togram and the experimental conditions are shown in Figure 4. The fraction indicated by the vertical marks (a colorless, air-sensitive liquid) was found to be the desired triene XVII, $n^{25}D$ 1.5292; the ultraviolet and nmr spectra are reported under Results. The infrared spectrum shows three distinctive peaks at 900, 960, and 985 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.01; H, 12.00.

Recovery Experiments. An approximate 8% w/v solution (0.857 g in 10 ml of 96% sulfuric acid) of the carbonium ion "pair" V–VI was prepared and decomposed (30 g of potassium hydroxide, 200 ml of ice-water, 50 ml of ether, more ice as addition proceeds) as previously described.[18,19] There was recovered 0.613 g (72%) of product, bp 82–85° (9 mm). The product is virtually identical in composition with that formed from the dehydration of the alcohol XX (nmr analysis). When put back into sulfuric acid the ions V–VI were again formed.

Area Calculations. The nmr peaks used to calculate the relative amounts of each isomer in the ions I–II, III–IV, and V–VI are essentially the same as those for the corresponding trialkyl ions, reported in the Appendix of part I.[1] For VII–VIII, the higher field isopropyl doublet was used to calculate the relative amount of isomer VIII. This area multiplied by two (the remaining isopropyl methyl group and the methyl part of the ethyl group) was subtracted from the rest of the area in the τ 8.4–9.3 region; the remainder represents the nine protons of isomer VII. In this analysis, one of the ions (VII) is obtained by difference and the experimental error is certainly larger than in the other ion "pairs." For IX–X, the relative amounts of the two isomers were calculated directly from the areas of the respective C2 methyl groups. Some rough resolution (hand estimated) of these peaks was necessary in the low-temperature spectra and even a minor amount in the higher temperature spectra.

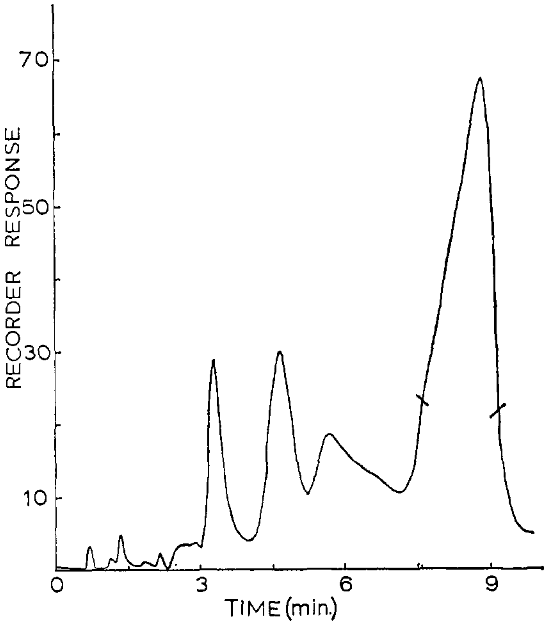

Figure 4. The preparative vapor phase chromatogram of the fraction used to isolate the triene XVII: column, 145°, collector, 165°, injector, 230°, He flow rate *ca.* 200 cc/min, injector sample, *ca.* 0.15 ml.

Acknowledgments. The author wishes to thank the National Research Council of Canada and the Petroleum Research Fund for financial support. The author is also grateful for the technical assistance provided by Mrs. V. Boon and Mr. P. Campbell.

A Nuclear Magnetic Resonance Study of Transmission of Electronic Effects. Ethylbenzenes, Dihydrocinnamic Acids, and *cis*- and *trans*-Cinnamic Acids[1]

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Abstract: The proton magnetic resonance spectra of a series of *meta*- and *para*-substituted styrenes, ethylbenzenes, dihydrocinnamic acids, and *cis*- and *trans*-cinnamic acids have been determined in acetone solution. Based on analysis of the β-hydrogens of the styrenes, it is concluded that perturbations in their chemical shifts are caused mainly by inductive and resonance effects rather than by electric and magnetic field effects. Comparison of internal chemical shifts in the various acid series to those in the styrenes and ethylbenzenes reveals that *trans*-cinnamic acids show marked conjugation when substituted with electron-releasing groups, that the side chains of *cis*-cinnamic acids are sufficiently twisted out of coplanarity with the phenyl ring as to markedly dampen conjugation, and that electronic effects can be effectively transmitted from the phenyl ring to the β-carboxyl group of the dihydrocinnamic acids through solvent.

Numerous papers have appeared in the past few years dealing with the origin of the chemical shift. Attempts have been made to relate it to specific substituent properties such as electronegativity[3] or dipole moment[4] as well as to correlate it with more general expressions of substituent ability to affect electronic density such as, for example, the well-known

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(1) Taken in part from the Ph.D. dissertation of T. A. Wittstruck.

(2) National Science Foundation Cooperative Fellow, 1964–1965.

(3) (a) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951); (b) H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952); (c) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953); (d) J. N. Shoolery, *J. Chem. Phys.*, **21**, 1899 (1953); (e) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955); (f) A. L. Allred and E. G. Rochow, *ibid.*, **79**, 5361 (1961); (g) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961); (h) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 722 (1961); (i) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963); (j) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962).

(4) (a) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958); (b) S. Reddy, J. H. Goldstein, and L. Mandell, *ibid.*, **83**, 1300 (1961).

