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Studies on the Linear Free Energy Relationship in Methyl Cinnamates by ^{1}H-NMR Spectrometry

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(Received January 30, 1981)

Chemical shift values of α-proton of *trans*- and *cis*-methyl cinnamates are well correlated with σ (σ_I, σ_R°), and and (F, R) (r=0.999−0.879). It is observed that (1) the degree of variation of δH_α value by varying the substituents in *trans*-cinnamates is similar to that of *cis*-cinnamates (ρ_{trans}=0.296, ρ_{cis}=0.284), (2) resonance contribution is larger in the *trans*-cinnamates than that in the *cis*-cinnamates, but inductive contribution is reversed, (3) for *m*-substituted derivatives, resonance contribution is very small compared to that for *p*-substituted derivatives.

Introduction

Attempts have been made by many workers to relate ^{1}H chemical shifts of various type of compounds to specific substituent properties such as electronegativity[1] or dipole moment[2] as well as to correlate them with more general expressions of substituent ability to affect electron density such as, for example, the well known Hammett σ constants and variations[3] thereof. Explanations involving either the magnetic[4] or electric field[5] arising in a substituent have been advanced.

Wittstruck and Trachtenberg[6] found that perturbations in their chemical shifts are caused mainly by inductive and resonance effects rather than by electric and magnetic field effects in the case of cinnamic acid. Wehrli, *et al.*[7] calculated π-electron density of vinyl proton by LCAO-MO method, and they could observe that there is a linear correlation between chemical shift of vinly proton and electron density on the side chain of *trans*-cinnamic acid (r=0.77). It is found by Katritzky and Swinbourne[8] that there is a good correlationship between the chemical shifts of α-proton and Hammett σ-constants of ring substituents in cinnamic acids (r=0.973 in dimethyl sulfoxide, r=0.912 in trifluoroacetic acid), but less so for the β-protons (r=0.850). They proposed that steric and magnetic anisotropic effects (possibly including ring current) are the cause of the poor relationship for the β-protons.

In order to exclude the possibility of interfering effect of hydroxyl group and to increase the solubility in organic solvents, the acid is esterified. Thus we determined the chemical shifts of vinyl protons of *trans*- and *cis*-methyl cinnamates, and corerlated them with Hammett equation (eq. 1) and its variations (eq. 2, eq.3).[9-11]

$$\delta H_{\alpha,x}=\rho\sigma+\delta H_{\alpha,0} \quad \text{(eq. 1)}$$
$$\delta H_{\alpha,x}=\rho_I\sigma_I+\rho_R\sigma_R+\delta H_{\alpha,0} \quad \text{(eq. 2)}$$
$$\delta H_{\alpha,x}=fF+rR+\delta H_{\alpha,0} \quad \text{(eq. 3)}$$
$$\lambda_p=(\rho_R/\rho_I)_p \quad \text{(eq. 4)}$$
$$\lambda'_p=(r/f)_p \quad \text{(eq. 5)}$$
$$\lambda_m=(\rho_R/\rho_I)_m \quad \text{(eq. 6)}$$
$$\lambda_m'=(r/f)_m \quad \text{(eq. 7)}$$
$$N_p=(\lambda_p)_{trans}/(\lambda_p)_{cis} \quad \text{(eq. 8)}$$
$$N_p'=(\lambda_p')_{trans}/(\lambda_p')_{cis} \quad \text{(eq. 9)}$$
$$N_m=(\lambda_m)_{trans}/(\lambda_m)_{cis} \quad \text{(eq. 10)}$$
$$N_m'=(\lambda_m')_{trans}/(\lambda_m')_{cis} \quad \text{(eq. 11)}$$

where F and R are the substituent constants corresponding

to the field and resonance contribution proposed by Williamson and Norrington and f and r are their weighting factors. $\lambda_p(\lambda_p')$ and $\lambda_m(\lambda_m')$, so called the blending coefficients, represent the ratio of resonance and inductive (field) contribution of *para* and *meta* substituents and $N_p(N_p')$ and $N_m(N_m')$ represent the ratio of λ.

