Effect of substituents on the ^{1}H-NMR chemical shifts of 3-methylene-2-substituted-1,4-pentadienes

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Abstract: The principle of linear free energy relationships was applied to the ^{1}H chemical shifts of the β-vinyl proton atoms of 3-methylene-2-substituted-1,4-pentadienes. The correlations of the proton chemical shifts with Swain and Lupton substituent parameters provide a mutually consistent picture of the electronic effects in these compounds. The overall pattern of proton chemical shifts can be largely accounted for by a model of substituent effects based on field, resonance and π polarization effects. Owing to the particular geometric arrangement of the vinyl group in 3-methylene-2-substituted-1,4-pentadienes, the β-vinyl protons H_B and H_C have different sensitivities to polar and resonance effects. The different sensitivities of the ^{1}H chemical shifts to resonance effects reveals some effects not predicted by the model outlined above. Evidence is presented that demonstrates that both the ^{1}H and ^{13}C chemical shifts for these compounds reflect their ground-state charge densities.

Keywords: cross-conjugated trienes, ring substituted α-(*s-cis*-2-butadienyl)styrenes, β-vinyl proton chemical shifts, substituent effects.

INTRODUCTION

In a preceding paper,[1] ^{13}C substituent chemical shifts (SCS) of the carbon atoms in the unsaturated chain of 3-methylene-2-substituted-1,4-pentadienes, **1**-R (Scheme 1), were correlated with the substituent parameters of Swain and Lupton.[2] The correlations of the ^{13}C SCS were used to deduce the mechanisms of the transmission of substituent effects in these compounds. It was concluded that the pattern of electronic effects can be fully rationalized by a model based on the direct transmission of substituent effects through-space (direct through-space field effects), and *via* conjugative interactions (resonance effects), or by substituent-induced polarization of the π-system in the unsaturated chain (π-polarization effect).

The resonance effects of aromatic ring substituents of the *s-cis*-conformer[1] **1**-R have a superior influence on the carbon chemical shifts of the unsaturated chain terminal π-unit **1**,

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$\mathbf{Y}$ = *s-cis*-2-butadienyl

1-R
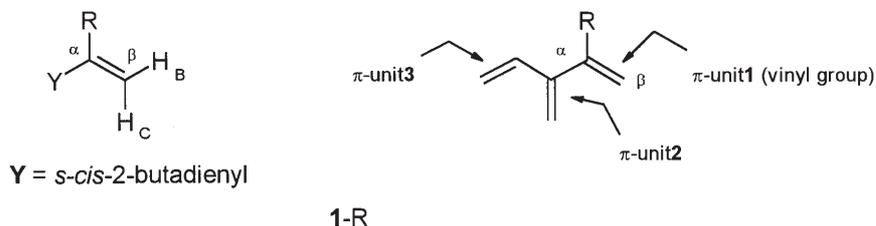
$\mathbf{R}$ = X-C_6H_4 (X = H, *m*-CH_3, *p*-CH_3, *p*-CH_2OH, *o*-CH_2OH, *p*-OH, *p*-OCH_3, *p*-I, 3N, 2N)
  2-Thienyl
  2-Bromopyridine-6-yl

Scheme 1. Methylene-2-substituted-1,4-pentadiens (**1**-R)

and have an inferior influence on those of the distant unsaturated chain terminal/non-terminal π-unit. The observed alternation of polar effects in the unsaturated chain of the investigated cross-conjugated trienes, **1**-R, bears evidence for the transfer of polar effects by the π-polarization mechanism in this molecular framework.[1]

In the present work, linear free energy relationships (LFER) have been applied to proton chemical shifts in the unsaturated chain of 3-methylene-2-substituted-1,4-pentadienes **1**-R, with the aim of gaining insight into their substituent dependence. In contrast to ^{1}H chemical shifts, ^{13}C chemical shifts are relatively insensitive to magnetic anisotropy effects (due to the much greater chemical shift range) and to solvent and concentration effects.[3] Carbon-13 chemical shifts primarily reflect substituent effects transmitted through the bonding network of the molecule. Although being fully aware of the complexity of determining factors of ^{1}H-NMR chemical shifts, we expected that the substituent dependence of proton chemical shifts (SCS) should bear a similarity to the pattern observed for ^{13}C SCS.[1]

EXPERIMENTAL

Synthesis of the compounds: The preparation of twelve 3-methylene-2-substituted-1,4-pentadienes has been described previously.[1] 3-Methylene-2-(4-hydroxyphenyl)-1,4-pentadiene, which was not mentioned in our preceding paper[1] because of the lack of data for its ^{13}C-NMR spectra, was synthesized by the same procedure as presented there.