Table I. Chemical Shifts of Side-Chain Hydrogens, in cps from Tetramethylsilane; Solvent, Acetone

	Styrenes			Ethylbenzenes		Dihydrocinnamic acids		Cinnamic acids			
								cis		trans	
Substit	$H_{\beta\text{-}t}$	$H_{\beta\text{-}c}$	H_α	H_β	H_α	H_β	H_α	$H_{\beta\text{-}t}$	H_α	$H_{\beta\text{-}c}$	H_α
p-OCH_3	304.4	336.8	401.8	69.5	153.9	153.0	170.4	350.6	412.0	382.9	458.5
p-CH_3	308.6	342.1	403.5	69.5	155.2	155.2	172.4	355.5	415.3	388.1	458.9
m-CH_3	311.5	345.0	404.0	71.6	155.4	...	...	357.1	415.1	390.0	459.3
None	313.6	347.3	407.6	72.2	156.4	155.2	174.0	359.8	418.0	392.6	460.8
p-Cl	316.8	348.5	407.3	72.0	160.0	155.6	172.6	362.0	419.5	393.3	460.3
m-Cl	318.3	351.3	406.4	...	...	...	...	363.9	417.1	397.5	460.0
m-CF_3	...	...	...	...	...	...	...	367.6	427.2	401.3	465.9
p-CF_3	...	...	...	...	...	...	...	...	...	401.7	465.1
m-CN	...	...	...	...	...	...	...	...	...	400.9	462.5
p-CN	...	...	...	...	...	...	...	...	...	402.0	463.2
m-NO_2	327.5	360.1	417.5	...	...	...	...	372.4	431.2	404.6	468.4
p-NO_2	330.7	363.0	416.9	75.0	168.4	162.2	183.0	378.5	433.7	...	...

Hammett σ constants and variations thereof.[5] Explanations invoking either magnetic[6] or electric field effects[7] arising in a substituent have been advanced. Outside of the fact that there is clear consensus that the chemical shift is dependent on the electronic properties of the molecule, there does not seem to be any general agreement as to the exact nature of this dependence.

The field theories of the chemical shift all involve a steric relationship between the substituent, X, or its bond, C–X, and the proton under consideration. For electric fields, the field at the proton is given by

$$E = \frac{\mu(1 + 3\cos^2\theta)^{1/2}}{r^3} \qquad (1)$$

where μ is the electric dipole moment giving rise to the field (usually considered to be that of the C–X group), r is the distance between the locus of the dipole and the proton, and θ is the angle between r and μ. The component along the C–H bond, E_Z, is given by

$$E_Z = E\cos\varphi \qquad (2)$$

where φ is the angle between the vector E and the C–H bond. Buckingham[7a] has given the relationship between the shielding arising from the electric field, σ_E, and the electric field as

$$\sigma_E = -2 \times 10^{-12}E_Z - 10^{-18}E^2 \qquad (3)$$

whereas Musher[7b] has proposed a slightly different relationship

$$\sigma_E = -2.9 \times 10^{-12}E_Z - 7.3 \times 10^{-19}E^2 \qquad (4)$$

The electric field of a polar substituent acting across space will thus either shield or deshield the protons of a molecule and hence give rise to a chemical shift. Buckingham also includes in his treatment additional shielding or deshielding arising from solvent orientation by the substituent dipole.[7c]

For magnetic fields, if they are anisotropic, McConnell[6a] has shown that the shielding, σ_M, is approximated by

$$\sigma_M = \sum_g[\Delta\chi_g(1 - 3\cos^2\theta_g)/3r_g^3] \qquad (5)$$

where $\Delta\chi_g$ is the anisotropy in the magnetic susceptibility of the gth bond, r_g is the distance between the proton and that bond, and θ_g is the angle between r_g and the bond axis.

Both of these theories involve steric parameters, and thus the chemical shifts predicted by their application are strongly dependent upon the relative orientation between the protons and the substituent. Although invoked in many cases to rationalize chemical shifts, they have not always proved adequate.[8]

Another approach which has met with widespread use for explaining chemical shifts not only of protons but also of carbon[5m] and fluorine[3a–c,5b–g] involves correlation with Hammett σ or similar substituent constants. Although there are some exceptions, excellent correlations have been found in many cases involving both proton and fluorine chemical shifts. However, it is not obvious why the chemical shift should be a linear function of the σ constant, and there is no agreement as to which factors of σ are affecting the chemical shift.[9]

In the present problem, we wished to investigate whether nmr chemical shifts could be used to evaluate the effectiveness of transmission of conjugative effects. Because of the general uncertainty indicated above, it was decided to examine first the nmr spectra of a series of *meta-* and *para*-substituted ethylbenzenes, styrenes, *cis-* and *trans*-cinnamic acids, and dihydrocinnamic acids, in which the conjugative properties are fairly well understood.[10]

Results and Discussion

The chemical shifts in cps from tetramethylsilane at 60 Mcps are given in Table I. All the spectra are

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(5) (a) K. L. Williamson, N. C. Jacobus, and K. T. Soucy, *J. Am. Chem. Soc.*, **86**, 4021 (1964); (b) R. W. Taft, *ibid.*, **79**, 1045 (1957); (c) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 3146 (1963); (d) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 709 (1963); (e) R. W. Taft and L. D. McKeever, *ibid.*, **87**, 2489 (1965); (f) G. E. Maciel, *ibid.*, **86**, 1269 (1964); (g) M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 3318 (1966); (h) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964); (i) P. L. Corio and B. P. Dailey, *ibid.*, **78**, 3043 (1956); (j) C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962); (k) R. E. Klinck and J. B. Stothers, *ibid.*, **40**, 1071 (1962); (l) S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966); (m) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); (n) R. O. Kan, *J. Am. Chem. Soc.*, **86**, 5180 (1964).

(6) (a) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957); (b) J. I. Musher, *ibid.*, **35**, 1159 (1961); (c) P. T. Narasimhan and M. T. Rogers, *J. Phys. Chem.*, **63**, 1388 (1959); (d) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961); (e) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 731 (1961); (f) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

(7) (a) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960); (b) J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962); (c) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *ibid.*, **32**, 1227 (1960); (d) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

(8) (a) R. F. Fraser, *Can. J. Chem.*, **38**, 2226 (1960); (b) W. G. Paterson and N. R. Tipman, *ibid.*, **40**, 2122 (1962); (c) C. D. Cook and S. S. Danyluk, *Tetrahedron*, **19**, 177 (1963).