Experimental

1. *Materials.* *trans*-Methyl cinnamate was obtained from *trans*-cinnamic acid (practical, Eastman) by the method reported,[12] and recrystallized from methanol. White crystal (needle), m.p 34.5~5.5 °C, λ_{max}^{abs} ($\varepsilon\times10^{-4}$) in methanol=273 nm, (2.25), 214 nm (1.66), 202 nm(1.49), λ_{max}^{the} in chloroform =277 nm, δH(ppm) in chloroform-d=3.77(s, 3H), 6.37 (d, 1H, AB, J=16 Hz), 7.63(d, 1H, AB, J=16 Hz), 7.32 (m, 5H), ν_{CO}(KBr)=1713 cm^{-1}, $\nu_{C=C}$ (KBr)=1634 cm^{-1}.

trans-Methyl *p*-nitro cinnamate was obtained from the corresponding acid (TCI, G.R.).[12] Pale yellow crystal, m.p 158.0-9.0 °C, λ_{max}^{the} ($\varepsilon\times10^{-4}$) in methanol=295 nm (2.10), λ_{max}^{abs} in chloroform=304 nm, δH (ppm) in chloroform-d= 3.80(s, 3H), 6.58 (d, 1H, AB, J=16 Hz) 7.70 (d, 1H, AB, J=16 Hz), 7.67, 7.80, 8.17, 8.30 (dd, 4H, AA'BB'), ν_{CO} (KBr)=1724 cm^{-1}, $\nu_{C=C}$ (KBr)=1640 cm^{-1}.

trans-Methyl *p*-methoxy cinnamate was obtained from the correspondin g acid (TCI),[12] and recrystallized from methanol. White crystal, m.p 87.0-8.0 °C, λ_{max}^{abs} ($\varepsilon\times10^{-4}$) in methanol=306 nm(2.40), 224 nm(1.28), 208 nm(1.09), λ_{max}^{abs} in chloroform=308 nm, δH(ppm) in chloroform-d=3.73 (s, 3H), 3.75(s, 3H), 6.20 (d, 1H, AB, J=16 Hz), 7.55 (d, 1H, AB, J=16 Hz), 6.73, 6.84, 7.30, 7.41 (dd, 4H, AA'BB'), ν_{CO}(KBr)=1713 cm^{-1}, $\nu_{C=C}$(KBr)=1640 cm^{-1}.

trans-Methyl *p*-methyl cinnamate was obtained from the corresponding acid (99%, Aldrich),[12] and recrystallized from methanol. White crystal, m.p 56.0-7.0 °C, λ_{max}^{abs} ($\varepsilon\times10^{-4}$) in methanol=283nm (2.56), 291nm(1.53), 206nm (0.76), λ_{max}^{abs} in chloroform=286nm, δH(ppm) in chloroform-d=2.30(s, 3H), 3.72(s, 3H), 6.28(d, 1H, AB, J=16 Hz), 7.60(d, 1H, AB, J=16 Hz), 7.00, 7.13, 7.27, 7.40 (dd, 4H, AA'BB'), ν_{CO}(KBr)=1702 cm^{-1}, $\nu_{C=C}$=(KBr)= 1629 cm^{-1}.

trans-Methyl *p*-hydroxy cinnamate was obtained from the correspon ding acid (98 %, Aldrich),[12] and recrystallized from methanol. White crystal, m.p 135-6 °C, λ_{max}^{abs}($\varepsilon\times10^{-4}$) in methanol=310 nm(2.40), 226 nm(1.19), 208 nm(0.67), λ_{max}^{abs} in chloroform=308 nm, δH(ppm) in chloroform-d=3.70 (s, 3H), 6.15(d, 1H, AB, J=16 Hz), 7.50(d, 1H, AB, J=16 H), 6.67, 6.83, 7.22, 7.38(dd, 4H, AA'BB'), ν_{CO}(KBr)= 1683 cm^{-1}, $\nu_{C=C}$(KBr)=1632 cm^{-1}.

