Investigations of Substituent Effects by Nuclear Magnetic Resonance Spectroscopy and All-valence Electron Molecular Orbital Calculations.
II. 4-Substituted α-Methylstyrenes and α-*t*-Butylstyrenes

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Received June 14, 1972

Substituent-induced ^1H chemical shifts (S.C.S.) for 19 4-substituted α-methyl- and α-*t*-butylstyrenes have been determined at infinite dilution in C_6H_{12} and ^{13}C S.C.S. have been determined for 0.4 *M* solutions in CCl_4. S.C.S. are correlated with field and resonance substituent parameters and compared with charge densities determined by CNDO/2 MO calculations. The variation of S.C.S. with the dihedral angle, ρ, between phenyl and vinyl groups and the overall pattern of S.C.S. can be largely accounted for by a model of substituent effects based on field, resonance, and π polarization effects, with conjugative interactions varying as $\cos^2\rho$. Both ^{13}C chemical shifts and charge densities indicate that the π polarization effect consists of two components: (*1*) a through-space polarization of the vinyl system by the polar C—X bond and (*2*) polarization of the entire conjugated styrene π electron system. However, significant deviations are noted for some of the ^1H S.C.S. correlations. The CNDO/2 calculations indicate that these deviations are primarily due to electronic effects not predicted by the model outlined above. CNDO/2 calculations for related compounds provide a partial explanation by indicating that the magnitude of the field effect depends upon the nature of the molecular framework.

Les déplacements chimiques en ^1H induits par des substituants (S.C.S.) pour 19 α-méthyl et α-*t*-butylstyrènes substitués en position 4 ont été déterminés à dilution infinie dans le C_6H_{12}; ceux-ci en ^{13}C ont été déterminés en solution 0.4 *M* dans le CCl_4. Les déplacements chimiques induits par des substituants sont reliés aux paramètres de champ et de résonance caractéristiques des substituants et comparés avec les densités de charge obtenues par des calculs CNDO/2 MO. La variation dans les déplacements chimiques avec l'angle dièdre, ρ, entre les groupes phényle et vinyl ainsi que le schéma général de ces déplacements chimiques peuvent très bien s'interpréter à partir d'un modèle des effets de substituants basé sur le champ, la résonance et des effets de polarisation π avec des interactions de conjugaison variant selon le $\cos^2\rho$. Les déplacements chimiques en ^{13}C et les densités de charge indiquent tous les deux, que l'effet de polarisation π possède deux composantes: (*1*) une polarisation à travers l'espace du système vinylique par la liaison polaire C—X et (*2*) une polarisation du système d'électrons π du styrène conjugué en entier. Cependant, des écarts notables ont été observés pour quelques-unes des correlations dans les déplacements chimiques en ^1H. Les calculs CNDO/2 montrent que ces écarts sont imputables principalement à des effets électroniques imprévisibles selon le modèle illustré précédemment. Les calculs CNDO/2 pour des composés voisins permettent une explication partielle en montrant que l'amplitude des effets de champ dépend de la nature du squelette moléculaire.

[Traduit par le journal]

Can. J. Chem., **51**, 915 (1973)

Introduction

In the preceding paper (1), ^1H and ^{13}C chemical shifts for 4-substituted styrenes were correlated with field (*F*) and resonance (*R*) substituent parameters (2):

$$[1] \qquad \delta = fF + rR + \delta_0$$

These correlations of substituent-induced chemical shifts (S.C.S.) were used in conjunction with charge densities estimated by CNDO/2 molecular orbital calculations (3) to deduce mechanisms of transmission of substituent effects in these compounds. However, since the use of *F* and *R* correlations for this purpose has been severely criticized (4), several criteria were proposed to test the validity of the correlations (1). One of these criteria was that *f* and *r* values should vary in a regular and predictable fashion for related series of compounds. To test this criterion, a series of 4-substituted derivatives of 2-phenylpropene (**1**) and 2-phenyl-3,3-dimethylbutene (**2**) were synthesized. These compounds will hence-

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forth be referred to as derivatives of α-methylstyrene (AMS) and α-*t*-butylstyrene (ATBS). These compounds were chosen on the assumption that through-bond electronic effects should vary as a function of the dihedral angle, ρ, between phenyl and vinyl groups.

Results of investigations of S.C.S. for AMS and ATBS derivatives are presented below.

Experimental

(a) Preparation and Purification of Compounds

α-Methylstyrene and its 4-fluoro and 4-chloro derivatives were obtained from Aldrich Chemicals, Inc. Other AMS derivatives were known compounds and were synthesized by previously reported methods. Full details are reported elsewhere (5).

Of the ATBS derivatives only the parent α-*t*-butylstyrene (6, 7) and its 4-methoxy derivative (7) have been previously described in the literature. The remaining compounds were synthesized by modifying known methods; in most cases, the olefin was obtained by catalytic dehydration of the appropriate 3,3-dimethyl-2-phenyl-2-butanol over activated alumina. Synthetic procedures and analytical data are outlined below.

3,3-Dimethyl-2-phenyl-1-butene

3,3-Dimethyl-2-phenyl-2-butanol, b.p. 108–109.5°/10 mm (lit. 128°/20 mm (6), 95.5°/4.5 mm (7)), was obtained from the reaction of 3,3-dimethyl-2-butanone and phenyllithium in refluxing ether (6). The alcohol was dehydrated over activated alumina and purified by v.p.c. An analytical sample had b.p. 56.5–57°/3.4 mm (lit. 75°/10 mm (6)).

Anal. Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 90.02; H, 10.13.

3,3-Dimethyl-2-(4′-methylphenyl)-1-butene

The required butanol, b.p. 93–97°/2 mm (lit. 98°/2.5 mm (7)), was prepared from 4-methylphenyllithium and 3,3-dimethyl-2-butanone and dehydrated over alumina. Purification by v.p.c. gave the styrene, b.p. 74.8–75°/2.6 mm.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.50; H, 10.39.

3,3-Dimethyl-2-(4′-t-butylphenyl)-1-butene

4-Bromo-*t*-butylbenzene, b.p. 82–84°/5 mm (lit. 113–114°/20 mm (8)), was obtained by addition of chlorosulphonic acid to an ice-cold solution of bromobenzene and *t*-butanol (9). The lithium reagent prepared from this product was treated with 3,3-dimethyl-2-butanone to give the required butanol, b.p. 99–102°/2 mm. Dehydration of the alcohol with alumina, followed by preparative v.p.c., gave a white crystalline solid, m.p. 46.5–47.5°, b.p. 86–86.3°/0.8 mm.

Anal. Calcd. for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.64; H, 11.29.