(9) Many of the references cited previously are pertinent; there are too many to list, but two very recent papers with lead references are ref. 3g and 3l.

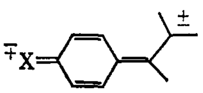
(10) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

determined in acetone (and in some cases repeated in deuteriochloroform and deuterioacetone) and the results extrapolated to infinite dilution. Acetone was used as the solvent because some of the cinnamic acids are not sufficiently soluble in chloroform to obtain good spectra. The data in Table I are for the side-chain protons only, designated according to Figure 1.

The chemical shifts of the side-chain hydrogens are determined primarily by their proximity to the aromatic ring. Because of the anisotropy in the magnetic susceptibility of the phenyl ring, protons lying in the plane of the ring experience maximum deshielding. This is predicted to decrease as the protons are located further above or below the plane; at some point this effect will reverse so that protons located directly above the center of the ring should be maximally shielded. According to eq 5, this effect decreases inversely with the cube of the distance from the center of the ring.

In all cases investigated here, the multiplets of the hydrogens on the carbon α to the phenyl ring are further downfield from those of the β-hydrogens. The spectra for the ethylbenzenes show quartets for the methylene protons and triplets for the methyl protons, indicating free rotation about the C–C bond. The styrene side-chain protons each give quartets; their assignments are based on the observed coupling constants. It is known that vicinal coupling of vinylic protons is greater between *trans* than between *cis* protons.[11] In the styrenes, this requires that $J(H_\alpha\text{–}H_{\beta\text{-}c}) > J(H_\alpha\text{–}H_{\beta\text{-}t})$. The geminal coupling, between $H_{\beta\text{-}c}$ and $H_{\beta\text{-}t}$, should yield the smallest constant. The assignments for the cinnamic acids are straightforward since in these cases only two side-chain hydrogens are involved. The lower field doublet in each case is assigned to H_α. The spectra for the dihydrocinnamic acids are those of an A_2B_2 system under the classification system of Pople.[12] In this particular case, $J = J'$, so that the chemical shifts of the α- and β-hydrogens may be obtained directly from the spectra.

The chemical shifts of the side-chain hydrogens for several *para*-substituted ethylbenzenes have previously been reported by Williamson[5a] who interpreted his data as indicating that the substituent effect decreases as the number of intervening bonds increases, in agreement with the present findings. Carbon-13 magnetic resonance spectra of *meta*- and *para*-substituted styrenes have been interpreted as reflecting changes in electron density at the β-carbon.[13] Contributions to the ground-state structure of the styrenes can include canonical forms such as



whereas these would not be present in the ethylbenzenes. Katritzky and Swinbourne[14] reported data for several *trans*-cinnamic acids. Plotting the chemical shifts for the side-chain hydrogens *vs.* Hammett σ constants, they found a good correlation for the β-protons but a less satisfactory one for the α-protons.

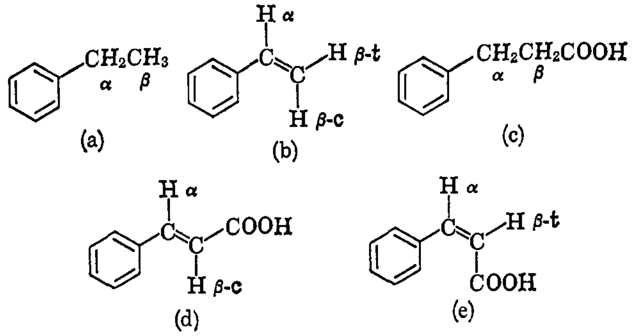


Figure 1. Designation of side-chain hydrogens for (a) ethylbenzene, (b) styrene, (c) dihydrocinnamic acid, (d) *trans*-cinnamic acid, and (e) *cis*-cinnamic acid.

Throughout any given series of compounds used in this study, the only variable is that of the substituent attached to the phenyl ring in the *meta* or *para* position relative to the side chain. The rest of the molecule and the solvent remain unchanged. Hence, the difference between the chemical shifts of the side-chain hydrogens of the substituted and unsubstituted compounds can be considered as arising solely from the effects of the substituent. To the extent that any substituent interacts with the solvent, its effect will be modified. The substituent effect is, therefore, either that due to the group itself or some solvent-induced modification of it.

Several difficulties are encountered in attempting to estimate directly the contribution of the chemical shift arising from the field effects of the substituents. The most critical, perhaps, is choice of the locus of the dipole, since this will govern the geometric factors found in eq 1 and 5. Serious problems arise in selecting values for the electric dipole moment, μ, in eq 1. Group moments might be used, or the dipole moment of the entire molecule might be chosen. There is also uncertainty as to the effective dielectric constant and as to the dependence on distance, especially when the dimensions of the dipole become comparable to its distance from the proton under investigation.[5g] There are also difficulties in evaluating $\Delta\chi_q$ in eq 5. Published values are very scarce, and those that are available show a rather wide range. For instance, values for the C–C bond have been reported as ranging from 2.2×10^{-30} to 16.7×10^{-30} cm/molecule^{-1}.[15]

One approximation for expressing the chemical shift, $\delta(i)$, of a proton, H(i), is to assume that it consists of several additive factors

$$\delta(i) = \delta^0(i) + \sum_j[\Delta\delta_j^{I}(i) + \Delta\delta_j^{R}(i) + \Delta\delta_j^{F}(i) + \Delta\delta_j^{M}(i)] \tag{6}$$

where $\delta^0(i)$ is the chemical shift of H(i) in some unsubstituted, symmetrical "parent" compound, and the summation is over j different substituents interacting through inductive (I), resonance (R), electric field (F), and magnetic field (M) effects. For example, styrene

[11] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd, London, 1959, p 85.