trans-Methyl *p*-chloro cinnamate was obtained from the corresponding acid (white crystal, m.p 244-5 °C)[12] which was prepared from *p*-chlorobenzaldehyde (practical, Kanto) by the known method,[13] and recrystallized from ethyl ether. White crystal, m.p 73.5-4.5 °C, λ_{max}^{abs} ($\varepsilon\times10^{-4}$) in methanol =279 nm(2.74), 218 nm(1.55), 206 nm(1.38), λ_{max}^{abs} in chloroform=284 nm, δH(ppm) in chloroform-d=3.73(s, 3H), 6.27 (d,1H, AB, J=16 Hz), 7.53 (d, 1H, AB, J=16 Hz), 7.28 (m, 4H), ν_{CO}(KBr)=1707 cm^{-1},$\nu_{C=C}$(KBr)=1633 cm^{-1}.

trans-Methyl *p*-dimethylamino cinnamate was obtained from the corresponding acid[12] which was prepared from *p*-dimethylaminobenzaldehyde (G.R., Kanto),[13] and recrysta-l lized from acetone. Yellow crystal (leaflet), m.p 132.5-3.5 °C, λ_{max}^{abs} ($\varepsilon\times10^{-4}$) in methanol=387 nm(3.15), 240 nm(1.08), λ_{max}^{the} in chloroform=362 nm, δH(ppm) in chloroform-d=2.96 (s, 6H), 3.73(s, 3H), 6.12 (d, 1H, AB, J=16 Hz), 7.53 (d, 1H, AB, J=16 Hz), 6.47, 6.63, 7.24, 7.40(dd, 4H, AA'BB'), ν_{CO}(KBr)=1702 cm^{-1},$\nu_{C=C}$(KBr)=1600 cm^{-1}.

trans-Methyl *m*-hydroxy cinnamate was obtained from the corresponding acid (99 %, Aldrich),[12] and recrystallized from ethyl ether and acetone two times. White crystal (prism), m.p 85.5-6.5 °C, λ_{max}^{abs} ($\varepsilon\times10^{-4}$) in methanol=315 nm(0.53), 277 nm(1.78), 232 nm(1.32), 212 nm(1.67), λ_{max}^{abs} in chloroform=276 nm, δH(ppm) in chloroform-d=3.80(s, 3H), 6.35(d, 1H, AB, J=16 Hz), 7.60 (d, 1H, AB, J=16 Hz), 6.7 -7.4(m, 4H), ν_{CO}(KBr)=1680 cm^{-1}, $\nu_{C=C}$(KBr)=1630 cm^{-1}, ν_{OH}(KBr)=3320 cm^{-1}.

trans-Methyl *m*-bromo cinnamate was obtained from the corresponding acid (Aldrich),[12] and recrystalliz ed from ethyl ether. White crystal (prism), m.p 54.0-5.0 °C, λ_{max}^{abs}($\varepsilon\times10^{-4}$) in methanol=271 nm(1.90), 222nm(2.23), λ_{max}^{abs} in chloroform=272 nm, δH(ppm) in chloroform-d=3.80(s, 3H), 6.39(d, 1H, AB, J=16 Hz), 7.57(d, 1H, AB, J=16 Hz), 7.1 -7.6(m, 4H), ν_{CO}(KBr)=1715 cm^{-1}, $\nu_{C=C}$(KBr)=1640 cm^{-1}

trans-Methyl *m*-chloro cinnamate was obtained from the corresponding acid (Aldrich),[12] and recrystallized from ethyl ether. White crystal (prism), m.p 46.0-7.0 °C, λ_{max}^{abs} ($\varepsilon\times10^{-4}$) in methanol=270 nm(2.00), 218 nm(2.33), λ_{max}^{abs} in chloroform =272 nm, δH(ppm) in chloroform-d=3.80 (s, 3H), 6.40 (d, 1H, AB, J=16 Hz), 7.61(d, 1H, AB, J=16 Hz), 7.0-7.5 (m, 4H), ν_{CO}(KBr)=1710 cm^{-1}, $\nu_{C=C}$(KBr)=1636 cm^{-1}.