3,3-Dimethyl-2-(4′-N,N-dimethylaminophenyl)-1-butene

The required butanol was prepared from 4-*N*,*N*-dimethylaminophenyllithium (10) and 3,3-dimethyl-2-butanone. The butanol did not readily dehydrate during distillation. Consequently the crude alcohol was refluxed with potassium hydrogen sulfate for 5 min at 140°, and vacuum distilled. An analytical sample of the olefin, recrystallized from methanol, had m.p. 26–27°.

Anal. Calcd. for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.88; H, 10.31; N, 6.95.

3,3-Dimethyl-2-(4′-fluorophenyl)-1-butene

The reaction of 3,3-dimethyl-2-butanone with 4-fluorophenylmagnesium bromide gave the required alcohol, b.p. 90–97°/5 mm. The alcohol was dehydrated over alumina. The olefin, purified by v.p.c., had b.p. 58°/1.9 mm.

Anal. Calcd. for $C_{12}H_{15}F$: C, 80.86; H, 8.48; F, 10.66. Found: C, 80.72; H, 8.51; F, 10.48.

3,3-Dimethyl-2-(4′-chlorophenyl)-1-butene

4-Chlorophenylmagnesium chloride (11) was converted to 3,3-dimethyl-2-(4′-chlorophenyl)-2-butanol, b.p. 98–103°/2 mm, by treatment with 3,3-dimethyl-2-butanone. The alcohol was dehydrated over alumina; purification of the distillate by v.p.c. gave the styrene, b.p. 81–81.2°/1.9 mm.

Anal. Calcd. for $C_{12}H_{15}Cl$: C, 74.02; H, 7.77; Cl, 18.21. Found: C, 73.95; H, 8.04; Cl, 17.96.

3,3-Dimethyl-2-(4′-bromophenyl)-1-butene

The bromophenylbutanol, b.p. 110–115°/2 mm, was obtained from the reaction of 3,3-dimethyl-2-butanone with 4-bromophenylmagnesium bromide. Purification of the alumina catalyzed dehydration product by v.p.c. gave the desired olefin, b.p. 98–99°/2 mm.

Anal. Calcd. for $C_{12}H_{15}Br$: C, 60.26; H, 6.32; Br, 33.42. Found: C, 60.46; H, 6.27; Br, 33.24.

3,3-Dimethyl-2-(4′-methoxyphenyl)-1-butene

4-Methoxypivalophenone, b.p. 130–132°/5 mm (lit. 138–140°/8 mm (12)), was prepared by Friedel–Crafts acylation of anisole with pivaloyl chloride and aluminum chloride (12). The ketone was converted directly to the required styrene by the Wittig synthesis (13) and the crude reaction product purified by v.p.c. (column A; 160°, 200 ml/min helium). An analytical sample had b.p. 84°/1 mm (lit. 63°/0.6 mm (7)).

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.18; H, 9.33.

3,3-Dimethyl-2-(4′-nitrophenyl)-1-butene

3,3-Dimethyl-2-butanol was added to an ice-cold suspension of aluminum chloride in benzene while dry hydrogen chloride was bubbled into the mixture (14). The isolated product, 3,3-dimethyl-2-phenylbutane, b.p. 205–207°/756 mm (lit. 205–207°/760 mm (14)), was nitrated by the method of Stirling and Bogert (15). Distillation of the crude 3,3-dimethyl-2-(4′-nitrophenyl)-butane gave a fraction, b.p. 119–124°/2 mm (lit. 117–124°/2 mm (14)), which solidified on standing; m.p. 37.5–38.5°, recrystallized from methanol. Treatment of this material with *N*-bromosuccinimide and benzoyl peroxide (16) gave the benzyl bromide, m.p. 122–123°, recrystallized from methanol. The bromide was dehydrohalogenated with ethanolic potassium hydroxide (4 h at 60°) (16) to give 3,3-dimethyl-2-(4′-nitrophenyl)-1-butene, m.p. 42–43°, recrystallized from pentane.

Anal. Calcd. for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.83. Found: C, 70.16; H, 7.32; N, 6.94.

Catalytic dehydrations were carried out using activated alumina (Matheson Coleman and Bell; 8–14 mesh) which was washed with ammonium hydroxide and dried for 24 h at 100° before packing into the reaction tube. 3,3-Dimethyl-2-phenyl-2-butanols were passed through the heated (250°) reaction tube at a flow rate of 0.5 ml/min, using N_2 as a carrier gas and with the apparatus main-

TABLE 1. Vinyl proton chemical shifts (in p.p.m. relative to $(CH_3)_4Si$) and coupling constants (in Hz) for 4-substituted α-methylstyrenes at infinite dilution in C_6H_{12}

Substituent	δ_{H_B}	δ_{H_C}	$\Delta\delta(B - C)$	$^4J_{AB}$	$^4J_{AC}$	J_{BC}
H	5.2751	4.9965	0.2786	−0.82	−1.51	1.62
CH_3	5.2285	4.9306	0.2979	−0.81	−1.50	1.68
$C(CH_3)_3$	5.2511	4.9503	0.3008	−0.81	−1.47	1.70
F	5.2219	4.9843	0.2376	−0.81	−1.49	1.53
Cl	5.2639	5.0173	0.2466	−0.81	−1.49	1.36
OCH_3	5.1848	4.8957	0.2891	−0.81	−1.49	1.60
$N(CH_3)_2$	5.1533	4.8125	0.3408	−0.79	−1.47	1.74
NO_2	5.4266	5.2041	0.2225	−0.82	−1.50	1.07
$Si(CH_3)_3$	5.2811	4.9963	0.2848	−0.82	−1.50	1.63
$Sn(CH_3)_3$	5.2581	4.9710	0.2873	−0.81	−1.48	1.65

tained at 130–150 mm pressure. Products were trapped in a receiver flask immersed in a Dry Ice – acetone slurry.

ATBS derivatives were dried over Linde 4A molecular sieve. They were then purified by preparative v.p.c., using a Varian Aerograph Autoprep 700 and a 20 ft × 3/8 in. column packed with 30% SE-30 on 45/60 mesh Chromosorb W. Melting points were determined on a Fisher–Johns hot-stage apparatus and are uncorrected. Elemental analyses were carried out by A. B. Gygli, Microanalyses Laboratories Limited, Toronto, Ontario.

