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INVERSE SUBSTITUENT EFFECT IN THE ^{13}C CHEMICAL SHIFTS OF TRANS-1-SUBSTITUTED-1,3-BUTADIENES. DIRECT EVIDENCE OF BOND POLARIZATION EFFECTED BY SUBSTITUENTS.

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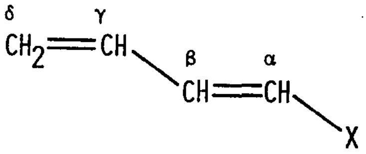
We wish to report the alternation of substituent effect on the ^{13}C substituent chemical shifts (SCS) along the conjugated framework of trans-1-substituted-1,3-butadienes. The observed alternation is considered as direct evidence of bond polarization which Pople and Gordon[1] predicted in their earlier CNDO/2 calculations of substituent effect.



The ^{13}C nmr spectra were recorded on a JEOL C-60HL spectrometer for neat liquids at room temperature by the proton decoupling technique. The signal assignment was based on the splittings of peaks by partial decoupling and on the estimation from the additivity rule. The results are summarized in Table I.

It is generally accepted that an electron-withdrawing substituent usually causes lower-field shifts of ^{13}C peaks.[2,3] This is indeed the case for the β and δ carbons of trans-1-substituted-1,3-butadienes, as can be seen in Table I. With the α and γ carbons, however, the reverse is true; that is, an electron-donating substituent shifts the peaks to lower field. This can be more clearly seen by

Table I. Observed ^{13}C Chemical Shifts and Calculated Electron Densities of Various Carbons in trans-1-Substituted-1,3-butadienes

No.	X	^{13}C Chemical shift[a]				π-Electron density[b]				σ-Electron density[b]			
		α	β	γ	δ	α	β	γ	δ	α	β	γ	δ
1	C_2H_5O[c]	-24.5	15.3	-7.5	19.3	0.9811	1.0589	0.9772	1.0352	3.8915	2.9948	2.9973	3.0170
2	CH_3	-4.4	-0.5	-9.0	14.5	0.9847	1.0254	0.9767	1.0301	3.0064	2.9869	3.0083	3.0189
3	C_6H_5	-1.3	-5.0[d]	-9.3[d]	10.6	0.9990	1.0001	0.9795	1.0224	3.0085	3.0030	3.0076	3.0225
4	H	11.7	-8.8	-8.8	11.7	1.0177	0.9823	0.9823	1.0177	3.0246	3.0028	3.0028	3.0246
5	$COOCH_3$	6.1	-16.3	-6.9	3.1	1.0521	0.9158	0.9963	0.9859	3.0241	3.0284	3.0029	3.0378
6	CN	29.5	-21.3	-4.6	1.1	1.0240	0.9652	0.9915	1.0010	2.9829	3.0047	3.0019	3.0312

[a] ppm from benzene. [b] Electron unit. [c] Calculation was carried out for CH_3O. [d] Assignment is somewhat uncertain.

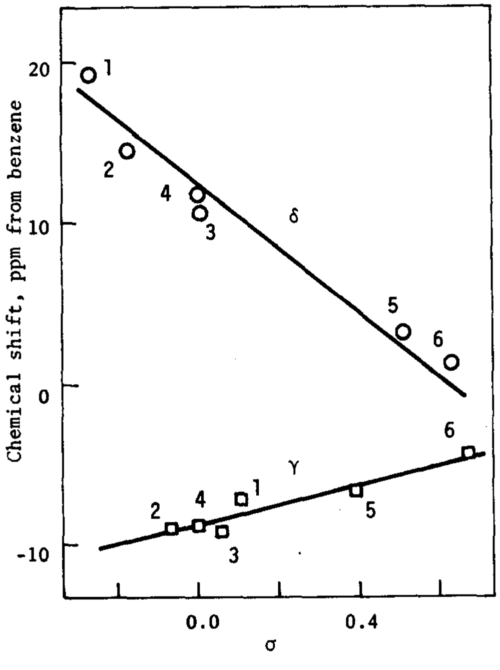


Fig. 1. Hammett plots of the ^{13}C SCS for the δ- and γ-carbons of trans-1-substituted-1,3-butadienes.