trans-Methyl *m*-methoxy cinnamate was obtained from the corresponding acid (Aldrich),[12] and purified by distillation under reduced pressure. White solid or liquid, b.p at 50 mmHg 183 °C, m.p 25.0-6.0 °C, λ_{max}^{abs} ($\varepsilon\times10^{-4}$) in methanol=312 nm(0.54), 276 nm(1.86), 231 nm(1.47), 215 nm (1.63), λ_{max}^{abs} in chloroform=277 nm, δH(ppm) in chloroform-d=3.80 (s, 3H), 6.40 (d, 1H, AB, J=16 Hz), 7.67 (d, 1H, AB, J=16 Hz), 6.7-7.3(m, 4H), ν_{CO}(neat on NaCl)=1705 cm^{-1}, $\nu_{C=C}$(neat on NaCl)=1638 cm^{-1}.

trans-Methyl *m*-nitro cinnamate was obtained from the corresponding acid (99 %, Aldrich),[12] and recrystallized from acetone. Yellow crystal (prism), m.p 121.0-2.0 °C, λ_{max}^{abs} ($\varepsilon\times10^{-4}$) in methanol=259 nm(3.19), λ_{max}^{abs} in chloroform =262 nm, δH(ppm) in chloroform-d 3.83(s, 3H), 6.57 (d, 1H, AB, J=16 Hz), 7.72 (d, 1H, AB, J=16 Hz), 7.3-8.3 (m,4H), ν_{CO}=(KBr)=1710 cm^{-1}, $\nu_{C=C}$(KBr)=1640 cm^{-1}.

2. *Spectral Data.* ^{1}H-NMR spectra were measured on a Varian T-60A Nuclear Magnetic Resonance Spectrometer using tetramethylsilane (TMS) as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 267 Model using potassium bromide pellets and Ultraviolet-visible spectra were recorded on a Cary-17 spectrophotomteter.

3. *Preparation of cis-Methyl Cinnamates.* *trans*-Methyl Cinnamates (30-40 mg) were dissolved in organic solvents (chloform, acetonitrile, or methanol) and irradiated in a

TABLE 1: Chemical Shifts of α-Proton of Methyl Cinnamates and Values of Substituent Constants

Substituent	δH_α (ppm)		σ^a	$\sigma_I{}^b$	$\sigma_R{}^{ob}$	F	R^c
	trans	*cis*					
p-NO_2	6.58	6.07	0.78	0.64	0.19	1.109	0.155
p-Cl	6.27	5.90	0.23	0.47	−0.20	0.690	−0.161
H	6.37	5.85	0.00	0.00	0.00	0.00	0.00
p-CH_3	6.28	5.80	−0.17	−0.05	−0.10	−0.052	−0.141
p-CH_3O	6.20	5.78	−0.27	0.26	−0.41	0.413	−0.500
p-OH	6.15	5.75	−0.37	0.27	−0.44	0.487	−0.643
p-$N(CH_3)_2$	6.12	5.62	−0.83	0.05	−0.52	0.032	−0.863
m-NO_2	6.57	6.08	0.71	0.64	0.19	1.109	0.155
m-Br	6.39	5.95	0.39	0.45	−0.16	0.727	−0.176
m-Cl	6.40	5.94	0.37	0.47	−0.20	0.690	−0.161
m-OH	6.35	5.91	0.12	0.27	−0.44	−0.487	−0.643
m-CH_3O	6.40	5.92	0.12	0.26	−0.41	0.413	−0.500

[a]From ref. 14, [b]from ref. 10, [c] from ref. 11.

Pyrex cell using Rayonet Photochemical Reactor (The Southern New England Ultraviolet Co., Model RPR-208 and RPR-100) for 1 day. For *trans*-methyl *p*-dimethyl amino cinnamate, 350 nm light was used and for others 300 nm light was used. Chemical shifts of α-and β-protons of *cis*-methyl cinnamates were determined from NMR spectra of *cis* and *trans* mixtures (*cis* major) which was obtained from the irradiation.

