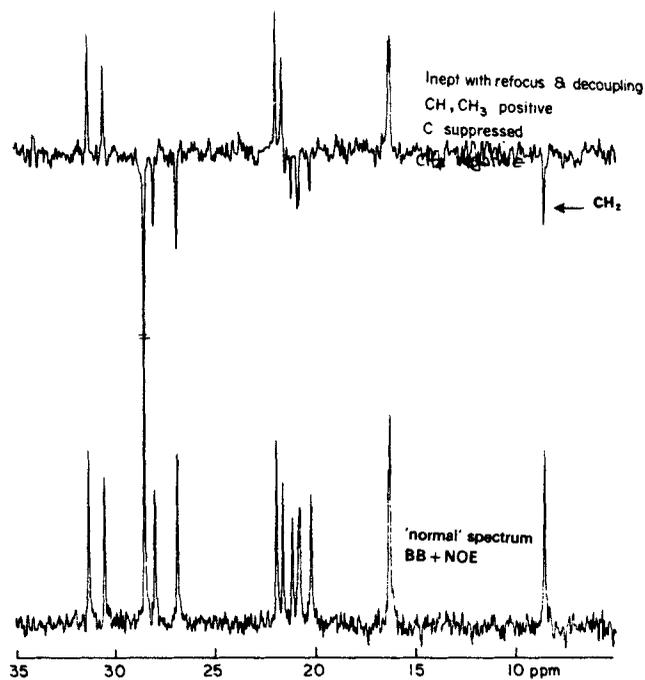


Figure 3. Insensitive nuclei enhancement by polarization transfer (INEPT) 72 hr.

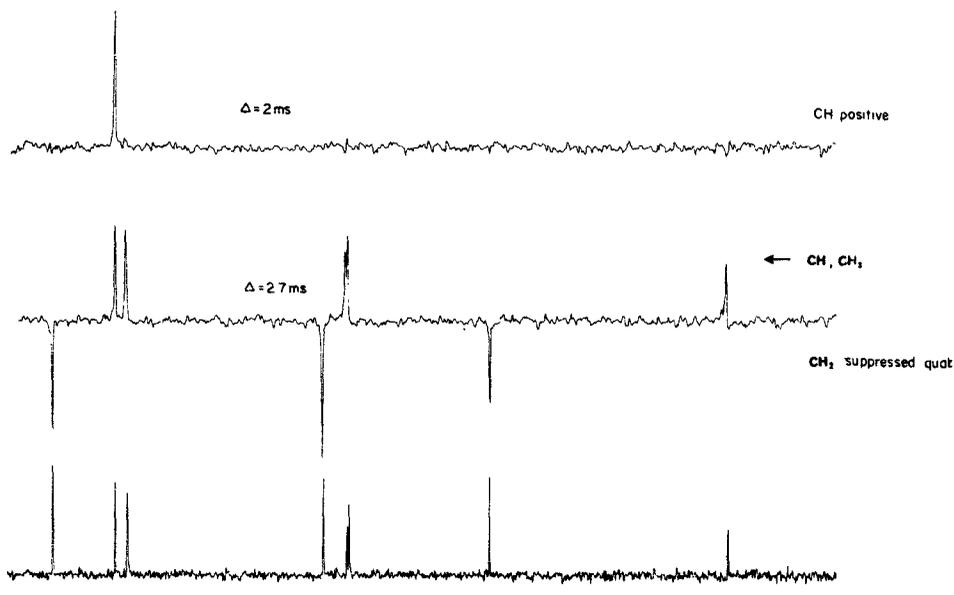
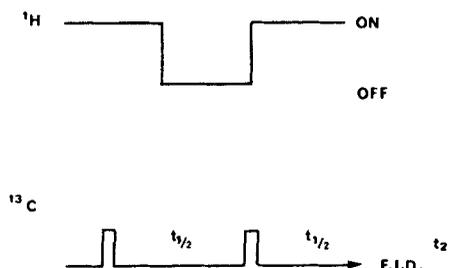


Figure 4. INEPT 6 hr.

The 2D experiments were obtained by the gated decoupling method in which broadband decoupled ^{13}C spectra are acquired. The broadband decoupled signals are modulated by heteronuclear coupling during t_1 , so the second transform gives ^{13}C - ^1H information in F_1 . The method is schematically shown below:



A total of 128 t_1 increments were used with a 2K acquisition in the ^{13}C F_2 domain, 500 pulses were used to build up S/N . The F_1 domain was zero-filled once with gaussian multiplication being used in both F_1 and F_2 . The total transform time was 20 min.

Acknowledgements

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