Recording of the spectra: The ^{1}H-NMR spectra were obtained in deuterated chloroform ($CDCl_3$) with tetramethylsilane (Me_4Si) as the internal reference signal using a Bruker AM 250 spectrometer operating at 250 MHz and 25 °C.

RESULTS AND DISCUSSION

The chemical shifts of the unsaturated chain protons for the 12 compounds in the series **1**-R are given in Table I. The assignment of these signals was accomplished through analysis of their coupling models, as well as of the estimated chemical shifts of 3-methylene-1,4-pentadiene,[4,5] ring substituted styrenes (Scheme 2; **2**-H)[3] and ring substituted α-alkylstyrenes (Scheme 2; **2**-Me and **2**-*t*-Bu).[6]

All the **1**-R π-unit **1** proton spectra were analysed as AB spectra (there was no resolvable coupling to the *s-cis*-2-butadienyl group). The protons (Scheme 1) are not labelled

conventionally in order of increasing field but rather by analogy to **2**-H,[3] to facilitate comparisons between the different series.

TABLE I. π-Unit **1** proton chemical shifts (in ppm relative to Me$_4$Si) and coupling constants (Hz) for 3-methylene-2-substituted-1,4-pentadienes (**1**-R) in CDCl$_3$ [a]

R	δ_{H_B}	δ_{H_C}	$\Delta\delta(B-C)$[b]	$^2J_{BC}$
Phenyl	5.5370	5.2580	0.2790	1.50
3-Tolyl	5.5150	5.2305	0.2845	1.50
4-Tolyl	5.5030	5.1985	0.3045	1.50
4-(Hydroxymethyl)phenyl	5.5370	5.2525	0.2845	1.00
4-Hydroxyphenyl	5.4400	5.1485	0.2915	1.50
4-Methoxyphenyl	5.4585	5.1595	0.2990	1.25
4-Iodophenyl	5.5305	5.2615	0.2690	1.25
3-Pyridyl [c]	5.5845	5.3575	0.2270	1.25
2-Pyridyl [c]	6.1185	5.3960	0.7225	2.25
2-Thienyl [c]	5.5952	5.0861	0.5091	1.00
2-(Hydroxymethyl)phenyl	5.5370	4.7510 [d]	0.7860	1.50
2-Bromopyridin-6-yl [c]	6.3510	5.4230	0.9280	2.00

[a] The π-unit **1** proton spectra of 3-methylene-2-substituted-1,4-pentadienes were analysed as AB spectra (there was no resolvable coupling to the π-unit **2** protons). $^2J_{H,H}$ coupling constants were calculated. [b] Internal chemical shift difference for the π-unit **1** protons. [c] Heteroaromatic nuclei were treated as benzenoid structure where one CH or CH:CH fragment is replaced with a heteroatom. [d] Assignment uncertain.

3-Methylene-2-substituted-1,4-pentadienes, **1**-R, can be treated as α-alkylstyrenes (Schemes 1 and 2) with an *s-cis*-2-butadienyl group in the α-position. It is particularly instructive to compare the internal chemical shift differences for the vinyl β-protons H$_B$ and H$_C$, $\Delta\delta(B-C)$, in the **1**-R and **2**-G derivatives. The internal chemical shift difference for the π-unit **1** protons in **1**-R (Table I, R = Phenyl) amounts to 0.279, which is much smaller than $\Delta\delta(B-C) = 0.517$, established for **2**-H[3] but the same as $\Delta\delta(B-C)$ established for **2**-Me.[6] For **2**-t-Bu, $\Delta\delta(B-C)$ has a large negative value – 0.417.[6]

It is known that the vinyl proton chemical shifts in styrene, **2**-H, are not solely due to ring current effects.[3] All-valence electron theoretical calculations of the CNDO/2 type[7] indicate that differences in charge density (q) for H$_B$ and H$_C$ contribute substantially to $\Delta\delta(B-C)$.[6] The large positive charge density for H$_B$ in styrene is apparently due to steric interaction between H$_B$ and H$_2$ since q_{H_B} decreases as the phenyl-vinyl dihedral angle, θ, increases: Similarly, H$_2$ has a smaller negative charge than H$_6$ with q_{H_2} becoming more negative as θ increases (see Scheme 2 for labelling of the nuclei). By contrast, q_{H_C} is much less sensitive to θ.[6]