[12] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 144.

[13] K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **43**, 510 (1965).

[14] A. R. Katritzky and F. J. Swinbourne, *J. Chem. Soc.*, 6707 (1965).

[15] (a) J. Guy and J. Tillieu, *J. Chem. Phys.*, **24**, 1117 (1956); (b) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958); (c) P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **31**, 1302 (1959); (d) J. I. Musher, *ibid.*, **35**, 1159 (1961); (e) S. Reddy and J. H. Goldstein, *ibid.*, **38**, 2736 (1963).

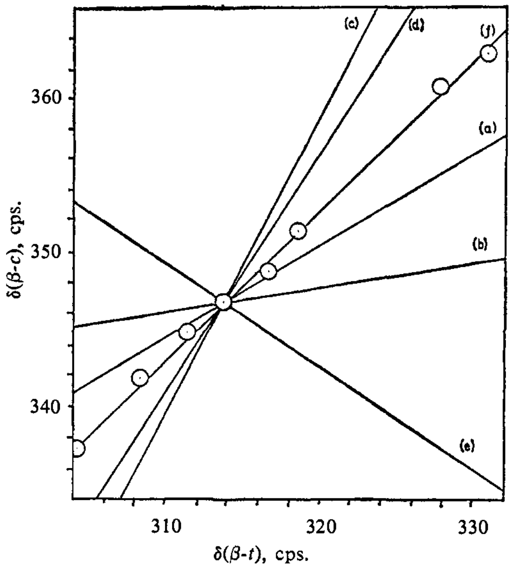


Figure 2. Chemical shifts of $H_{\beta\text{-}c}$ *vs.* $H_{\beta\text{-}t}$ for styrenes. The circles represent the observed values. Lines a–b are calculated for electric field effects of substituents in *meta* and *para* positions (slopes: 0.57 and 0.14); lines c–e for magnetic field effects (slopes: *meta–trans*, −0.68; *meta–cis*, 1.89; *para*, 1.54). Line f is calculated assuming no effect of electric and magnetic fields (slope, 1.00).

can be considered to be composed of ethylene to which a substituent phenyl ring is attached. Thus, $\delta^0(i)$ is the chemical shift of a proton on ethylene itself, $\Delta\delta_\varphi{}^{\mathrm{I}}$ is the perturbation in the chemical shift caused by the phenyl ring and transmitted inductively through the bonds separating the proton from the ring, $\Delta\delta_\varphi{}^{\mathrm{R}}$ is the change in chemical shift caused by the resonance effect of the phenyl ring, etc. For substituted styrenes, additional terms of the same type but reflecting the effects of the phenyl substituents must be included.

For two hydrogens, H(1) and H(2), *on the same carbon atom*, the perturbations involving either inductive or resonance effects will have the same value, but this will not, in general, be true of the electric and magnetic field effects. In these, there is a steric relationship between the substituent and the proton such that $\Delta\delta(1) \neq \Delta\delta(2)$. These two terms may be related, however, as

$$\Delta\delta_j{}^{\mathrm{F}}(2) = G_j{}^{\mathrm{F}}\Delta\delta_j{}^{\mathrm{F}}(1) \qquad (7)$$

where $G_j{}^{\mathrm{F}}$ is the geometric factor between H(2) and H(1) and the *j*th substituent for an electric field effect. A similar expression will obtain for the $\Delta\delta_j{}^{\mathrm{M}}$ terms, where the geometric factor will be given from eq 5 as

$$G_j{}^{\mathrm{M}} = \frac{(1 - 3\cos^2\theta_2)r_1{}^3}{(1 - 3\cos^2\theta_1)r_2{}^3} \qquad (8)$$

These geometric factors must be evaluated for each substituent and, of course, will be different generally for substituents located in different positions relative to the protons under consideration. Application of eq 6 to hydrogens on the same carbon atom shows that

$$\delta(2) = \delta(1) + \sum_j[(G_j{}^{\mathrm{F}} - 1)\Delta\delta_j{}^{\mathrm{F}}(1) + (G_j{}^{\mathrm{M}} - 1)\Delta\delta_j{}^{\mathrm{M}}(1)] \qquad (9)$$

Differentiating both sides of (9) with respect to δ(1) gives

$$\frac{\mathrm{d}\delta(2)}{\mathrm{d}\delta(1)} = 1 + \sum_j\left[\Delta\delta_j{}^{\mathrm{F}}(1)\frac{\mathrm{d}(G_j{}^{\mathrm{F}} - 1)}{\mathrm{d}\delta(1)} + (G_j{}^{\mathrm{F}} - 1) \times \frac{\mathrm{d}\Delta\delta_j{}^{\mathrm{F}}(1)}{\mathrm{d}\delta(1)} + \Delta\delta_j{}^{\mathrm{M}}(1)\frac{\mathrm{d}(G_j{}^{\mathrm{M}} - 1)}{\mathrm{d}\delta(1)} + (G_j{}^{\mathrm{M}} - 1)\frac{\mathrm{d}\Delta\delta_j{}^{\mathrm{M}}(1)}{\mathrm{d}\delta(1)}\right] \qquad (10)$$