(b) Sample Preparations and Recording of Spectra

All styrene derivatives were either used immediately after synthesis and purification or else were redistilled or recrystallized immediately before use. AMS derivatives were dissolved in cyclohexane which was used as a lock and reference signal. The cyclohexane (Fisher A.C.S. grade) was fractionally distilled from sodium and stored over Linde 4A molecular sieve. ATBS derivatives were dissolved in cyclohexane-d_{12} (Merck Sharp and Dhome Canada Ltd.) with 4% tetramethylsilane as lock and reference signal, to avoid interference between *t*-butyl and cyclohexane peaks. Measurements were made at three concentrations in the range of 1–5 mol %.

Proton spectra were obtained on a Varian HA-100 operating in frequency sweep mode at a probe temperature of 30°. Experimental conditions were identical to those previously described (17). Nuclear Overhauser effects for α-*t*-butylstyrene were determined according to the procedure of Bell and Saunders (18), using the electronic integrator of the HA-100 and a Hewlett–Packard 4204A digital oscillator. The sample (5 mol % in $CDCl_3$ containing 5 mol % tetramethylsilane as lock and reference) was filtered, degassed by five freeze–pump–thaw cycles on a high vacuum line and sealed at 0.01 mm.

^{13}C n.m.r. spectra were obtained in CCl_4 for 0.4 *M* solutions, using previously reported procedures (1).

Results

A complete A_3BC spectral analysis was carried out for the α-methyl and vinyl proton spectrum of α-methylstyrene, using the iterative computer program LAME (19) (protons are not labelled conventionally in order of increasing field but rather by analogy to styrene (1) to facilitate comparisons between different series).

TABLE 2. Vinyl proton chemical shifts (in p.p.m. relative to $(CH_3)_4Si$) and coupling constants (in Hz) for 4-substituted α-*t*-butylstyrenes at infinite dilution in cyclohexane-d_{12}

Substituent	δ_{H_B}	δ_{H_C}	$\Delta\delta(B - C)$	J_{BC}
H	4.7200	5.1367	−0.4167	1.79
CH_3	4.7256	5.1513	−0.4257	1.68
$C(CH_3)_3$	4.7247	5.1538	−0.4291	1.60
F	4.7247	5.1518	−0.4271	1.58
Cl	4.6958	5.1092	−0.4134	1.87
Br	4.7110	5.1156	−0.4046	1.87
OCH_3	4.6896	5.0776	−0.3880	2.07
$N(CH_3)_2$	4.7035	5.1088	−0.4053	1.91
NO_2	4.7780	5.2399	−0.4619	1.19

However, it was found that all chemical shifts and coupling constants and also the chemical shift difference Δδ(B − C) agreed within 0.05 Hz of those obtained from a first order A_3MX analysis. Consequently, all AMS spectra were analyzed by first order analysis. ATBS derivatives were analyzed as AB spectra (there was no resolvable coupling to the *t*-butyl group).

Infinite dilution proton chemical shifts were determined by least squares fitting of the linear dilution curves. Standard errors of intercepts never exceeded 0.0008 p.p.m. Proton chemical shifts and coupling constants for AMS derivatives are summarized in Table 1 with results for ATBS derivatives in Table 2. ^{13}C chemical shift data for both compounds are given in Table 3.

CNDO/2 calculations were carried out on an IBM 360-65 computer using a standard program (19). Most bond lengths and bond angles for styrene were identical to those previously reported (1) with the C_1—C_α—C_β valence angle α fixed at 120°. The C_1—C_α bond length was varied as a function of ρ

$$[2] \qquad r_{C_1—C\alpha} = (1.52 - 0.06 \cos \rho)\text{Å}$$

TABLE 3. ^{13}C chemical shifts (in p.p.m. relative to $^{13}CH_3Si(CH_3)_3$) for 0.4 *M* solutions of 4-substituted α-methyl- and α-*t*-butylstyrene derivatives in CCl_4

Substituent	C-4	C-3,5	C-2,6	C-1	C-α	C-β
(a) α-Methylstyrenes						
H	127.05	127.87	125.25	141.07	142.97	112.13
CH_3	136.23	128.53	125.18	138.26	142.74	111.28
$C(CH_3)_3$	149.55	124.66	125.02	138.21	142.74	111.39
F	162.21	114.78	126.84	137.15	141.99	112.09
Cl	133.20	128.14	126.50	139.42	141.89	112.73
OCH_3	158.98	113.28	126.30	133.61	142.30	110.37
$N(CH_3)_2$	149.59	112.03	125.97	129.62	142.28	108.65
NO_2	147.23	123.27	125.85	146.96	141.50	115.82
$Si(CH_3)_3$	138.62	132.93	124.65	141.49	143.04	112.23
$Sn(CH_3)_3$	140.36	135.35	124.96	141.05	143.08	112.03
(b) α-t-Butylstyrenes						
H	126.05	127.05	128.70	143.08	159.43	111.39
CH_3	134.99	127.73	128.64	140.21	159.34	111.27
$C(CH_3)_3$	148.31	123.84	128.51	140.23	159.33	111.29
F	161.55	113.99	130.15	138.86	158.49	112.06
Cl	132.05	127.38	130.01	141.40	158.39	112.04
Br	120.53	130.35	130.35	141.85	158.39	112.03
OCH_3	158.09	112.52	129.61	135.39	159.04	111.49
$N(CH_3)_2$	148.79	111.68	129.30	131.90	159.37	111.03
NO_2	146.96	122.40	129.37	149.59	157.94	112.86

TABLE 4. Excess charge densities (× 10^4, relative to the parent styrene) for C-1 and vinyl protons and carbons of 4-substituted styrenes with ρ = 90° (phenyl and vinyl groups at right angles)

	$N(CH_3)_2$	NH_2	OCH_3	CH_3	$C(CH_3)_3$	C≡CH	F	Cl*	CF_3	C≡N	NO_2	$Si(CH_3)_3$*
$C\text{-}1_\sigma$	+214	+176	+145	+54	+76	+8	+70	−17	−109	−51	−178	+10
$C\text{-}1_\pi$	−574	−460	−409	−159	−215	−30	−245	−86	+263	+94	+396	−24
$C\text{-}\alpha_\sigma$	−2	+2	+11	−4	−4	+11	+37	+36	+44	+26	+72	−7
$C\text{-}\alpha_\pi$	+41	+31	+15	+11	+17	−12	−27	−36	−78	−45	−118	+4
$C\text{-}\beta_\sigma$	+9	+3	−4	+5	+5	−6	−23	−23	−34	−19	−53	+5
$C\text{-}\beta_\pi$	−41	−30	−12	−11	−17	+14	+35	+43	+88	+52	+133	−5
H_B	−18	−11	−7	−5	−8	+3	+7	+11	+25	+14	+38	−3
H_C	−25	−18	−8	−7	−10	+7	+17	+22	+46	+27	+71	−3
Δ†	+7	+7	+1	+2	+2	−4	−10	−11	−21	−13	−33	0