2-G
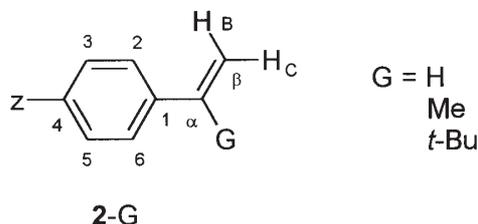
Chemicals shifts of the β-Vinyl proton (in ppm relative to Me$_4$Si) for **2**-G[a] at infinite dilution in cyclohexane-d_{12}

Compound	δ_{HB}	δ_{HC}	$\Delta\delta$(B–C)[b]
2-H	5.6302[c]	5.1135[c]	0.5167
2-Me	5.2751[d]	4.9965[d]	0.2786
2-*t*-Bu	4.7200[d]	5.1367[d]	−0.4167

[a]Z=H. [b]Internal $\delta_{HB} - \delta_{HC}$. [c]Data from Ref. (3). [d]Data from Ref. (6).

Scheme 2. 4-substituted styrene (**2**-H) and its α-alkyl derivatives: α-methyl-(**2**-Me) and α-*t*-butilstyrene (**2**-*t*-Bu), and corresponding chemical shifts.

While styrene, **2**-H, has a well defined geometry (planar or nearly planar[3]), the phenyl-vinyl dihedral angle, θ, for **2**-Me is 30º while that for **2**-*t*-Bu is 64º.[6] Thus, there are apparently two electronic contributions to the high field shift of H$_B$ on going from **2**-H to **2**-*t*-Bu: (1) relief of steric hidrance and (2) the electron-releasing effect of the alkyl substituent (as evidenced by the additional negative contribution to q_{HB} for the alkylstyrenes as compared to the styrenes for the same θ). This combines with the decreased ring current effect to give a large high field shift for H$_B$, By contrast, the near constancy of δ_{HC} reflects a lower sensitivity to both ring current and charge density effects.[6]

In a preceding paper,[1] the suggestion that cross-conjugated triene **1**-R prefers the *s-cis* conformation (with a minimal heat of formation) was reported. According to this conformation of **1**-R, the π-unit **1** is neither coplanar with the aromatic/heteroaromatic ring (defined by the dihedral angle θ) nor coplanar with the *s-cis*-butadiene fragment. The disturbed planarity of the extended π-system consisting of the aromatic/heteroaromatic ring and the π-unit **1** (caused by the presence of the *cis*-butadiene fragment, **Y**) positively contributes to decreased steric hindrance, as compared to **2**-H. This, together with the peculiarity of the π-electron arrangement in the cross-conjugated chain of series **1**-R,[1] apparently are electronic contributions to the high field shift of H$_B$ on going from **1**-R to **2**-H. The mentioned two electronic contributions combine with the decreased ring current to give the high field shift of H$_B$. There is no large difference between δ_{HC} for **1**-R and for **2**-G. This suggests a lower sensitivity of δ_{HC} to both charge density and ring current effects caused by α-substitution in **2**-H, as well as to small changes in θ.

All heteroaryl derivatives of **1**-R were treated as benzenoid structures where one CH/CH:CH fragment is replaced with a heteroatom. As is known, pyridinium rings (benzenoid

structures where one CH fragment is replaced with nitrogen) are known to be strongly electron-attracting at all positions.[8] Inductive and/or field effects of pyridyl groups appear to be more important than the resonance effects, as the Hammett σ substituent constant (reaction: ^{1}H-NMR chemical shifts of α-protons in β-pyridylacrylic acids in DMSO[8]) is lower for the 4-substituted pyridinium ring than for the 3-substituted analogue.[8] It should be noted that *ortho*-values of the Hammett σ substituent constants suffer from some of the same disadvantages that are found for *o*-substituted benzenes: although steric effects will be low for N: direct field effects could be important, and, for NMR work, anisotropic effects.[8]

By analogy with arguments presented for the Hammett σ constants, the chemical shifts of the β-vinyl protons for individual members of **1**-R are likely to be affected by the anisotropic magnetic susceptibility of the heteroatoms present in 2-thienyl, 3-pyridyl, 2-pyridyl and 2-bromopyridin-6-yl groups. The heteroaromatic ring current effects differ from those in the phenyl group and very likely contribute significantly to the large positive value of $\Delta\delta(B - C)$ in **1**-R (Table I; R = heteroaromatic nuclei). Accordingly, the possible proximity effects of the *o*-substituted hydroxymethyl group to $\Delta\delta(B - C)$ for **1**-R [Table I; R = 2-(Hydroxymethyl)phenyl] will not be considered.

