

¹³C NMR SPECTRA OF ALKENYLBORANES. EVIDENCE FOR THE PRESENCE OF π-CHARACTER IN THE B-C BOND

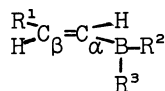
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The strong deshielding of the β-carbon atom in the ¹³C NMR spectra of α,β-unsaturated alkenylboranes supports the presence of π-character in the B-C bond.

The π-interaction between a π-electron system and a vacant orbital of a boron atom has been postulated for α,β-unsaturated alkenylboranes.¹⁾ A substantial body of evidence now exists supporting this type of interaction. On the other hand, evidence against such π-bonding has been presented.²⁾ These topics are frequently discussed with the aid of various spectroscopic techniques. Vinylboranes have been studied with infrared,^{3,4,5,6)} Raman,⁶⁾ ultraviolet,^{4,5,8)} ¹H NMR,⁵⁾ ¹¹B NMR,^{4,5)} and photoelectron⁷⁾ spectroscopy, and have also been the subject of LCAO-MO-SCF⁸⁾ and CNDO⁹⁾ calculations. However, ¹³C NMR spectra of alkenylboranes have not previously been published, although the chemical shifts can much directly provide insights into the bonding situation.¹⁰⁾

In the course of systematic investigations of chemical reactivity and structures of organoboranes,¹¹⁾ it was required to clarify the bonding character of alkenylboranes. Accordingly, we prepared various kinds of alkenylboranes¹²⁾ and measured their ¹³C NMR spectra. The data are summarized in the Table.

Table. ¹³C Chemical Shifts for Alkenylboranes.^a



Compound	R ¹	R ²	R ³	δC _β	δC _α
I	H	-O(CH ₂) ₃ CH ₃	-O(CH ₂) ₃ CH ₃	135.5 (134.1) ^b	127.8 ^b
II	-(CH ₂) ₃ CH ₃	-CH=CH(CH ₂) ₃ CH ₃	Cl	160.9	133.0
III	-(CH ₂) ₃ CH ₃	-CH=CH(CH ₂) ₃ CH ₃	-OCH ₃	153.8	129.1
IV	-(CH ₂) ₃ CH ₃	-CH(CH ₃)CH(CH ₃) ₂	-CH(CH ₃)CH(CH ₃) ₂	155.2	134.6

^a ¹³C FT NMR spectra were examined with a Varian XL-100-15 spectrometer at 25.2 MHz; compounds were dissolved in C₆D₆ with an internal standard of C₆D₆. Chemical shifts are converted to δ_c, using δ_c^{C₆D₆} 128.7; errors are ± 0.02. ^b in CDCl₃ with TMS as an internal standard.

Assignments of ¹³C signals were made by (i) single-frequency off-resonance decouplings, (ii) comparison of the chemical shifts with those for related hydrocarbons, and (iii) broadening and weakening of signal peaks corresponding to ¹³C directly attached to boron. The last phenomenon (iii) is generally observed for organoboranes such as trialkylboranes and boronates, probably owing to the coupling of C_α to boron.^{11,13)} However, ¹³C-¹¹B coupling constants can not

precisely be defined at the present stage. The $^{13}\text{C}_\beta\text{-H}$ coupling constants of di-*n*-butylvinylboronate (I) are 158 and 164 Hz, indicating that the C_β has a normal sp^2 -hybridization. The $^{13}\text{C}_\alpha\text{-H}$ coupling constant was not obvious, owing to the boron atom bonded to the C_α .

A characteristic feature of the Table is the strong deshielding of C_β . This deshielding might be explained in terms of the inductive effect of boron. However, the chemical shifts of triethylborane (δC_α 19.7, δC_β 7.9)¹³⁾ and 2-ethyl-1,3,2-dioxaborinane (δC_β 7.7) indicate that α and β effects due to the boron substituents are relatively small. Therefore, it is difficult to explain the deshielding merely by the inductive effect of the boron group.

The chemical shifts in I are similar to those in acrylic acid (δC_α 128.0, δC_β 131.9).¹⁰⁾ The tendency of chemical shifts in II - IV is also analogous to that in α,β -unsaturated carbonyl derivatives, in which the contribution of such a form as (2) is important.¹⁰⁾



Consequently, the present ^{13}C spectral study supports that the resonance structure (4) contributes to the ground state of alkenylboranes, the conclusion being in agreement with other experimental results. We are continuing to explore the possibility that such contribution is reflected on new reactions of organoboranes. The suggestion that many of the reactions of aldehydes or ketones have counterparts in the reaction of trialkylboranes has been presented.¹⁴⁾

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(Received November 12, 1974)