*3s and 3p orbitals only.
†$\Delta = \Delta q(H_B - H_C)$.

to allow for decreased conjugation in the nonplanar forms. Assumed geometries for other substituents are tabulated elsewhere (5). For reasons of computational economy, most calculations were carried out for 4-substituted styrenes with ρ = 90° rather than for α-alkylstyrenes using the experimental ρ. Vinyl carbon and hydrogen charge densities are given in Table 4 (complete charge densities are on deposit in the Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Canada K1A 0S2). However, calculations were also performed for a limited number of styrene derivatives with ρ = 30 and 60° and AMS derivatives with the experimental ρ of 30°. These calculations showed that charge densities varied smoothly with ρ. In addition, nearly identical results were obtained for the substituent dependence of charge densities of styrene and AMS derivatives with ρ = 30°, demonstrating that no complications were introduced by the presence of the alkyl substituent.

Discussion

(a) Determination of Conformation of α-Alkylstyrenes

^1H and ^{13}C S.C.S. in 4-substituted α-alkylstyrenes are very sensitive to the dihedral angle, ρ, between the phenyl and vinyl groups. Consequently we attempted to determine this angle as accurately as possible. ρ was estimated from the

TABLE 5. Calculated ring current and charge density contributions to $\Delta\delta_0(B - C)$, the β proton chemical shift difference in unsubstituted styrene, AMS and ATBS

(*a*) Calculated charge densities for H_B and H_C in styrene, AMS and ATBS

	Charge density ($\times 10^4$)				
Proton	Styrene(0°)	Styrene(30°)	AMS(30°)	Styrene(64°)	ATBS(64°)
H_B	+169	+144	+58	+126	+30
H_C	+63	+66	+46	+70	+78

(*b*) Calculated ring current (r.c.) and charge density (c.d.) contributions to $\delta_0(B)$, $\delta_0(C)$ and $\Delta\delta_0(B - C)$

		δ (p.p.m.)		
Proton	Contribution	Styrene	AMS(30°)	ATBS(64°)
H_B	r.c.*	0.561	0.438	0.123
	c.d.†	0.355	0.122	0.063
	Total	0.916	0.560	0.186
	δ_0(calcd.)‡	5.630	5.274	4.900
	δ_0(exp.)	5.630	5.275	4.720
H_C	r.c.	0.258	0.246	0.218
	c.d.	0.132	0.097	0.164
	Total	0.390	0.343	0.382
	δ_0(calcd.)	5.104	5.057	5.096
	δ_0(exp.)	5.113	4.997	5.137
$H_B - H_C$	$\Delta\delta_0$(calcd.)§	0.526	0.217	−0.196
	$\Delta\delta_0$(exp.)	0.517	0.279	−0.417

*Calculated using Bovey–Johnson (42) calculations.

†Calculated assuming a scaling factor of 21 p.p.m./hydrogen 1s electron and expressed relative to zero charge density.

‡Calculated δ_0 obtained by assuming that the calculated value for δ(B) for styrene is equal to the experimental value and expressing other values relative to this value.

§Difference in total ring current and charge density contributions for H_B and H_C. It is not necessary to assume any chemical shift in this case.

electronic absorption spectrum using two different techniques.

Experimentally determined λ_{max} values for the conjugation bands of styrene AMS and ATBS were respectively 248, 243 and 223 mμ while the corresponding extinction coefficients were 14 310, 10 900, and 2630. ρ can be estimated from the extinction coefficients using the approach of Braude and Sondheimer (20):

$$[3] \qquad \varepsilon/\varepsilon_{0^\circ} = \cos^2\rho$$

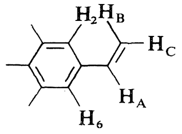
where ε_{0° is the extinction coefficient for styrene (assumed planar (1)). This approach gives ρ = 29° for AMS and ρ = 65° for ATBS. Alternatively one can determine ρ from conjugation band transition frequencies, using the method of Suzuki (21). This method yields ρ = 30° for AMS and ρ = 63° for ATBS (full details of the calculation are given elsewhere (5)). The two methods are in excellent agreement and average values of ρ = 30° for AMS and ρ = 64° for ATBS will be used in the following discussion.

(*b*) *Assignment of H_B and H_C for AMS and ATBS and Discussion of Factors Determining $\Delta\delta_0(B - C)$*

H_B and H_C for AMS have been previously assigned on the basis of specific deuteration experiments (22). It was found that $\delta_{H_B} > \delta_{H_C}$, as in styrene. However, $\Delta\delta_0(B - C)$ is much smaller for AMS (+0.279 p.p.m.) than for styrene (+0.517 p.p.m.). H_B and H_C for ATBS have not been previously assigned. These were assigned by utilizing the nuclear Overhauser effect (n.O.e.) (23,24). Irradiation of the *t*-butyl group gave a positive n.O.e. of 11 ± 2% for the low field vinylidene proton and negative n.O.e. of 3 ± 2% for the high field proton. This allows unambiguous assignment of the low field peak as H_C and the high field peak as H_B. This means that $\Delta\delta_0(B - C)$ has changed sign and now has a large negative value (−0.417 p.p.m.) for ATBS.

It is interesting to consider why this occurs. As shown in Table 5, δ_{H_C} is nearly constant while

δ_{H_B} moves continuously to low frequency (high field) on going from styrene to ATBS. It is known that the vinyl proton chemical shifts in styrene are not solely due to ring current effects (25). The CNDO/2 calculations indicate that differences in charge density for H_B and H_C contribute substantially to $\Delta\delta_0(B - C)$. Assuming an average scaling factor of 21 p.p.m./hydrogen 1s electron (1), then $\Delta\delta_0(B - C)$ for styrene and AMS are almost quantitatively predicted by a combination of ring current and charge density effects (Table 5). A somewhat larger error is found for ATBS although chemical shift trends are well reproduced, particularly for H_C. The large positive charge density for H_B in styrene (**3**) apparently is due to the steric interaction between H_B and H_2 since q_{H_B} decreases as ρ increases: Similarly, H_2 has a less negative charge (-18×10^{-4}) than H_6 (-54×10^{-4}) with q_{H_2} becoming more negative as ρ increases. By contrast, q_{H_C} is much less sensitive to ρ. Thus, there are apparently two electronic contributions to the high field shift of H_B on going from styrene to ATBS: (*1*) relief of steric hindrance and (*2*) the electron-releasing effect of the alkyl substituent (as evidenced by the additional negative contribution to q_{H_B} for the alkylstyrenes as compared to styrene for the same ρ). 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_{H_C} reflects a lesser sensitivity to both ring current and charge density effects. It is also possible that there is a van der Waals' or dispersion interaction (26) contributing to the low field shift of H_B in styrene. However, the results can be explained without invoking an effect of this kind.



