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A LINEAR RELATIONSHIP BETWEEN ^{13}CNMR CHEMICAL SHIFT OF VINYL CARBONS AND ELECTRONIC ABSORPTION WAVELENGTH IN POLYSILYLETHYLENES[1)]

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A very good linear correlation between ^{13}CNMR chemical shift of vinyl carbons and electronic absorption maxima (band II) of polysilylethylenes has been established. An explanation based on the theory of Karplus-Pople is presented.

In a series of papers,[2)] we have reported preparation and interesting physical and chemical properties of very crowded tetrasilylethylenes. The double bonds of tetrakis(trimethylsilyl)ethylene (1) and 1,1-bis(*t*-butyldimethylsilyl)-2,2-bis(trimethylsilyl)ethylene (2), as determined by X-ray crystallographic analyses, are twisted by 29.6°[2c)] and 49.6°,[2e)] respectively.

The ^{13}CNMR chemical shifts of these olefins appear at very low field almost in a carbonyl region. Electronic absorption maxima of 1 and 2 are observed also at an unusually long-wavelength region. Since the ^{13}CNMR chemical shifts are related to the excitation energy (*vide infra*),[3)] these findings suggest a considerable mixing of the excited state property to the ground state properties of these olefins, and it seemed very interesting to study the spectra in detail.

We have measured then both ^{13}CNMR chemical shifts and electronic absorption maxima for several other polysilylethylenes. Tables 1 and 2 list these values together with some data available from literatures.[4)] An excellent linear plot of ^{13}C chemical shifts of vinyl carbons against wavelengths of absorption maxima of Band-II in polysilylethylenes (correlation coefficient = 0.996) is obtained as shown in Figure 1. In cases of unsymmetric ethylenes such as 2, 5, and 6, average values of two ^{13}CNMR chemical shifts are shown in the Figure.

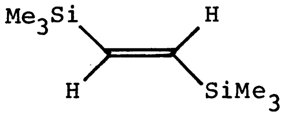
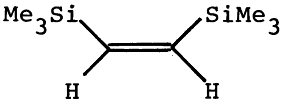
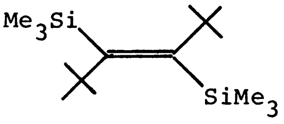
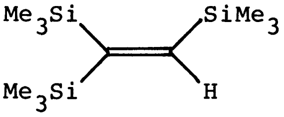
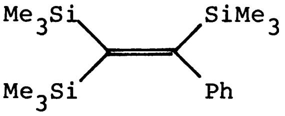
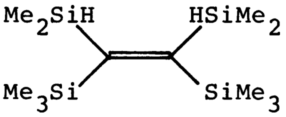
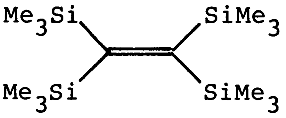
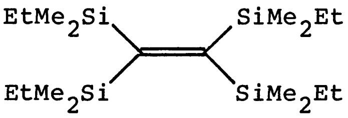
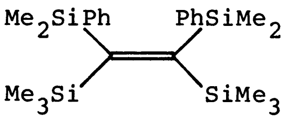
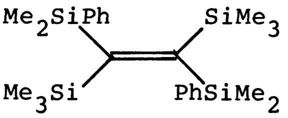
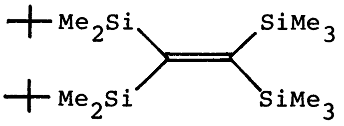
Such a linear relationship between NMR chemical shifts and electronic absorption maxima has been observed for ^{15}N[5)] and ^{195}Pt nuclei.[6)] Similar relations between $n \rightarrow \pi^*$ excitation energies and both ^{13}C[7a)] and ^{17}O[7b)] chemical shifts in carbonyl compounds have been reported, but no such relationship for C=C double bonds is known up to date.

The magnetic shielding constant σ_i is described by the following equation,

$$\sigma_i = \sigma^{dia} + \sigma^{para} + \sigma^{N}$$

where σ^{dia}, σ^{para} and σ^{N} stand for diamagnetic, paramagnetic shielding, and neighbor anisotropy terms, respectively.[3)] For ^{13}C nuclei, the paramagnetic shielding term σ^{para} predominates.[8)] According to Karplus and Pople,[8)] σ^{para} is inversely related to both the mean electronic excitation energy ΔE and the mean cube radius

Table 1. Electronic Absorption Maxima of Polysilylethylenes.a)

Compound		Band-I		Band-II	
		λmax / nm	ε	λmax / nm	ε
	(E-3)b)	195.5	20100	225	650
	(Z-3)b)	198	9600	233	920
	(4)	210.5	16500	253 284.5	860 1300
	(5)b)	211	17000	280	350
	(6)	211.5	18700	290	960
	(Z-7)	224.2	16500	344	370
	(1)	223.7	17900	370	710
	(8)	225.5 280 sh	16200 1700	383	610
	(Z-9)	214	23500	379	625
	(E-9)	214	23500	375	625
	(2)	245.5	9900	433	550

a) UV spectra were taken on a Hitachi 323 spectrometer in n-hexane.