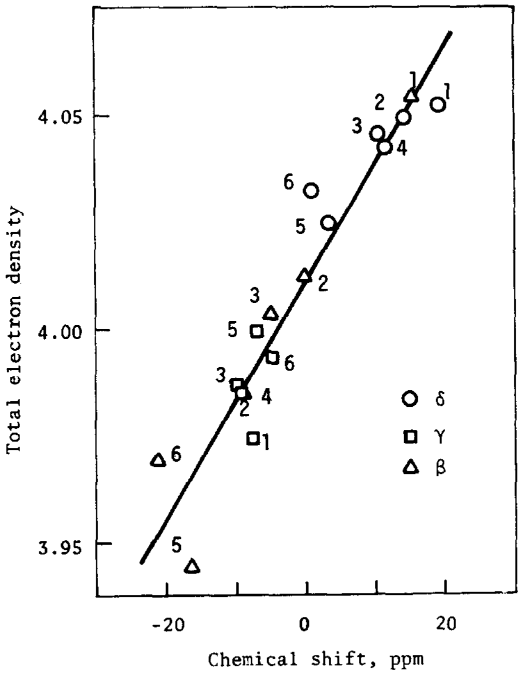


Fig. 2. Plots of the calculated total electron densities against the observed ^{13}C SCS of trans-1-substituted-1,3-butadienes.

plotting these SCS against Hammett's σ (Fig. 1). The positive slope of the plots for the γ carbon indicates the "inverse" substituent effect, though the magnitude is relatively small as compared with the "normal" substituent effect for the δ carbon. This is the first unambiguous observation of the inverse substituent effect in ^{13}C chemical shifts. A careful reexamination of available data revealed that a similar trend can be perceived in the ^{13}C SCS for the α carbons of ring-substituted styrenes,[3] benzonitriles[4] and 1-substituted 1-hexynes[5].

It is recognized that ^{13}C chemical shifts can be linearly related with the total electron density of the carbon atoms considered.[6,7] Accordingly, our present observation may be taken as an indication that the charge densities on carbon atoms alternate along the skeletal chain as follows:

$$X \longleftarrow \overset{\delta-}{C} \text{---} \overset{\delta+}{C} \text{---} \overset{\delta\delta-}{C} \text{---} \overset{\delta\delta+}{C}$$

The view is in line with the theoretical prediction of Pople and Gorgon[1], who noted that unsaturated bonds tend to be polarized by the introduction of a polar group.

The alternation of π-electron densities in polar-substituted compounds has been proposed by several authors[8,9] in terms of the π-inductive effect. Although the π-inductive effect cannot be distinguised clearly from the so-called π-mesomeric effect, such an alternation can well be reproduced even by the simple Hückel calculations. In σ-electron systems, on the other hand, substituent effects are usually thought to be transmitted through a carbon chain by way of simple attenuation such as

$$X \longleftarrow \overset{\delta+}{C} \text{---} \overset{\delta\delta+}{C} \text{---} \overset{\delta\delta\delta+}{C} \text{---} \overset{\delta\delta\delta\delta+}{C}$$

Therefore, the observed alternation can be considered to reflect the importance of the role of π-electrons to the transmission of substituent effects in this system.

In order to clarify the roles of π and σ electrons on a more quantitative basis, CNDO/2 calculations were carried out for <u>trans</u>-1-substituted-1,3-butadienes. All the geometries adopted were based on Pople's standard bond lengths and angles.[10]

Figure 2 shows that the calculated total electron densities are linearly related with the observed ^{13}C chemical shifts except for α carbons. This assures reliability of the CNDO/2 calculations of electron distribution. We may then look more closely into the effect of substituents on the distributions of π- and σ-electrons. As is shown in Table I, the calculated π-electron densities do alternate along the chain, in agreement with the trend of the ^{13}C chemical shifts observed. On the other hand, σ-electrons show no such tendency; even the reverse trend is observed for electron-withdrawing substituents. Thus, these calculations confirm the dominant role of π-electrons to cause the alternation of substituent effect.

In conclusion, the substituent effect in conjugated diene is considered to be transmitted mainly through its π-framework by successive polarization of the -CH=CH- groups involved. The inverse ^{13}C SCS observed for the α and γ carbons of trans-1-substituted-1,3-butadienes can be regarded as direct evidence for this mode of transmission of substituent effects.

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