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One final conclusion can be drawn from the above discussion and the data in Table 5: for a given styrene derivative, δ_{H_B} should be much more sensitive than δ_{H_C} to small changes in ρ.

(c) Interpretation of Substituent-induced Chemical Shifts

π-Conjugative effects should vary as $\cos^2\rho$ (27). Consequently, the expected weighting factors, *r*, for correlations of S.C.S. with *F* and *R* can be estimated from the observed values for styrene (1):

$$r_{\mathrm{HB}} = 0.414 \cos^2\rho \quad [4]$$

$$r_{\mathrm{HC}} = 0.420 \cos^2\rho \quad [5]$$

$$r_{\mathrm{C}\text{-}\alpha} = -0.35 \cos^2\rho \approx 0 \quad [6]$$

$$r_{\mathrm{C}\text{-}\beta} = 7.15 \cos^2\rho \quad [7]$$

It is more difficult to make predictions from the observed *f* values since they should reflect both through-space field effects and π polarization effects (1). As a first approximation it seemed reasonable to assume that the through-space field effect upon proton chemical shifts should be independent of ρ. To predict how π polarization effects vary with ρ it is necessary to determine the exact nature of these effects.

The $N(CH_3)_3^+$ group should have a large field effect and small resonance effect (zero according to Swain and Lupton (2)). Since σ inductive effects are unimportant (1), vinyl ^{13}C chemical shifts for $N(CH_3)_3^+$ derivatives should primarily reflect π inductive effects. Chemical shift data for $N(CH_3)_3^+$ derivatives of styrene and ATBS as well as charge densities for the styrene derivative at $\rho = 0$ and $\rho = 90°$ are given in Table 6. Comparison of π charge densities for $\rho = 90$ and $\rho = 0°$ suggests that there are two mechanisms of transmission of π inductive effects. For $\rho = 90°$, the phenyl and vinyl π electron systems appear to be independently polarized towards the positive group, leading to equal but opposite changes in π electron density for C-α and -β. This effect, which is probably transmitted through space, should be the only mechanism affecting the vinyl group for large values of ρ. For small values of ρ, the vinyl and phenyl groups are conjugated and the entire π electron system can be polarized. This additional polarization mechanism leads to electron transfer from the vinyl to the phenyl group with loss of electron density from C-β but little change in electron density for C-α. These two mechanisms can account for the *f* values obtained from the correlations of vinyl ^{13}C chemical shifts for 4-substituted styrenes with *F* and *R* (1). These correlations showed a small negative *f* value for C-α and a larger positive *f* value for C-β. The C-α and -β chemical shifts for $N(CH_3)_3^+$ derivatives of styrene and ATBS are also consistent with this interpretation of π

TABLE 6. (*a*) Calculated charge densities for 4-*N*,*N*,*N*-trimethylammoniostyrene at ρ = 0° and ρ = 90° (× 10^4, relative to styrene)

ρ	C-4	C-3,5	C-2,6	C-1	C-α	C-β
0°	+707* (−902)	−173 (−187)	+163 (+185)	+274 (+464)	−145 (−343)	+339 (+580)
90°	+737 (−840)	−185 (−212)	+201 (+257)	+238 (+447)	−116 (−360)	+231 (+413)

(*b*) Comparison of substituent-induced ^{13}C chemical shifts for *N*,*N*,*N*-trimethylammonio and *t*-butyl derivatives of styrene and α-*t*-butylstyrene in CD_3OD (in p.p.m. relative to parent styrenes)

Compound	Substituent	C-4	C-3,5	C-2,6	C-1	C-α	C-β
Styrene	$N(CH_3)_3^+$	+18.95	−7.90	+1.98	+2.42	−2.13	+3.90
	$C(CH_3)_3$	+22.69	−3.20	−0.18	−2.75	−0.26	−0.83
	Δ†	−3.74	−4.70	+2.16	+5.17	−1.87	+4.73
α-*t*-Butylstyrene	$N(CH_3)_3^+$	+18.60	−7.19	+2.08	+2.48	−1.82	+1.58
	$C(CH_3)_3$	+22.35	−3.22	−0.20	−2.84	−0.09	−0.13
	Δ	−3.75	−3.97	+2.28	+5.32	−1.73	+1.71

*Total charge density and (in brackets) π charge density.
†S.C.S. for $N(CH_3)_3^+$ derivative − S.C.S. for $C(CH_3)_3$ derivative.

polarization effects. Assuming a $\cos^2\rho$ dependence for the conjugative π polarization mechanism, this indicates that the residual through-space π polarization effect upon $\delta_{C\text{-}\beta}$ at ρ = 90° should be approximately 30% of the total π polarization effect at C-β for the planar styrene. By contrast, C-α is much less sensitive to ρ, as suggested by the calculations. Of the phenyl carbon chemical shifts, C-1 and -2,6 are consistent with the presence of a π polarization effect but C-3,5 and -4 apparently are not. However, the latter chemical shifts are likely to reflect structural effects similar to the α and β effects for linear hydrocarbons (28).[3] Since the $N(CH_3)_3^+$ group is isoelectronic with the $C(CH_3)_3$ group and similar in size, a comparison of chemical shifts for these pairs of styrene derivatives should minimize if not completely eliminate structural effects. The chemical shift differences should then reflect the effect of the positive charge on the $N(CH_3)_3^+$ group. As seen in Table 6, these chemical shift differences indicate a strong π polarization effect (the relatively small shift for C-4 may be due to the counteracting σ inductive effect of the $N(CH_3)_3^+$ group). This is a particularly interesting observation since π polarization effects are usually regarded as unimportant (32). However, we have obtained corroboratory evidence for π polarization effects from the ^{13}C chemical shifts of a large number of phenylalkane derivatives (31). In addition, ^{13}C chemical shift data and π charge densities for *trans*-1-substituted 1,3-butadienes indicate that π polarization effects are important in these derivatives (33).