Equation 10 represents the slope of a plot of the chemical shifts of H(2) *vs.* H(1). Shown in Figure 2 are the experimental results for the styrenes, where H(2) is the β_{cis}- and H(1) the β_{trans}-hydrogen. Also included in this figure are theoretical plots for these two hydrogens based on the following working hypotheses: the chemical shifts are predominantly affected by electric field effects (a–b); the chemical shifts are dominated by magnetic field effects (c–e); magnetic and electric field effects are insignificantly small or zero (f). Note that different slopes are obtained for *meta* and *para* substituents under either of the first two assumptions, since $G_j{}^{\mathrm{F}}$ and $G_j{}^{\mathrm{M}}$ both change significantly in going from *meta* to *para*. These theoretical curves were calculated assuming Dreiding bond distances,[16] angles of 120°, and a typical value of $l_{\mathrm{C-X}}$ (the distance between the locus of a C–X dipole and the aromatic ring carbon to which it is attached) of 2.0 A. The experimental results are seen to agree only with the last working hypothesis. The slope, calculated by the method of least squares, is 0.98 ± 0.02. The correlation is very good, with the standard error in each measurement being 0.5 cps, comparable to the experimental error of the measurements. In order for such a result to be obtained, the summation on the right-hand side of (10) must approximate to zero. This could occur through a fortuitous cancellation of all terms in the summation or it could arise if all the terms in the summation approximate to zero. If the latter assumption is correct, two interesting inferences may be drawn: (1) the contribution to the chemical shifts of side-chain hydrogens from electric field effects is either zero or very small; and (2) the contribution from the anisotropy of the phenyl ring is independent of the nature of the substituents, at least to a first approximation.

The possibility that the terms due to the electric field and magnetic field effects cancel cannot be dispensed with easily. It is certainly true that they have different geometric factors, for although both show r^{-3} dependence, their dependence on θ is quite different and the electric field is additionally dependent on cos φ as is seen from eq 2 and from the fact that the E_Z term in either (3) or (4) generally dominates. However, the two field effects must operate in opposite directions in the styrenes. Thus, electron-withdrawing groups must deshield by electric field effects and shield by magnetic field effects. The latter follows from the fact that the side-chain hydrogens are in the deshielding region of the phenyl ring and will be deshielded less by the π circulation of the aromatic ring if its electron density is decreased.

Whatever the explanation for the experimental observation that the styrenes show essentially unit slope in a plot of chemical shifts of $H_{\beta\text{-}cis}$ *vs.* $H_{\beta\text{-}trans}$, the

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(16) A. S. Dreiding, *Helv. Chim. Acta*, **42**, 1339 (1959).

conclusion is that the net effect of field effects is insignificantly small and that the chemical shifts are being determined by the field independent terms of eq 6, *i.e.*, induction and resonance terms. It follows that the chemical shifts can be used to evaluate conjugation.

If H(1) and H(2) are on adjacent carbon atoms, additional terms must appear in eq 9 to account for the fact that perturbations in the chemical shifts caused by inductive and resonance effects are different for H(1) and H(2), *i.e.*

$$\Delta\delta_j^{\mathrm{I}}(2) = F\Delta\delta_j^{\mathrm{I}}(1) \qquad (11)$$

$$\Delta\delta_j^{\mathrm{R}}(2) = C_j\Delta\delta_j^{\mathrm{R}}(1) \qquad (12)$$

where F is the transmittance factor of the bond separating the carbons to which H(1) and H(2) are attached, and C is a conjugation factor expressing the change in effectiveness of transmission of a resonance effect arising in the jth substituent to H(1) and H(2). The F factor is assumed to be constant for a given bond and to be independent of j. The C_j factor, however, will be a function of the substituent if there is a direct resonance interaction between the substituent and either or both of the atoms bearing H(1) or H(2). In this connection, it should be pointed out that C_j is much more likely to be substituent independent in proton magnetic resonance than it is in fluorine magnetic resonance. This, and the greater ease of synthesis of hydrocarbon as opposed to fluorocarbon derivatives, serve to cancel out much of the advantage of studying fluorine resonances which derives from their chemical shifts being considerably larger than those of protons.

The relationship between the chemical shifts of two vicinal hydrogens subject to inductive and resonance effects but independent of electric and magnetic field effects is given by

$$\delta(2) = \delta(1) + \sum_j[(F - 1)\Delta\delta_j^{\mathrm{I}}(1) + (C_j - 1)\Delta\delta_j^{\mathrm{R}}(1)] \qquad (13)$$

Differentiation with respect to δ(1) leads to

$$\frac{\mathrm{d}\delta(2)}{\mathrm{d}\delta(1)} = 1 + \sum_j\left[\frac{\mathrm{d}(F - 1)}{\mathrm{d}\delta(1)}\Delta\delta_j^{\mathrm{I}}(1) + (F - 1)\frac{\mathrm{d}\Delta\delta_j^{\mathrm{I}}(1)}{\mathrm{d}\delta(1)} + \frac{\mathrm{d}(C_j - 1)}{\mathrm{d}\delta(1)}\Delta\delta_j^{\mathrm{R}}(1) + (C_j - 1)\frac{\mathrm{d}\Delta\delta_j^{\mathrm{R}}(1)}{\mathrm{d}\delta(1)}\right] \qquad (14)$$

In the absence of direct resonance interaction between the substituents and the hydrogen-bearing carbons under consideration, C_j will be constant and can be combined with F to give F', a factor reflecting the differential effectiveness of transmission of electronic effects to two adjacent atoms both through induction and resonance. In this case, eq 13 reduces to the more simple relationship

$$\delta(2) = \delta(1) + \sum_j(F' - 1)\Delta\delta_j^{\mathrm{I}'}(1) \qquad (15)$$

where $\Delta\delta_j^{\mathrm{I}'}(i)$ represents the perturbation in the chemical shift of the ith proton caused by inductive and resonance effects arising in the jth substituent. Since in this case F' is independent of the substituent, j, and therefore a constant for any given bond between the carbons bearing H(1) and H(2), differentiation of (15) leads to

$$\frac{\mathrm{d}\delta(2)}{\mathrm{d}\delta(1)} = 1 + \sum_j(F' - 1)\frac{\mathrm{d}\Delta\delta_j^{\mathrm{I}'}(1)}{\mathrm{d}\delta(1)} \qquad (16)$$

Equations 10, 14, and 16 give expressions for the internal chemical shifts for the systems studied, under different conditions. The experimental values for these internal chemical shifts are in Table II. In Table III are recorded values for the relative sensitivity of the α-hydrogens to ring substitution, with styrene as standard.