Results and Discussion

Chemical shifts of α-proton of methyl cinnamates in chloroform-d and values of σ, σ_I, $\sigma_R{}^O$, F and R are shown in Table 1. When the chemical shifts are correlated with these substituent constants, the following results are obtained (respective curve fitting was obtained by virtue of computer optimization):

for all the *trans*-methyl cinnamates,

$$\delta H_\alpha = 0.296\sigma + 6.323,\ r = 0.932 \qquad \text{(Figure 1)}$$

for all the *cis*-methyl cinnamates,

$$\delta H_\alpha = 0.284\sigma + 5.855,\ r = 0.992 \qquad \text{(Figure 2)}$$

for only the *trans para* substituted methyl cinnamates

$$\delta H_\alpha = 0.284\sigma + 6.307,\ r = 0.917 \qquad \text{(Figure 3)}$$

$$\delta H_\alpha = 0.134\sigma_I + 0.536\sigma_R{}^\circ + 6.363$$

$$\lambda_p = 4.00,\ r = 0.982 \qquad \text{(Figure 4)}$$

$$\delta H_\alpha = 0.093F + 0.344R + 6.352$$

$$\lambda_p' = 3.70,\ r = 0.934 \qquad \text{(Figure 5)}$$

for only the *cis para* substituted methyl cinnamates,

$$\delta H_\alpha = 0.266\sigma + 5.848,\ r = 0.999 \qquad \text{(Figure 6)}$$

$$\delta H_\alpha = 0.262\sigma_I + 0.389\sigma_R{}^\circ + 5.845$$

$$\lambda_p = 1.48,\ r = 0.989 \qquad \text{(Figure 7)}$$

$$\delta H_\alpha = 0.157F + 0.274R + 5.845$$

$$\lambda_p' = 1.75,\ r = 0.999 \qquad \text{(Figure 8)}$$

for only the *trans meta* substituted methyl cinnamates,

$$\delta H_\alpha = 0.193\sigma_I + 0.183\sigma_R{}^O + 6.352$$

$$\lambda_m = 0.95,\ r = 0.898$$

$$\delta H_\alpha = 0.132F + 0.123R + 6.365$$

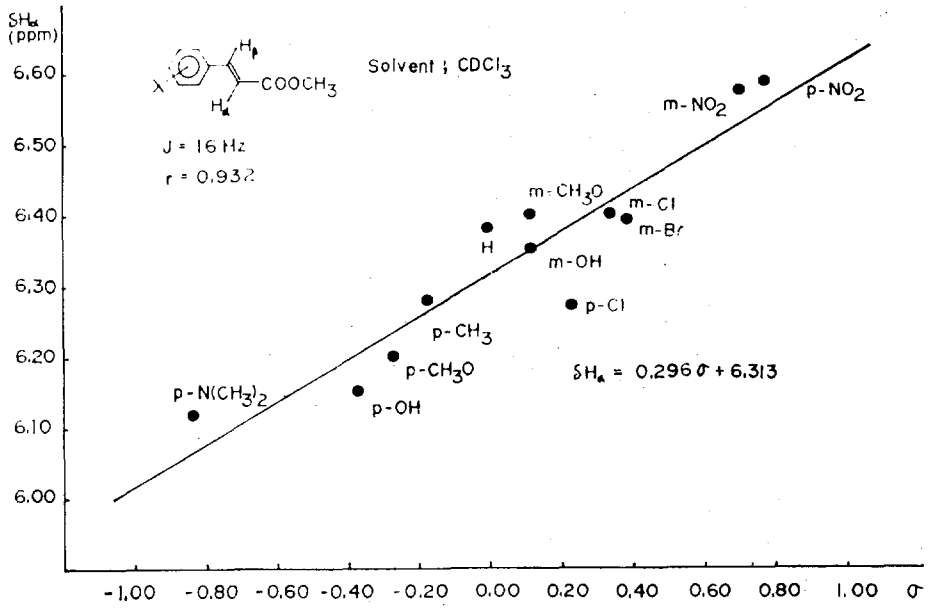

Figure 1. δH_α *vs.* σ for *trans-methyl* cinnamates.