The evidence presented above concerning the nature of π polarization effects can be used to predict f values for δ_{H_B}, δ_{H_C}, and $\delta_{C\text{-}\beta}$ as a function of ρ. Total f values for H_B and H_C of styrene are respectively 0.100 and 0.166 with estimated through-space field components of −0.007 and 0.060 and π polarization components of 0.107 and 0.106 (1). Assuming that 30% of the π polarization effect remains at ρ = 90° (see above) and that the field effect is independent of ρ:

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[3] The exact nature of these effects is still unclear (29) although it has been suggested that the α effect may be due to contributions to the diamagnetic and paramagnetic terms in the chemical shift equation arising from the electron distribution on the α substituent (29, 30). In any case, it appears improbable that the α and β effects will be totally reflected by changes in the ground state charge density at the carbon in question. γ-Effects were also noted for hydrocarbons (28). However, these effects apparently reflect *gauche* steric interactions (29) and should be insignificant in the case of C-2,6 S.C.S. since these carbons are *trans* to the substituent. The validity of correlating ^{13}C S.C.S. due to more remote substituents with ground state charge densities is discussed in detail elsewhere (31).

TABLE 7. Correlations of ^1H and ^{13}C S.C.S. (in p.p.m.) for styrene, α-methylstyrene (AMS) and α-*t*-butylstyrene (ATBS) derivatives with *F* and *R*

Compound	δ	*f**	*r**	S.D.†	*r*‡
(*a*) ^1H S.C.S.					
Styrene	H_B	$+0.100 \pm 0.011$	$+0.414 \pm 0.014$	0.012	0.996
	H_C	$+0.166 \pm 0.010$	$+0.420 \pm 0.014$	0.012	0.997
	$H_B - H_C$	-0.067 ± 0.002	—	0.002	0.997
AMS	H_B	$+0.094 \pm 0.011$ $(+0.08)$§	$+0.234 \pm 0.020$ $(+0.31)$	0.014	0.987
	H_C	$+0.140 \pm 0.008$ $(+0.15)$	$+0.313 \pm 0.013$ $(+0.32)$	0.010	0.997
	$H_B - H_C$	-0.046 ± 0.007 (-0.07)	-0.079 ± 0.011 (0)	0.008	0.977
ATBS	H_B	$+0.044 \pm 0.010$ $(+0.04)$	$+0.055 \pm 0.016$ $(+0.08)$	0.009	0.974
	H_C	$+0.077 \pm 0.008$ $(+0.11)$	$+0.104 \pm 0.014$ $(+0.08)$	0.008	0.995
	$H_B - H_C$	-0.032 ± 0.003 (-0.07)	-0.049 ± 0.006 (0)	0.004	0.994
(*b*) ^{13}C S.C.S.					
Styrene	C-2,6	$+0.89 \pm 0.17$	-1.90 ± 0.32	0.34	0.898
	C-1	$+2.98 \pm 0.37$	$+15.78 \pm 0.69$	0.73	0.985
	C-α	-1.30 ± 0.07	-0.35 ± 0.13	0.15	0.974
	C-β	$+2.82 \pm 0.15$	$+7.15 \pm 0.27$	0.29	0.991
AMS	C-1	$+3.11 \pm 0.29$	$+18.03 \pm 0.58$	0.43	0.996
	C-α	-1.02 ± 0.13 (≈ -1.3)	$+0.44 \pm 0.25$ (≈ 0)	0.20	0.947
	C-β	$+2.32 \pm 0.09$ $(+2.3)$	$+5.88 \pm 0.19$ $(+5.4)$	0.15	0.997
ATBS	C-1	$+3.03 \pm 0.31$	$+18.79 \pm 0.62$	0.41	0.997
	C-α	-1.18 ± 0.10 (≈ -1.3)	-0.14 ± 0.20 (≈ 0)	0.13	0.980
	C-β	$+1.04 \pm 0.05$ $(+1.2)$	$+0.57 \pm 0.10$ $(+1.4)$	0.07	0.994

*Weighting coefficients for equation $\delta = fF + rR + \delta_0$.
†Standard deviation between calculated and observed chemical shifts (in p.p.m.).
‡Correlation coefficient.
§Values for *f* and *r* estimated from **eqs.** 4–10 (in brackets).

$$[8] \quad f_{H_B} = -0.007 + 0.107\,(0.30 + 0.70 \times \cos^2\rho) = +0.025 + 0.075 \cos^2\rho$$

$$[9] \quad f_{H_C} = +0.060 + 0.106\,(0.30 + 0.70 \times \cos^2\rho) = +0.092 + 0.074 \cos^2\rho$$

$\delta_{C\text{-}\beta}$ should only reflect π polarization effects and resonance effects. Since $f_{C\text{-}\beta}$ for styrene $= +2.82$;

$$[10] \quad f_{C\text{-}\beta} = +2.82\,(0.30 + 0.70 \cos^2\rho) = +0.85 + 1.97 \cos^2\rho$$

By contrast, both calculations and chemical shift data for $N(CH_3)_3{}^+$ derivatives suggest that $f_{C\text{-}\alpha}$ should be nearly independent of ρ. While eqs. 4–10 appear complex, they are based on a very simple model for mechanisms of transmission of substituent effects, *i.e.*, that any conjugative interaction should vary as $\cos^2\rho$.

Results of correlations of ^1H and ^{13}C chemical shifts with *F* and *R* are summarized in Table 7. Halogens were excluded from the ^1H correlations but included in the ^{13}C correlations for reasons discussed in the previous paper (1). Previously determined *F* and *R* values were used for the $N(CH_3)_2$, $Sn(CH_3)_3$, and $Si(CH_3)_3$ groups (1) with other values taken from the original tabulation (2).

The *f* and *r* values predicted from eqs. 4–8 are also given in Table 7. In the case of ^{13}C correlations, there is a generally good agreement between predicted and observed *f* and *r* values. In particular the *f* values are entirely consistent

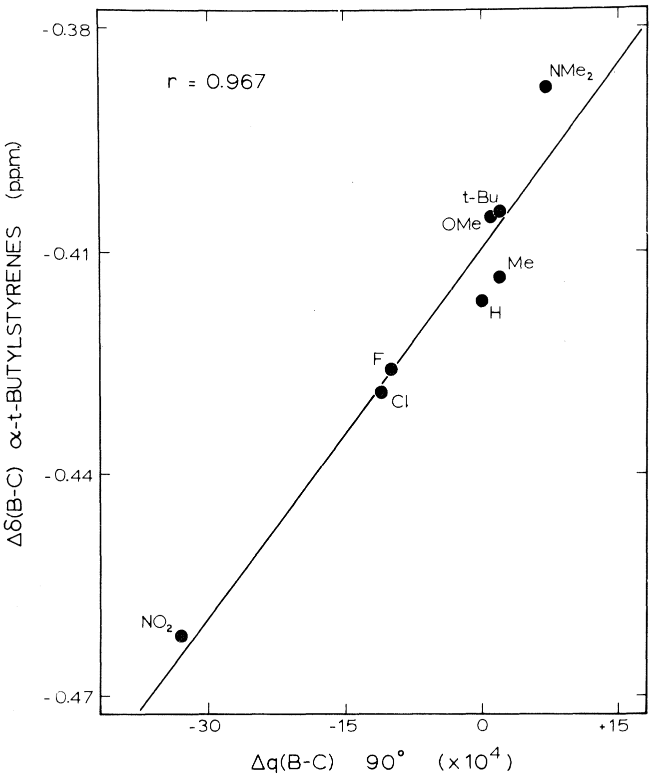


FIG. 1. Correlation of the β proton chemical shift difference, $\Delta\delta(B - C)$ of ATBS derivatives with the difference in charge density for the β protons of styrene derivatives (relative to styrene with $\rho = 90°$).