Table II. Transmission Factors for C–C Bonds

Compound	dδ(β)/dδ(α)
Styrene (for β-*trans*)	1.44 ± 0.16
Ethylbenzene	0.43 ± 0.05
Dihydrocinnamic acid	0.71 ± 0.07
trans-Cinnamic acid	1.81 ± 1.05
trans-Cinnamic acid (−σ groups)	3.89 ± 1.10
trans-Cinnamic acid (+σ groups)	0.64 ± 0.16
cis-Cinnamic acid	1.08 ± 0.22

Table III. Sensitivity of H$_\alpha$ to Ring Substitution Relative to H$_\alpha$ of Styrene as Standard

Compound	dδ(α)/dδ(α′)
Styrene	1.00
Ethylbenzene	0.98 ± 0.06
Dihydrocinnamic acid	0.86 ± 0.13
trans-Cinnamic acid	0.63 ± 0.09
cis-Cinnamic acid	1.33 ± 0.06

In the case of the styrenes, eq 16 should apply, at least to a first approximation, as one does not anticipate any strong specific resonance interactions with the vinyl group. Since it has already been demonstrated in this system that electric and magnetic field effects contribute insignificantly to the perturbation in the chemical shift by the various substituents, it follows that the derivative on the right-hand side of (16) must approximate to unity and that the internal chemical shift, 1.44, is F'. This result indicating that the substituent effects are felt about 40% more at the β-carbon is in good agreement with the results on C-13 studies.[13]

Equation 16 is also applicable to the ethylbenzenes, since there is no resonance possible with either the α- or β-carbons. In this case, therefore, $F = F'$. In view of the fact that the side-chain hydrogens in the ethylbenzenes (and in all the other systems included in this study) are approximately equally far removed from *meta* and *para* substituents as they are in the styrenes, it is probably safe to extrapolate the results on the internal chemical shifts for the two β-protons of styrene, *i.e.*, to ignore electric and magnetic field effects arising in the aromatic substituents and to ascribe all their perturbations on the chemical shifts to field-independent factors. If this is so, the internal chemical shift for the ethylbenzenes must measure the transmittance factor between the α- and β-carbons. The observed value of 0.43 ± 0.05 is in excellent agreement with that predicted on the basis of other studies of attenuation factors (transmittance^{-1}) for carbon–carbon single bonds.[17] The experimental results are shown in Figure 3 both for studies made in acetone and in chloroform. It is noteworthy that although the chemical shifts are quite different in these two solvents, as one might expect, the internal chemical shifts are identical within experimental

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(17) Reference 3g and references therein.

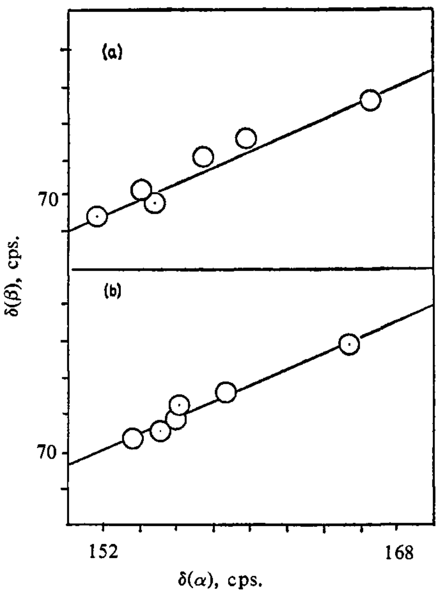

Figure 3. Chemical shifts of H_β *vs.* H_α for ethylbenzenes: (**a**) in in acetone, (b) in chloroform.

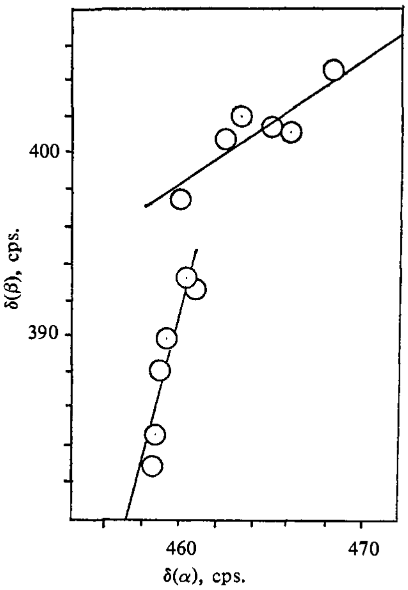

Figure 4. Chemical shifts of H_β *vs.* H_α for *trans*-cinnamic acids.

error. The errors in the estimates are 0.7 cps in acetone and 0.5 cps in chloroform.

It is interesting to note that the α-protons in both styrene and ethylbenzene are equally sensitive to ring substitution. In the latter case, the effect is presumably transmitted by induction from the adjacent ring carbon.[8c] In the case of the styrene, the electron density is also transmitted to the β-carbon by resonance, but both the ring atom and the β-carbon are adjacent to the α position and there is apparently no significant difference in inductive transmittal from these two sites.