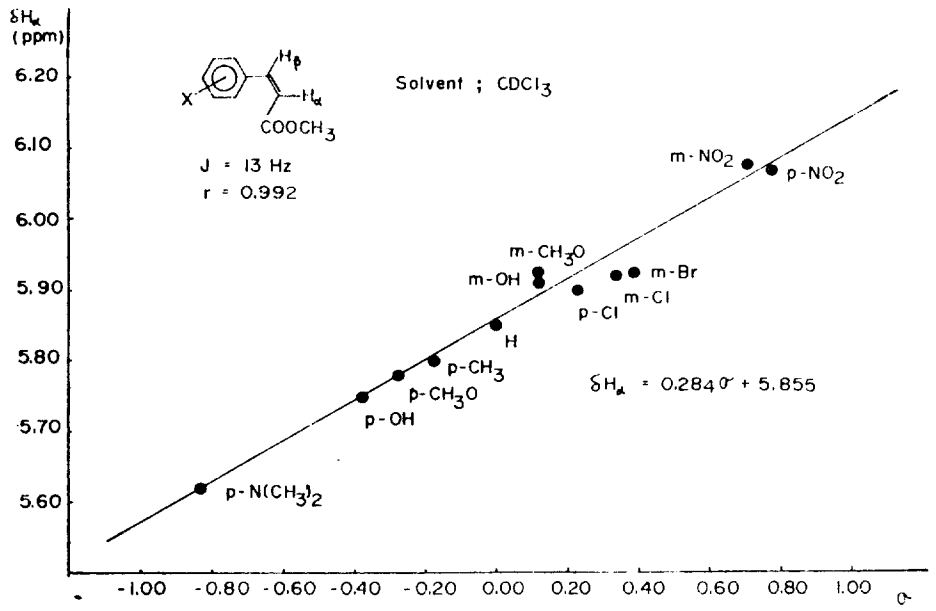

Figure 2. δH_α *vs.* σ for *cis*–methyl cinnamates.

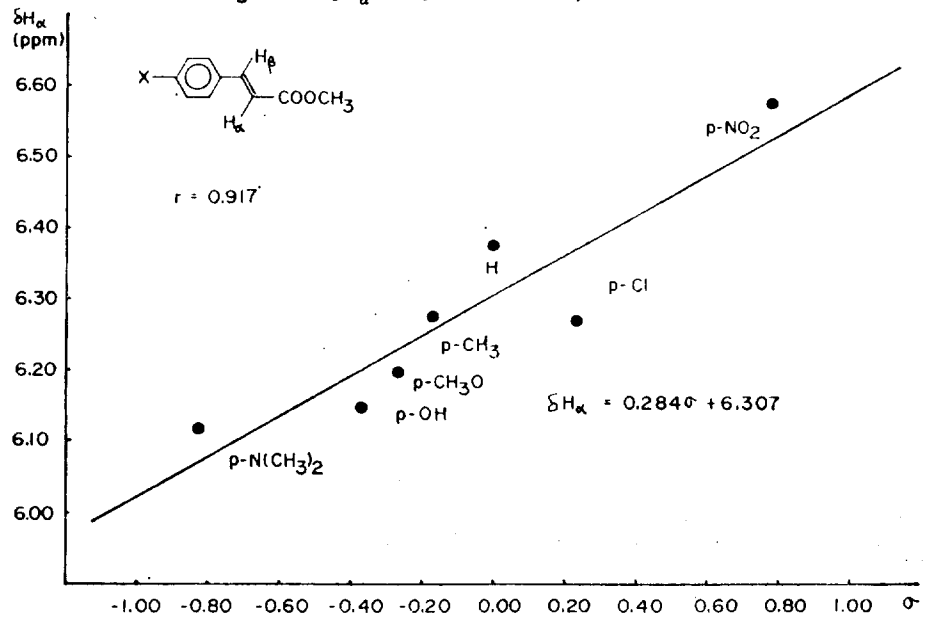

Figure 3. δH_α *vs.* σ for *trans para* substituted methyl cinnamates.