with the postulated nature of π polarization effects. The signs and magnitudes of the f values for C-2,6 and -1 are also consistent with phenyl group π polarization while the r values are consistent with normal pictures of resonance interactions (the increase in r with ρ for C-1 is logical since the resonance effect should be isolated in the phenyl group as conjugation between phenyl and vinyl groups decreases). No correlations were performed for C-3,5 and -4 because these chemical shifts are likely to be affected by structural effects. The ^{1}H chemical shift correlations also show good agreement between predicted f and r values. However, it appears that f for δ_{H_C} and r for δ_{H_B} both decrease more rapidly than predicted by eqs. 9 and 4. Consequently, $\Delta\delta(B - C)$ for AMS and ATBS derivatives depends upon both F and R with a smaller field dependence for $\Delta\delta(B - C)$ than in the case of styrene (1).

While the ^{1}H S.C.S. for H_B and H_C do not precisely follow the predictions based upon the model of electronic substituent effects outlined above, charge densities determined by the CNDO/2 calculations indicate a probable electronic origin for the deviations. For planar 4-substituted styrenes, $\Delta(\equiv q_{H_B} - q_{H_C}$, relative to styrene) is linearly related to F:

$$[11] \quad \Delta(0°) = -(33 \pm 4) \times 10^{-4}F$$

with a statistically insignificant dependence on R. On the other hand, when $\rho = 90°$, Δ depends upon both F and R:

$$[12] \quad \Delta(90°) = -(20 \pm 3) \times 10^{-4}F - (17 \pm 4) \times 10^{-4}R$$

Thus it is seen that both the decreased field dependence and the negative resonance dependence of $\Delta\delta(B - C)$ on going from styrene to non-planar α-alkylstyrenes are reproduced by the CNDO/2 calculations. This has been further confirmed by plotting $\Delta\delta(B - C)$ for ATBS *vs.* Δ(90°) (Fig. 1). There is a good correlation (better than for styrene (1)) and the slope of 17 p.p.m./hydrogen 1s electron is consistent with previously suggested scaling factors for proton chemical shifts (34, 35). While the good

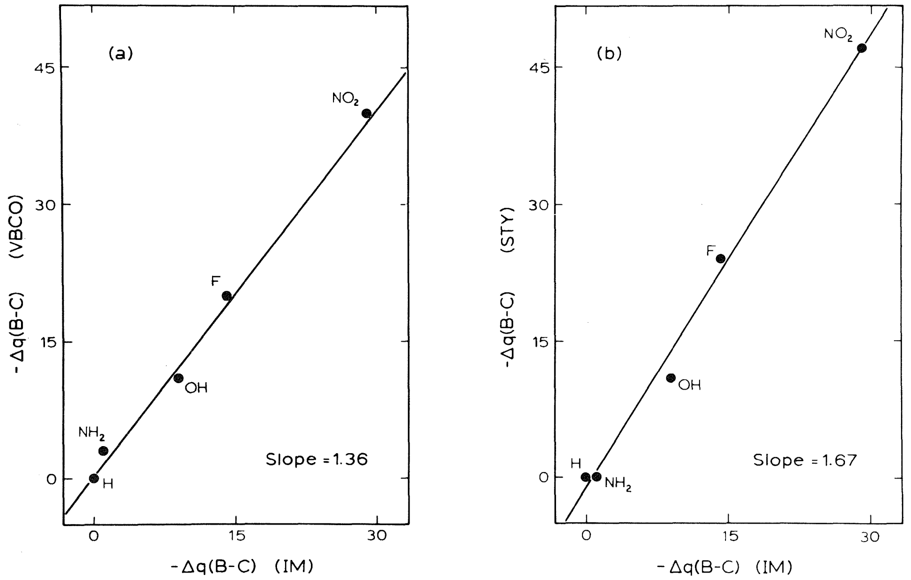


FIG. 2. Plots of differences in charge densities for H_B and H_C of (*a*) 4-substituted 1-vinylbicyclo[2.2.2]octanes (VBCO) and (*b*) 4-substituted styrenes (STY), both plotted against the corresponding difference in ethylene proton charge density for CH_3X—C_2H_4 pairs of molecules (IM).

correlation may be partly fortuitous since the calculations were carried out for styrene at 90° rather than ATBS at 64°, it is highly improbable that the agreement could be completely accidental. In addition, plots of $q_{H(90°)}$ *vs.* $q_{H(0°)}$ for each proton (not shown) revealed a linear plot for H_C while the plot for H_B was irregular, particularly for groups with large R values. This supports the conclusion from the F and R correlations that there is an unexpected resonance contribution to δ_{H_B}.

Thus the CNDO/2 calculations for 4-substituted styrenes with $\rho = 90°$ provide evidence for electronic effects which can apparently account for all deviations between predicted and observed f and r values for AMS and ATBS derivatives. In addition, CNDO/2 calculations for 4-substituted 1-vinylbicyclo[2.2.2]octanes (VBCO) and ethylene–CH_3X pairs (oriented so that the C—X bond and the ethylene group are in an identical orientation to the C—X bond and the vinyl group in VBCO) (1) provide a possible explanation for the reduced field dependence of δ_{H_B} and $\Delta\delta(B - C)$ on going from styrene to AMS to ATBS. These calculations indicate that the field effect of the substituent (as measured by Δ) strongly depends upon the nature of the intervening molecular framework (see Fig. 2). The field effect of the substituent should vary inversely as the effective dielectric constant within the cavity (36) where ε_{eff} is a function of both the molecule and the surrounding medium. Hermann (37) has calculated that ε_{eff} for 4-substituted bicyclo[2.2.2]octane carboxylic acids in vacuum is less than unity (0.73). This corresponds to an enhancement of the field effect by 1.37, in exact agreement with the calculated enhanced field effect for VBCO derivatives relative to CH_3X–ethylene pairs. The field effect is apparently even larger for styrene where the field acts in the nodal plane of the phenyl π system, *i.e.* in a cavity inside a polarizable system. It is entirely conceivable that ε_{eff} is increased by rotating the vinyl group so that the field no longer acts through the cavity formed by the phenyl π electron system. An increased ε_{eff} would lead to a decreased field effect. This would primarily effect the f coefficient for δ_{H_C}, as observed.