The results for the dihydrocinnamic acids indicate that the β-hydrogens are significantly more sensitive to substituent effects than are those in ethylbenzene. Although this might be due to some enhancement in carbon–carbon single bond electronic transmission, this hardly seems likely. A more plausible explanation is that the carboxyl feels the effect of the ring substituents through some external pathway and in turn shields or deshields the β-protons. One can envisage an intramolecular acid–base interaction between the carboxyl group and the phenyl π-electron cloud. Since the carboxyl can coordinate its proton better the more electron rich the aromatic ring, it follows that there should be a differential transmittance of electron density to the carboxyl based on the nature of ring substitution. In essence, the carboxyl will be behaving as a dependently variable substituent. If this explanation is valid, the ring should suffer a decrease in its capability to affect the chemical shifts of the α-hydrogens. It does!

The *trans*-cinnamic acids present an interesting situation in which it would appear necessary to use the more extended treatment of eq 14. The plot given in Figure 4 shows that the data are not adequately fit by a single line and that a much better correlation can be had with two discontinuous lines, one for $-\sigma$ (electron feeding) substituents and one for $+\sigma$ groups. It appears that the $-\sigma$ groups are directly interacting with the carboxyl by a resonance effect such that the β-hydrogens are almost four times more sensitive to the substituents than are the α-hydrogens and 2.5 times that of the β-protons in styrenes. In the case of $+\sigma$ groups, the situation is reversed. Now, the β-hydrogens are considerably less affected than even the α-protons and appear no better off than if there were a saturated bond between the α- and β-carbons.

In the *cis*-cinnamic acids, the internal chemical shift is intermediate between the saturated analog (dihydrocinnamic acid) and the noncarboxylated analog, styrene. It is possible to explain this result since one expects the side chain to be forced out of coplanarity with the phenyl ring in order to relieve steric strain. This should attenuate the resonance effect compared to a completely planar system such as styrene but not completely destroy it as would be true in one of the saturated analogs or appears to be true in the *trans*-cinnamic acids with $+\sigma$ groups. One can predict that the shifting of the side chain from coplanarity will remove the α-hydrogen away from the maximum deshielding region due to the magnetic anisotropy of the phenyl ring and should shift the resonance signal upfield. One can also predict that the rotation should be more favorable the more electron rich the ring, since one can compensate then for loss of π-orbital overlap by increased acid–base interaction (as in the dihydrocinnamic case discussed above). This would then result in an enhanced sensitivity to electron density of the α-hydrogens. Both of these predictions are confirmed experimentally.

Experimental Section

Reagents. The deuterated solvents, deuteriochloroform and acetone-d_6, were obtained from Ciba. The ethylbenzenes and styrenes were obtained from commercial sources and their physical constants checked with literature values. The cinnamic acids and dihydrocinnamic acids were synthesized in these laboratories. The physical constants of the known ones are listed in Table IV, and the syntheses and analyses of the others are shown below.

***cis-p*-Methylcinnamic Acid.** A solution of 11.5 g (0.0625 mole) of sodium *trans-p*-methylcinnamate in 100 ml of water was irradiated in an open quartz beaker at 15–25° for 100 hr with the full input of a low-intensity mercury arc lamp. After removal of nonacidic impurities by ether extraction, the solution was acidified with 6 *N* hydrochloric acid to precipitate a mixture of the *cis* and *trans* acids. A second crop was obtained by salting out the filtrate, extracting with three 20-ml portions of ether, and concentrating the ether. The combined precipitates weighed 7.5 g (0.046 mole).

Table IV. Melting Points of *cis*- and *trans*-Cinnamic Acids and Dihydrocinnamic Acids, °C

	trans-Cinnamic acids			*cis*-Cinnamic acids			Dihydrocinnamic acids		
Substituent	Found	Lit.	Ref	Found	Lit.	Ref	Found	Lit.	Ref
p-Methoxy	174.0–174.6	174	*a*	67.5–68.5	66	*g,h*	107–108	107	*a*
p-Methyl	198.2–199.0	199	*a*	...	...	...	116–117	116	*a*
m-Methyl	119–120	119	*a*	...	...	...	...	...	...
None	133–134	133	*c,f*	67–68	68	*f,g*	48.5–49.5	47.5–48.0	*a*
p-Chloro	249–250	247	*b,i*	110.5–111.5	113.8–116.2	*i*	122–123	122	*a*
m-Chloro	162–163.5	163.5–164.5	*j*	66.0–66.5	65.0–66.5	*j*	...	...	...
m-Cyano	247–248	247	*e*	...	...	...	...	...	...
p-Cyano	256.0–256.5	254	*d*	...	...	...	...	...	...
m-Nitro	203–204	202	*a*	157.0–157.5	155–156	*k,l*	...	...	...
p-Nitro	287–289	288	*a*	142.8–143.3	146–147 141	*l* *m*	166–167	168	*a*

[a] J. F. J. Dippy and J. E. Page, *J. Chem. Soc.*, 357 (1938). [b] K. C. Pandya and R. B. Pandya, *Proc. Indian Acad. Sci.*, **14A**, 112 (1941); *Chem. Abstr.*, **36**, 1599 (1942). [c] F. Weger, *Ann.*, **221**, 73 (1883). [d] C. W. Shoppee, *J. Chem. Soc.*, 968 (1930). [e] R. H. Wiley and N. R. Smith, *J. Am. Chem. Soc.*, **70**, 1560 (1948). [f] C. Paal and W. Hartmann, *Ber.*, **42**, 3930 (1909). [g] W. A. Roth and R. Stoermer, *ibid.*, **46**, 260 (1913). [h] Y. Urushibara and M. Hirota, *Nippon Kagaku Zasshi*, **82**, 351 (1961); *Chem. Abstr.*, **56**, 10025 (1962). [i] S. Lindenfors, *Arkiv Kemi*, **10**, 561 (1956). [j] S. Lindenfors, *ibid.*, **12**, 267 (1958). [k] S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 632 (1953). [l] F. Wollring, *Ber.*, **47**, 111 (1914). [m] Y. Urushibara and M. Hirota, *Nippon Kagaku Zasshi*, **82**, 358 (1961); *Chem. Abstr.*, **56**, 10026 (1962).