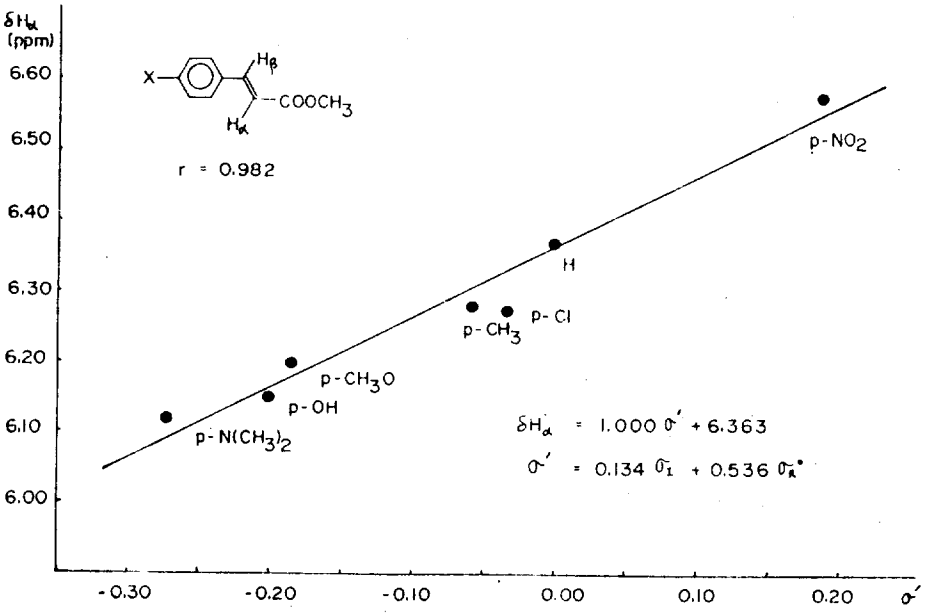

Figure 4. δH_α *vs.* $(\sigma_I.\sigma_R^\circ)$ for *trans para* substituted methyl cinnamates.

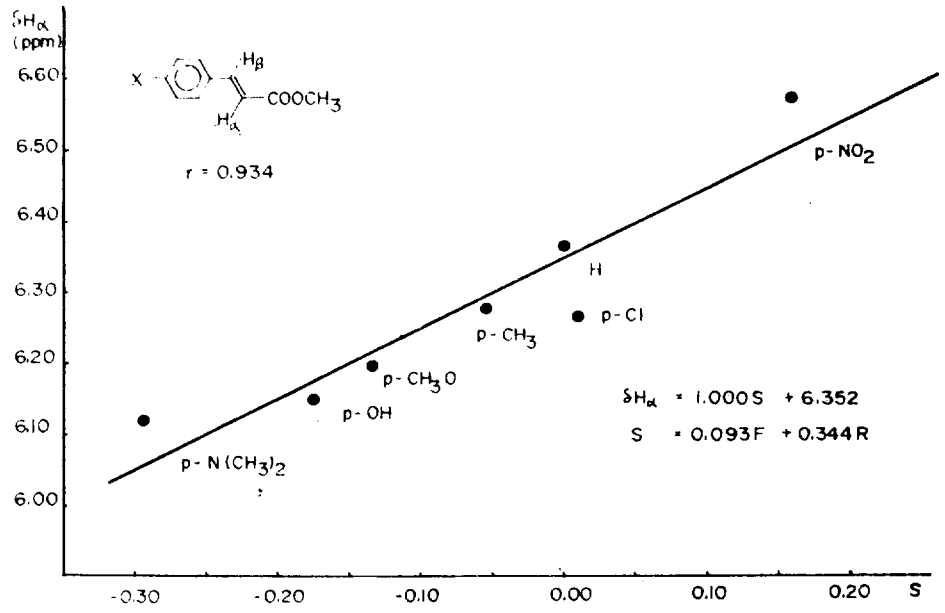

Figure 5. δH_α *vs.* *(F, R)* for *trans para* substituted methyl cinnamates.