The effects of substituents in the aromatic ring on the ^{1}H SCS (δ^H) are usually analysed using the Swain-Lupton equation.[2] We used this DSP equation in the following form:

$$\delta^H = fF + rR + h \tag{1}$$

where δ^H is the chemical shift induced by the substituent X, and F and R are substituent parameters reflecting the field and resonance effects, respectively. Parameters h (the intercept on the ordinate), f and r (measures of the sensitivity of the chemical shift to the field and resonance effects of the substituents, respectively), are obtained by polylinear regression analysis.

Not all available **1**-R derivatives were included in the correlations. The limited availability of F and R values in the literature[2,9] resulted in only five members (X = H, CH_3, CH_2OH, OCH_3 and I) remaining in the substituent set. Iodine was not omitted although halogens often give anomalous results.[3] There is a conviction that these anomalies are magnetic in origin.[3] Application of multiple linear regression analysis to the observed ^{1}H SCS using the Swain-Lupton equation (1) yields the following relationships (2-3):

$$\delta_{H_B} = 0.093(\pm 0.007)F + 0.191(\pm 0.006)R + 5.5378$$
$$(R = 0.999, s = 0.002, F = 582.1, n = 5, r/f = 2.05)^1 \tag{2}$$

$$\delta_{H_C} = 0.178(\pm 0.027)F + 0.266(\pm 0.023)R + 5.2529$$
$$(R = 0.993, s = 0.008, F = 66.6, n = 5, r/f = 1.49) \tag{3}$$

The observed f and r values in Eqs. (2–3) indicate a prevalent resonance effect at both β protons. It should be noted that the r/f ratio for H_C ($r/f = 1.49$) is smaller than that for H_B ($r/f = 2.05$) revealing the larger influence of the resonance effect at H_B. Owing to the particular geometric arrangement of the vinyl group (π-unit **1**) in **1**-R, the vinyl β protons H_B and

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1   *R*-regression coefficient; *s*-standard error of estimate; *F*-F test for significance of regression; *n*-number of points in the set

H_C should have different sensitivities to polar and resonance effects. This is consistent with the different magnitudes of the f and r values observed in Eqs. (2–3). The weighting factors f and r are larger for δ_{HC} than for δ_{HB}. A similar pattern of f and r values was previously established for α-alkylstyrenes (See Table II).

TABLE II. Correlations [a] of the chemical shifts of the β-vinyl protons [b] for 4-substituted derivatives of **2**-G (G = H, Me, t-Bu), with F and R parameters of Swain and Lupton[2]

Compound [b]	δ	f [c]	r [c]	r [d]	r/f [c]
2-H	H_B	0.100 ± 0.011	0.414 ± 0.014	0.996	4.14
	H_C	0.166 ± 0.010	0.420 ± 0.014	0.997	2.53
	$(H_B - H_C)$ [f]	-0.067 ± 0.002	_[f]	0.997	_[f]
2-Me	H_B	0.094 ± 0.011	0.234 ± 0.020	0.987	2.49
	H_C	0.140 ± 0.008	0.313 ± 0.013	0.997	2.24
	$H_B - H_C$	-0.046 ± 0.007	-0.079 ± 0.011	0.977	1.72
2-t-Bu	H_B	0.044 ± 0.010	0.055 ± 0.016	0.974	1.25
	H_C	0.077 ± 0.008	0.104 ± 0.014	0.995	1.35
	$H_B - H_C$	-0.032 ± 0.003	-0.049 ± 0.006	0.994	1.53

[a] Data from Ref. 6. [b] See Scheme 2 for labeling of the nuclei and compounds. [c] Weighting coefficients for Eq. $\delta = fF + rR + \delta_0$. [d] Correlation coefficient. [e] Weighting coefficient ratio. [f] Internal proton chemical shifts difference shows pure field dependence.
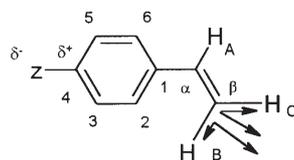
2-H

Scheme 3.