Previous experimental investigations (1, 38, 39) of field effects upon proton chemical shifts provide support for the suggestion that the A constant in the Buckingham equation (40) depends upon the system (see Table 8). Calculated A values are based upon Musher's calculated value of 3.1×10^{-12} for the effect of an isolated dipole upon a C—H bond (39) and the proportionality factors shown in Fig. 2. An experimental investigation of 1-vinylbicyclo[2.2.2]octane derivatives has been undertaken in an attempt to confirm this point.

TABLE 8. Comparison of observed and calculated values of A constant in the Buckingham equation for various systems

	$A(\times 10^{12})$	
System	Observed	Calculated
CH bond in gas phase	2.9*	3.1§
CH bond in alicyclic compounds	4.2†	4.2‖
CH bond in aromatic compounds	4.6–6.5‡	5.5‖

*Estimated from CHF_3 in gas phase (43).

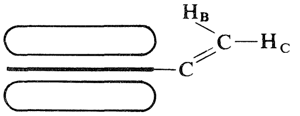
†Estimated from S.C.S. for steroids (38) (field evaluated at the proton).

‡Estimated from S.C.S. for 4-substituted styrenes (1) (field evaluated at the proton).

§Calculated value for isolated C—H bond in gas phase (39).

‖Calculated values for 4-substituted 1-vinylbicyclo[2.2.2]octanes and styrenes, using $A = 3.1 \times 10^{-12}$ for a C—H bond in the gas phase and the slopes of the plots of Δ for these compounds *vs.* Δ for C_2H_4–CH_3X pairs (Fig. 2).

The CNDO/2 calculations strongly suggest that the smaller than predicted R dependence of δ_{H_B} for AMS and ATBS derivatives is, at least in part, due to electronic interactions. Since there is no apparent reason why conjugative interactions should affect δ_{H_B} and δ_{H_C} differently, the small r values apparently reflect some additional negative resonance contribution to δ_{H_B}, *i.e.* a contribution by which electron-withdrawing $(+R)$ groups cause high field shifts while $-R$ groups cause low field shifts. This is unexpected and the nature of the electronic effect is unclear to us. However, it is possible that it may be associated with an interaction of the C_α—C_β—H_B σ bond system with the phenyl π electron system. C_β—H_C would be much less likely to interact with the π electron system.



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While the CNDO/2 calculations indicate that S.C.S. for the vinyl protons of AMS and ATBS derivatives are primarily due to electronic effects, one substituent effect which is primarily magnetic in origin may also be present. This is associated with substituent-induced changes in the dihedral angle ρ. The vinyl group can either accept or donate electrons by resonance. Therefore any substituent with a significant resonance effect should increase the conjugation between phenyl and vinyl groups. This is supported by CNDO/2 calculations since the calculated C_1—C_α bond order is greater for both 4-*N*,*N*-dimethylaminostyrene (0.2949) and 4-nitrostyrene (0.2952) than for styrene (0.2919).

As shown in Table 5, δ_{H_B} is much more sensitive than δ_{H_C} to changes in ρ, primarily due to changes in ring current effect. Since δ_{H_B} increases with decreasing ρ, substituent-induced changes in ρ should be reflected by a positive dependence of δ_{H_B} and $\Delta\delta(B - C)$ on $|R|$ (since both $+R$ and $-R$ substituents should decrease ρ).[4] Since all substituents had either $-R$ effects or very small $+R$ effects, this is difficult to distinguish from the observed negative R dependence (*i.e.* $-R \approx +|R|$). Based on the data from Table 5, the predicted angular dependence of δ_{H_B} at $\rho = 30°$ is approximately -0.01 p.p.m./degree. Thus the additional resonance contribution to δ_{H_B} could arise from very small changes in ρ, probably not exceeding 5°. This does not appear unreasonable.

There is conflicting evidence for the existence of a magnetic effect due to changes in ρ. 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 AMS than for ATBS, whereas a purely electronic effect might be expected to have a maximum for $\rho = 90°$. 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.

In conclusion, correlations of vinyl ^1H and ^{13}C S.C.S. for AMS and ATBS derivatives with F and R give f and r values which are in good agreement with values predicted from experimental results for styrenes and a model for transmission of substituent effects which assumes a $\cos^2\rho$ dependence for transmission of any conjugative interaction. In cases where discrepancies are observed between calculated and observed f and r values, CNDO/2 calculations indicate that the deviations are primarily due to unanticipated electronic interactions, although one possible magnetic effect is postulated. Since the ^1H and ^{13}C chemical shifts and CNDO/2 charge densities all reflect similar trends in substituent effects and since the variation of f and r with ρ is in overall good agreement with a simple model of substituent effects, we conclude that the F and R

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[4] This effect is completely different from a substituent-induced decrease in the total ring current effect of the phenyl group (38). The latter effect, which should have a *negative* $|R|$ dependence, is not important in 4-substituted styrenes (1) and therefore is unlikely to be important here.

correlations reflect electronic effects for these compounds and can be used to deduce mechanisms of transmission of substituent effects. As in the case of 4-substituted styrenes (1), the three main mechanisms of transmission of substituent effects are through-space field effects, resonance or mesomeric effects and π polarization effects. The magnitude of the field effect appears to depend upon the nature of the intervening molecular framework. Both CNDO/2 calculations and vinyl and phenyl ^{13}C chemical shifts suggest that the π polarization effect can be divided into two effects. When there is no conjugation between phenyl and vinyl groups ($\rho = 90°$) the two groups are independently polarized by the substituent (presumably acting through space) but for $\rho < 90°$ an additional polarization of the entire conjugated styrene π electron system can occur. The observation of π polarization effects is particularly important since these effects have often been considered to be unimportant.

Our conclusion that the correlations of S.C.S. for styrene derivatives with *F* and *R* reflect intramolecular electronic effects in these compounds is contradictory to the conclusion of Miller and Wiley based on S.C.S. for other systems (4). We have reinvestigated some of the systems on which the latter conclusions were based. This is the subject of the following paper.

W.F.R. thanks the National Research Council of Canada for financial support. I.R.P. thanks Gulf Oil Canada Ltd. for a Fellowship.

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