The *cis* acid was leached from the mixture with three 50-ml portions of boiling water. This aqueous solution was salted out and extracted with ether, and the ether was then concentrated to yield the *cis* acid as a colorless oil. It was further purified by extraction with three 50-ml portions of petroleum ether (in which the *cis*, but not the *trans*, isomer is quite soluble). Finally, the acid was fractionally crystallized from petroleum ether (bp 30–60°) and then from hexane to give 1.5 g (37%) of colorless prisms, mp 77.5–79.0°. This compound has the expected infrared and ultraviolet spectra.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22. Found: C, 73.88; H, 6.21.

cis-m-**Methylcinnamic Acid.** A solution of 11.5 g (0.0625 mole) of sodium *trans-m*-methylcinnamate in 100 ml of water was irradiated in an open quartz beaker at 15–25° for 70 hr. After removal of nonacidic organic impurities by ether extraction, the filtrate was acidified by gradual addition of 6 *N* hydrochloric acid. The *trans* acid precipitated first and could be fractionated by this acidification process. The *cis* acid which remained in solution was then salted out and extracted with three 20-ml portions of ether and the ether concentrated to a colorless oil. A total of 8 g of acid was recovered of which 2 g was *cis*. The latter was taken up in petroleum ether and evaporated on a Rinco rotary evaporator at −80° to precipitate a white powder, mp 36–38°. Slow recrystallization from *n*-hexane yielded 1.2 g of colorless prisms, mp 39.5–40.0°. This compound has the expected infrared and ultraviolet spectra.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22. Found: C, 74.30; H, 5.99.

trans-m-**Trifluoromethylcinnamic Acid.** *m*-Bromobenzotrifluoride was synthesized in 45% yield from benzotrifluoride by the method of Simons and Ramler.[18] It, in turn, was converted to *m*-trifluoromethylbenzaldehyde in 80% yield by the method of Gilman.[19] This was transformed by the Doebner reaction into *trans-m*-trifluoromethylcinnamic acid in 50% yield by the method of Rapoport.[20] The product was obtained as white needles, mp 135.5–136.5°.

Anal. Calcd for $C_{10}H_7O_2F_3$: C, 55.56; H, 3.26. Found: C, 55.83; H, 3.60.

cis-m-**Trifluoromethylcinnamic Acid.** A solution of 11.0 g (0.046 mole) of sodium *trans-m*-trifluoromethylcinnamate in 100 ml of water was irradiated with the full intensity of a low-intensity mercury arc lamp at room temperature for 120 hr. The solution was acidified with hydrochloric acid and then extracted with ether. The ether was concentrated and the residue dissolved in hot water from which the *trans* acid crystallized readily but in which the *cis* is considerably more soluble. After the solution had been cooled and the *trans* acid filtered off, the filtrate was put on an Amberlite IR-4B ion-exchange column as its sodium salt and gradiently eluted with sodium citrate (0–0.5 *M*). The eluted fractions were acidified with dilute hydrochloric acid to yield 0.5 g of pure *cis* compound, mp 53.5–54.5°.

Anal. Calcd for $C_{10}H_7O_2F_3$: C, 55.56; H, 3.26. Found: C, 55.38; H, 3.38.

trans-p-**Trifluoromethylcinnamic Acid.** *p*-Bromobenzotrifluoride was synthesized in 33% yield from *p*-bromotoluene by the method of Markarian.[21] This was converted to *p*-trifluoromethylbenzaldehyde by the method of Gilman;[19] the crude product (57% yield) was used in the next step without further purification. Condensation of this aldehyde with malonic acid by the method of Rapoport[20] gave 54% *trans*-trifluoromethylcinnamic acid as white crystals, mp 229.5–230.0°.

Anal. Calcd for $C_{10}H_7O_2F_3$: C, 55.56; H, 3.26. Found: C, 55.68; H, 3.61.

Spectra. The nmr spectra were obtained on a Varian Associates HA-60 spectrometer operating at a frequency of 60 Mcps. The samples were weighed into tared 5-mm o.d. precision bore Pyrex tubes and dissolved in sufficient solvent to make exactly 0.25 cc of solution. The solvents contained tetramethylsilane as an internal reference. The sample tubes were spun at 1800 rpm. The magnetic field was swept at a rate of approximately 1 cps/sec. In order to minimize errors, the spectra were obtained by both increasing and then immediately decreasing the field through the whole spectrum while maintaining all instrumental settings constant. The average frequency of the peaks observed for these two consecutive runs was taken to represent the value for that particular sample. Frequent checks on duplicate runs showed that the variation in frequency with respect to tetramethylsilane for a given peak was less than 0.5 cps. Hence this is taken to represent the average uncertainty in peak position.

The spectra were obtained with side bands occurring at a known frequency (usually 500 cps) which was introduced by the use of a Hewlett-Packard audiooscillator, Model 200 CDR. The individual frequencies of the peaks of a spectrum were then measured by interpolation. The average values of the frequency with respect to tetramethylsilane for each peak, taken from the two consecutive runs, were then tabulated. From these values the chemical shifts for the side-chain protons were obtained by appropriate spectral analysis.

Spectra were obtained for the compounds at three concentrations. In the case of a few difficultly soluble compounds, only one concentration was investigated. The chemical shifts for the respective side-chain hydrogens were plotted *vs.* concentration, and the chemical shift at infinite dilution was taken to represent the true chemical shift for that hydrogen. When only one concentration was employed, the chemical shift at this concentration is reported. These cases usually represent dilute solutions and, as such, the errors involved in not being able to extrapolate to infinite dilution are probably small.

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