It has been pointed out that polar effects of the substituent on the chemical shifts of the β protons of **2**-G strongly depend upon the nature of the intervening molecular framework.[6] According to the pattern of the regression coefficients for individual terms in σ_I, σ^0_R correlations,[10] as well as the weighting factors f and r (see Table II) observed for the β-vinyl protons of **2**-H, two points are apparent. Firstly, the very similar values for ρ_R or r essentially confirm equal through-bond transmission to H_B and H_C. Secondly, since δ_{HB} should be almost insensitive to field effects (see Scheme 3), the difference between ρ_I for H_B and H_C, suggests an almost equal contribution to δ_{HC} from direct field and π polarization effects[11,12] and the only electronic substituent effect contributing to $\Delta\delta(B - C)$ should

be the field effect.[3] This is consistent with both the excellent correlation of $\Delta\delta(B-C)$ for **2**-H with F (see Table II) and the excellent correlation of $\Delta\delta(B-C)$ for **2**-H with the difference in substituent-induced electric fields[3] acting along the $C_\beta - H_B$ and $C_\beta - H_C$ bonds.

It appears that the β vinyl protons of the **2**-Me and **2**-*t*-Bu derivatives have different sensitivities to both resonance and field effects.[6] Since there is no apparent reason why conjugative interactions should affect δ_{HB} and δ_{HC} differently, the smaller r values for H_B apparently reflect some additional negative resonance contribution to δ_{HB} *i.e.*, a contribution by which resonance electron-withdrawing groups cause high field shifts while resonance electron-releasing groups cause low field shifts.[6] This is unexpected and the nature of the observed effect is unclear.[6] However, it is possible that it may be associated with an interaction of the $C_\alpha - C_\beta - H_B \sigma$ bond system with the phenyl π-electron system. $C_\beta - H_C$ would be much less likely to interact with the π-electron system.[6]

While the CNDO/2 calculations indicate that the SCS for the vinyl protons of the **2**-Me and **2**-*t*-Bu derivatives are primarily due to electronic effects, a substituent effect, which is primarily magnetic in origin, may also be present. This is associated with substituent-induced changes in the dihedral angle θ.[6] The vinyl group can either accept or donate electrons by resonance. Therefore, any substituent with a significant resonance effect should increase the conjugation between the phenyl and vinyl groups (supported by CNDO/2 calculations[6]). δ_{HB} is much more sensitive to changes in θ than δ_{HC}, primarily due to changes in ring current effects. Since δ_{HB} increases with decreasing θ, substituent-induced changes in θ should be reflected by a positive dependence of δ_{HB} and $\Delta\delta(B-C)$ on $|R|$ (since both resonance electron-acceptors and donors should decrease θ).[6] In support of an effect of this type is the observation that the negative R dependence for $\Delta\delta(B-C)$ is apparently greater for the **2**-Me series than for the **2**-*t*-Bu series, whereas a purely electronic effect might be expected to have a maximum for $\theta = 90º$.[6] However, the CNDO/2 results provide strong evidence for the presence of an electronic effect. It is probable that both effects are present, but their relative importance is uncertain.[6]

While $\Delta\delta(B-C)$ shows a pure field dependence for **2**-H series, $\Delta\delta(B-C)$ for the **2**-Me and **2**-*t*-Bu derivatives depend upon both F and R with a relatively smaller field dependence for $\Delta\delta(B-C)$ than in the case of styrene (see Table II). By analogy with arguments presented previously for **2**-G derivatives, $\Delta\delta(B-C)$ for **1**-R should reflect both polar and resonance effects on the proton chemical shifts. The obtained f and r values for the correlation of the $\Delta\delta(B-C)$ of the **1**-R derivatives with the F and R substituent parameters indicate that these differences in the proton chemical shifts are influenced not only by the polar but also, to a smaller extent, by the resonance effect. The corresponding relationship is as follows:

$$\Delta\delta(B-C) = -0.085(\pm0.024)F - 0.075(\pm0.021)R + 0.2848$$
$$(R = 0.941, s = 0.007, F = 7.7, n = 5) \tag{4}$$