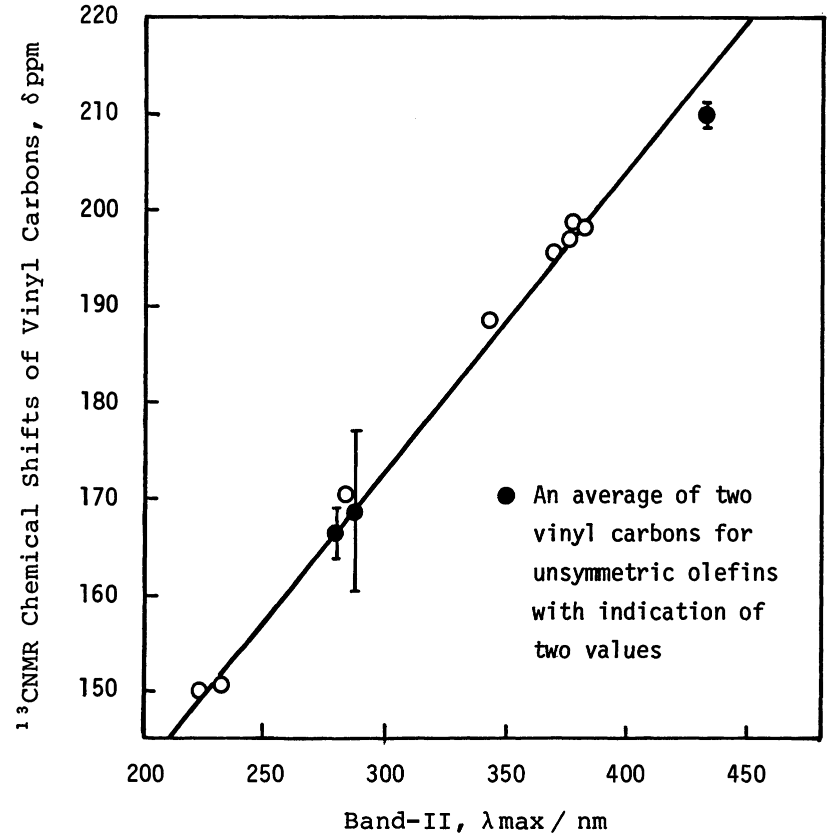
b) Values taken from ref. 4c.

Table 2. The ^{13}CNMR Chemical Shifts of Polysilylethylenes.[a)]

Compound	δ ppm		
	CH_3 ($SiMe_3$)	CH_3 ($SiMe_2R$)	C (vinyl)
(E-3)[b)]	-1.7		150.0
(Z-3)[b)]	-0.7		150.5
(4)	8.2		170.3
(5)[b)]	0.3, 1.0, 2.1		163.5, 169.0
(6)	2.42, 3.39, 4.31		160.2, 176.8
(Z-7)	3.6	-1.55	188.2
(1)	4.2		195.3
(8)		1.50	197.9
(Z-9)	3.55	1.56	198.3
(E-9)	3.66	3.00	197.0
(2)	5.94	0.20	208.4, 210.8

a) δ Values in $CDCl_3$ but only these of 4 in C_6D_6.
b) Values taken from ref. 4a and 4b.

Figure 1. Plot of ^{13}CNMR Chemical Shifts *vs.* Absorption Maxima.



for carbon 2p orbitals, $r_{2p}{}^{3}$.

$$\sigma^{para} = -(e^2h^2 / m^2c^2) \cdot \Delta E^{-1} \cdot r_{2p}^{-3} \cdot [Q_{AA} + \Sigma\, Q_{AX}]$$

The $[Q_{AA}$ and $\Sigma Q_{AX}]$ factor is charge density bond order matrix in the MO formalism. Since we are dealing with a system composed of a localized C=C double bond, both r_{2p}^{-3} and $[Q_{AA} + \Sigma\, Q_{AX}]$ terms can be regarded as constant. Then the shielding constant or the chemical shift becomes proportional to ΔE^{-1}, hence to the transition wavelength λmax.[9)]

The case of polysilylethylenes is unique since the double bonds have only nonconjugating substituents and hence electronic absorptions can easily be ascribed to localized double bonds except for **6**.[10)] Moreover, bulky trimethylsilyl groups exert dramatic effects on the electronic character of the compounds.[11)] As a result, both ^{13}CNMR chemical shifts and λmax extend over a wide range and are correlated each other nicely.

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7) (a) G. B. Savitsky, K. Namikawa, and G. Zweifel, *J. Phys. Chem.*, **69**, 3105 (1965); (b) W. H. de Jen, *Mol. Phys.*, **18**, 31 (1970), and references cited therein.

8) (a) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963); (b) J. A. Pople, *Mol. Phys.*, **7**, 301 (1964).

9) The r_{2p}^{-3} dependence of chemical shifts has been reported for nonbenzenoid monocyclic aromatic ions and benzene by H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).

10) However, an examination of the molecule by the Dreiding Stereomodels shows that the phenyl group **6** is almost perpendicular to the double bond.

11) The effect of d- (or σ^*-) orbitals may be considered as well.

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