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UNEQUIVOCAL ASSIGNMENT OF THE δ RESONANCES OF 2-SUBSTITUTED ADAMANTANES BY TWO-DIMENSIONAL INADEQUATE ^{13}C NMR SPECTROSCOPY

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Abstract: Two-dimensional INADEQUATE NMR spectroscopy was used to assign unequivocally the *syn* and *anti* δ ^{13}C resonances of 2-substituted adamantanes.

Adamantanes, being well-defined geometrically, minimally strained, and conformationally rigid, represent ideal models for studying NMR parameters. A number of investigators have reported on the ^{13}C NMR spectra of 2-substituted adamantanes.[1-7] Chemical shift assignments were straightforward except for distinguishing between the *syn* and *anti* δ resonances (δ_s *vs.* δ_a).

In an analysis of ^{13}C NMR data of 4-substituted adamantanones, Duddeck[3] showed that the δ effect is opposite to the γ effect and he reversed the prior assignment[2] of the chemical shifts for the *syn* and *anti* δ carbons. Duddeck's assignment was later supported by NMR studies of lanthanide-induced shifts in 2-adamantanol and 2-adamantanethiol,[4] dipolar relaxation times of 2-substituted adamantanes,[5] and the spectra of deuterated 2-adamantanol.[6] We now report an unequivocal proof of Duddeck's assignment of these two δ resonances.

Our work is based on the observation of ^{13}C-^{13}C one-bond coupling in natural abundance using the two-dimensional (2D) INADEQUATE experiment.[8-10] Contour plots of the 2D-INADEQUATE spectra of 2-phenyladamantane (**1**) and 2-bromoadamantane (**2**) are shown in Figures 1 and 2, respectively. The ^{13}C-^{13}C satellites are separated in the second frequency dimension (F_1) according to their characteristic double-quantum frequencies. Connectivity between two carbons is established by the appearance of the satellites on the same horizontal line in the 2-D spectrum. The assignment of the two δ resonances is thus straightforward based on connectivity with the corresponding γ signals.

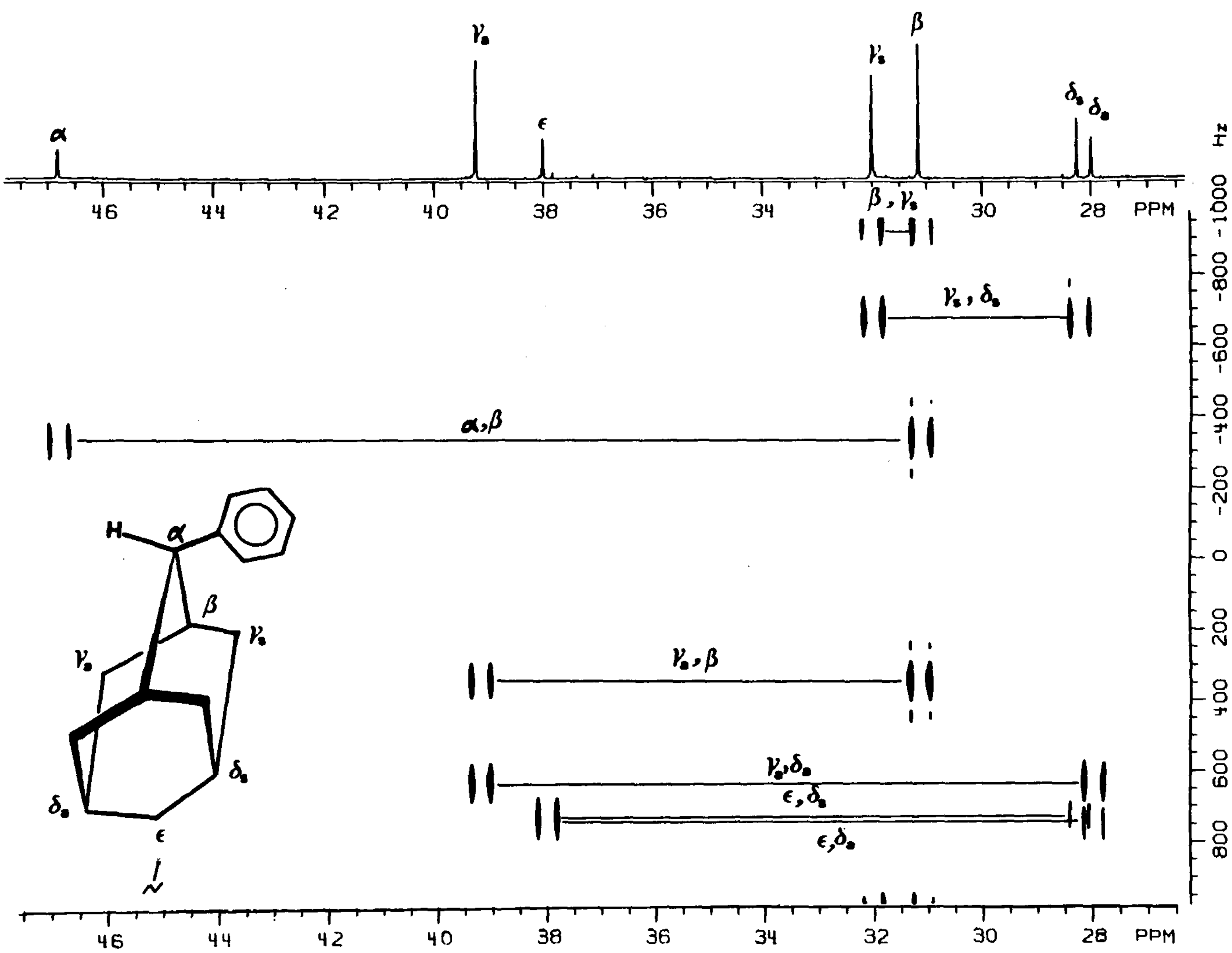

Fig. 1 Two-dimensional INADEQUATE spectrum of the aliphatic part of 2-phenyladamantane.