According to the pattern of f and r values observed for terminal π-unit **1** carbon chemical shifts in the **1**-R derivatives,[1] $\delta_{C\beta}$, it is apparent that those carbon chemical shifts show an increased field dependence and a decreased resonance dependence in comparison with

those for C_β in the **2**-H series. We have pointed out that this can be reasonably explained in terms of conformational effects arising from a disturbed planarity of the extended π-system consisting of the aromatic ring and the π-unit **1** (vinyl group), caused by the presence of the *cis*-butadiene fragment. The *r/f* values for both the δ_{HB} and δ_{HC} correlations indicate smaller resonance/field effects for the **1**-R relative to the **2**-H series. This together with relatively larger field dependence of $\Delta\delta(B-C)$ for the **1**-R than for **2**-H series reveals a likely increased π polarization of the π-unit **1** in the **1**-R (vinyl group) by polar substituents. There is a generally good agreement between the ^{13}C and ^{1}H correlations for the β-vinyl atoms in **1**-R, which reveals a similarity in the patterns of their substituent dependence.

The weighting coefficient ratio *r/f* is nearly equal for δ_{HC} [Eq. (3); *r/f* = 1.49] and $\delta_{C\beta}$ (*r/f* = 1.251[1]). In a specific case like this, a cross-correlation of the two chemical shifts should be linear, provided that intramolecular electronic effects are dominant. On the other hand, if there are significant contributions from magnetic anisotropy effects and solvent-solute interactions or if *r/f* is not nearly equal for the two nuclei, then the $\delta - \delta$ plot should be nonlinear.[13] In fact the $\delta_{HC} - \delta_{C\beta}$ plot for **1**-R is linear (Fig. 1). Only the 2-thienyl and 2-(hydroxymethyl)phenyl derivatives show significant deviation, which is probably due to ring current effects of the heteroaromatic group and proximity effects of the *ortho*-substituted hydroxymethyl group. In contrast, δ_{HB} for **1**-R (with the same data set) gives a poorer correlation with $\delta_{C\beta}$ ($R = 0.844$), which is expected since δ_{HB} is relatively less sensitive to field effects [Eq. (2); *r/f* = 2.05] than $\delta_{C\beta}$ and δ_{HC}.
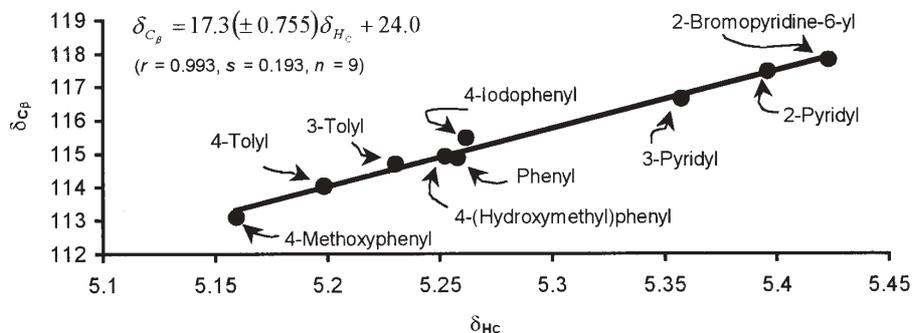

$$\delta_{C_\beta} = 17.3\left(\pm 0.755\right)\delta_{H_c} + 24.0$$
$$(r = 0.993,\ s = 0.193,\ n = 9)$$

Fig. 1. Plot of β ^{13}C chemical shifts[1] ($\delta_{C\beta}$) *vs.* β ^{1}H chemical shifts (δ_{HC}) for **1**-R. Points for 4-hydroxyphenyl, 2-thienyl and 2-(hydroxymethyl)phenyl derivatives were omitted.