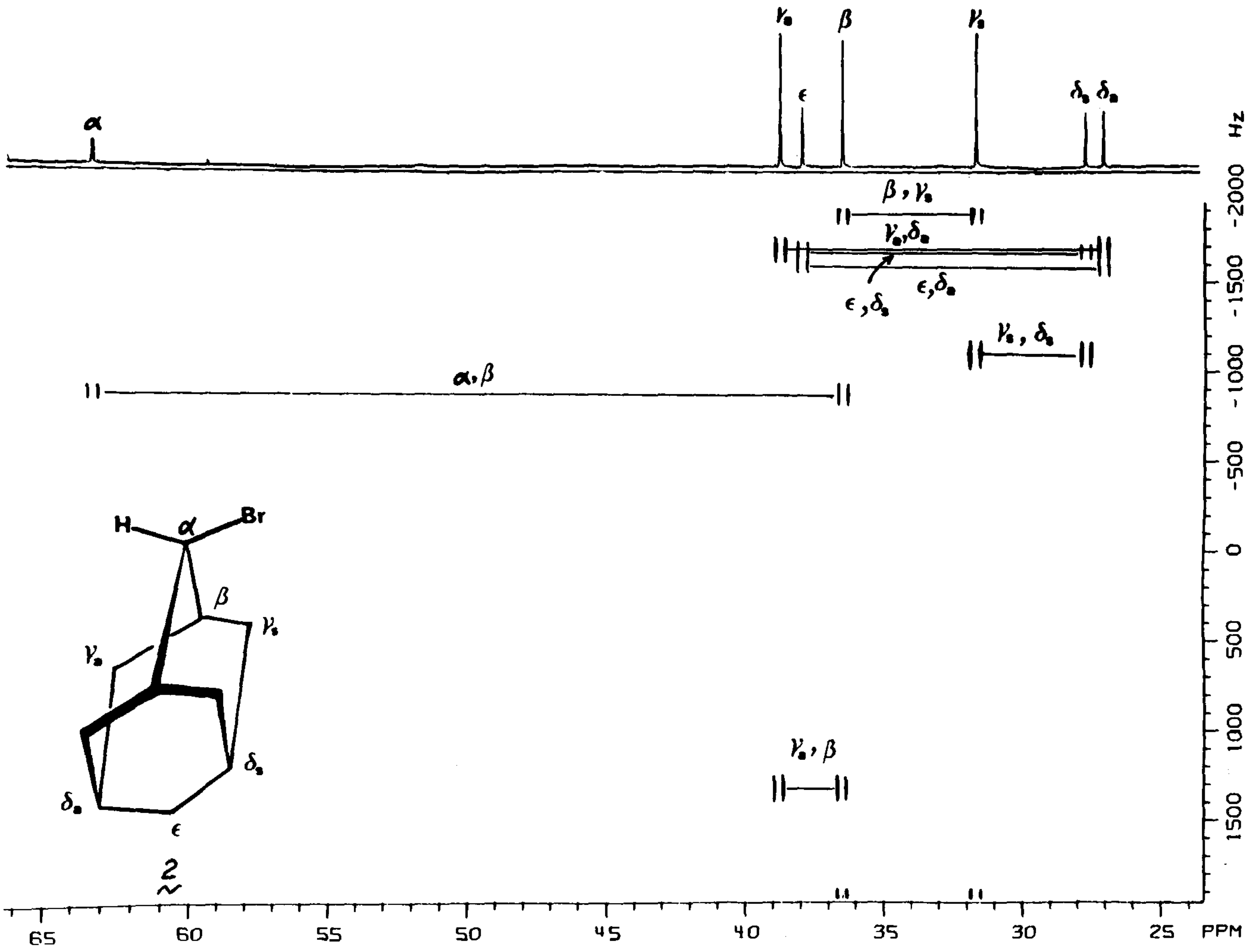

Fig. 2 Two-dimensional INADEQUATE spectrum of 2-bromoadamantane.

The experiments were performed on a Nicolet NT-360 NB spectrometer at 90.8 MHz using the pulse sequence of Bax et al.[8] with τ = 8.7 ms and a read pulse of 135° to achieve quadrature detection in F_1.[9] Identical sampling rates were used in both frequency dimensions which caused some resonances to foldover in F_1.[10] Concentrated solutions in $CDCl_3$ (3.3 M for **1** and 4.5 M for **2**) in 12 mm tubes were used to obtain reasonable signal-to-noise ratios in overnight runs. The initial data matrices were 29x4096 and 44x4096 for **1** and **2**, respectively, and were zero-filled in F_1 to 256x4096. Gaussian line broadening was used in both dimensions.

In conclusion, the 2D-INADEQUATE ^{13}C NMR spectra provided conclusive assignments for the syn and anti δ resonances in 2-substituted adamantanes. We are currently investigating the ^{13}C NMR spectra of a series 1,2-disubstituted adamantanes and shall report on their complete NMR spectral analyses later on.

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