The established $\delta_{HC} - \delta_{C\beta}$ correlation for **2**-H is also linear.[13] The corresponding relationship is as follows:

$$\delta_{C\beta} = 18.2\,\delta_{HC}$$
$$(r = 0.996)\ [2] \tag{5}$$

The basic assumption in utilizing substituent-induced changes in ^{1}H and ^{13}C chemical shifts of aromatic derivatives to monitor electronic effects is that these parameters re-

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2   Correlation coefficient.

flect changes in the ground-state electronic density.[14] The $\delta_{HC} - \delta_{C\beta}$ correlations for **1**-R (see Fig. 1) and **2**-H [see Eq. (5)] suggest that both β ^{13}C and ^{1}H chemical shifts in these aromatic systems are dominated by changes in the charge density at C_β. Changes in a carbon π charge density alter the ^{1}H chemical shifts by polarizing the C–H bond.[13] For aromatic derivatives a unit change in the π charge density for an sp^2 carbon should induce ^{13}C and ^{1}H chemical shifts of 160–200 ppm and 10 ppm, respectively.[13] Thus, the expected slope of the $\delta_{HC} - \delta_{C\beta}$ plot for **1**-R is 16–20, in quantitative agreement with the observed value (see Fig. 1), provided that both parameters reflect the ground-state electron density. The slope for the **1**-R $\delta_{HC} - \delta_{C\beta}$ plot amounts to 17.3 which is smaller than the slope in Eq. (5). This seems to suggest lower sensitivities of the ^{13}C chemical shifts of sp^2 carbons to charge density changes in **1**-R in comparison to those for C_β in **2**-H.

CONCLUSIONS

It has been shown that ^{1}H and ^{13}C chemical shifts in **1**-R can be used to monitor electronic substituent effects. It was pointed out that the observed relatively increased field dependence and the decreased resonance dependence for the carbon chemical shifts of the terminal π-unit **1** (β-vinyl) in 3-methylene-2-substituted-1,4-pentadienes, **1**-R, in comparison with those in **2**-H, can be reasonably explained in terms of increased π-polarization effects and increased localization of resonance interactions in the aromatic group.[1] Since r/f is nearly equal for δ_{HC} and $\delta_{C\beta}$ in **1**-R, a similarity in the pattern of their substituent dependence must exist.

The cross-correlation $\delta_{HC} - \delta_{C\beta}$ for **1**-R is linear ($R = 0.993$), with a slope amounting to 17.3, showing that both parameters reflect ground-state electron density. This is in good agreement with the predicted lower sensitivity of δ_{HC} to both ring current and charge density effects. The poorer cross-correlation $\delta_{HB} - \delta_{C\beta}$ for **1**-R ($R = 0.844$) suggests that some factors other than the electron density of the attached carbon contribute to the determination of δ_{HB} (such as magnetic anisotropy and steric effects). This is consistent with suggestions[15] that ^{1}H chemical shifts are influenced by electron densities on both the hydrogen atoms in question and the carbon atom directly bonded to them and that they very often show different dependencies on structural perturbations.

In summary, correlations of ^{1}H and ^{13}C chemical shifts with F and R parameters provide a consistent picture of electronic effects transmitted through the carbon framework of **1**-R. The transmission of electron effects in 3-methylene-2-substituted-1,4-pentadienes can be well explained in terms of a combination of polar effects with resonance effects. The observed different sensitivities of the chemical shifts of the β-vinyl protons (for **1**-R) to polar and resonance effects are in a good agreement with those established for H_B and H_C in other α-alkyl substituted **2**-H analogues.[6]

И З В О Д

ЕФЕКТИ СУПСТИТУЕНАТА НА ^{1}H-NMR ХЕМИЈСКА ПОМЕРАЊА 3-МЕТИЛЕН-2-СУПСТИТУИСАНИХ-1,4-ПЕНТАДИЕНА

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На ^{1}H хемијска померања β-винил-протона у 3-метилен-2-супституисаним-1,4-пента-диенима је примењен принцип линеарне корелације слободних енергија. Корелације протон-ских хемијских померања са супституентским параметрима Swain-a и Lupton-a пружају усагла-шену слику електронских ефеката у овим једињењима. Свеукупни концепт хемијских поме-рања протона у великој се мери може објаснити моделом ефеката супституената заснованих на ефектима поља, резонанционим и π поларизационим ефектима. У складу са посебним геометријским распоредом винил-групе у 3-метилен-2-супституисаним-1,4-пентадиенима, β-ви-нил протони H$_B$ и H$_C$ имају различиту осетљивост на поларне и резонанционе ефекте. раз-личита осетљивост ^{1}H хемијских померања на резонанционе ефекте открива непознати ефекат који није предвиђен поменутим моделом. Показано је да ^{1}H и ^{13}C хемијска померања за ова једињења одражавају електронске густине основног стања.

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