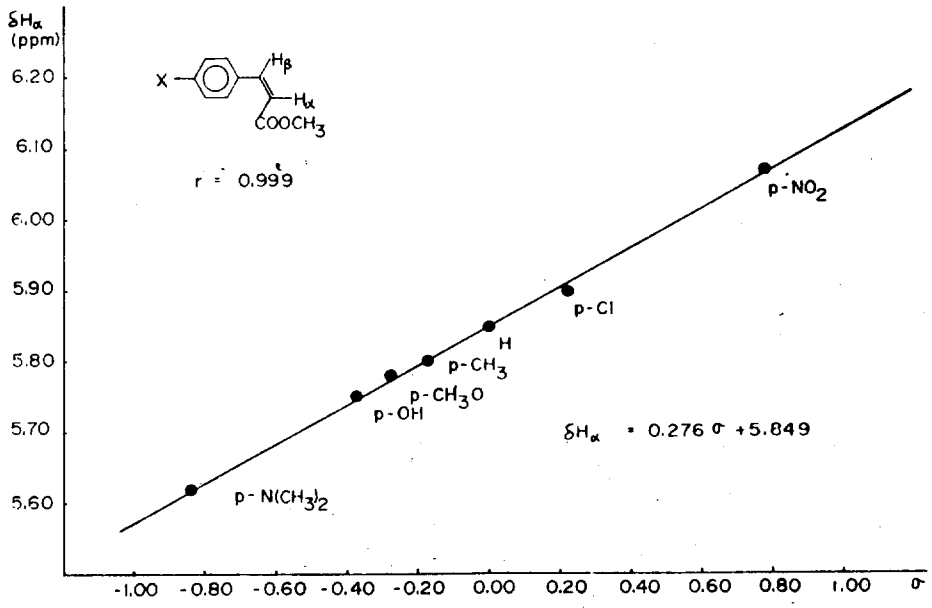

Figure 6. δH_α *vs.* σ for *cis para* substituted methyl cinnamates.

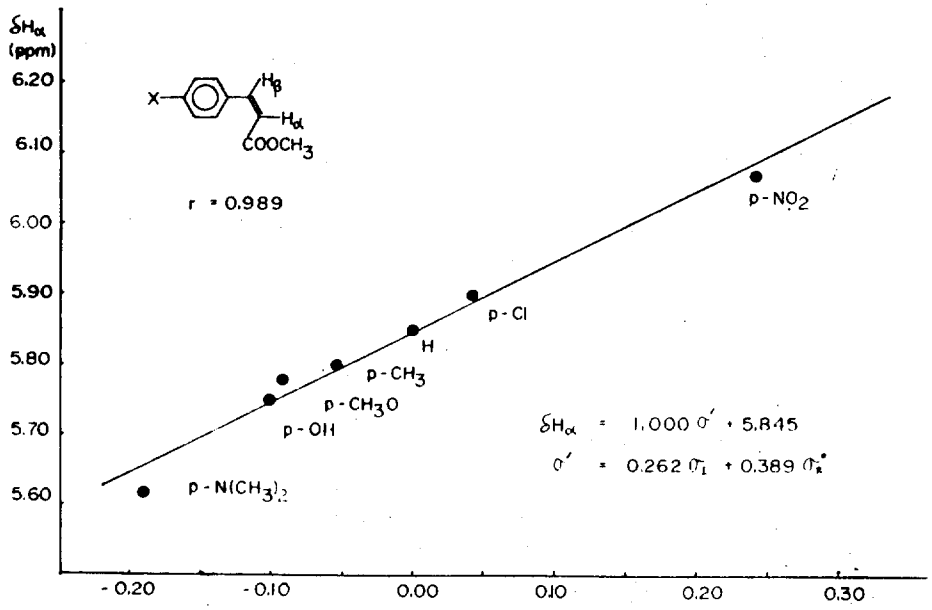

Figure 7. δH_α *vs.* σ $(\sigma_I, \sigma_R^\circ)$ for *cis para* substituted methyl cinnamates.

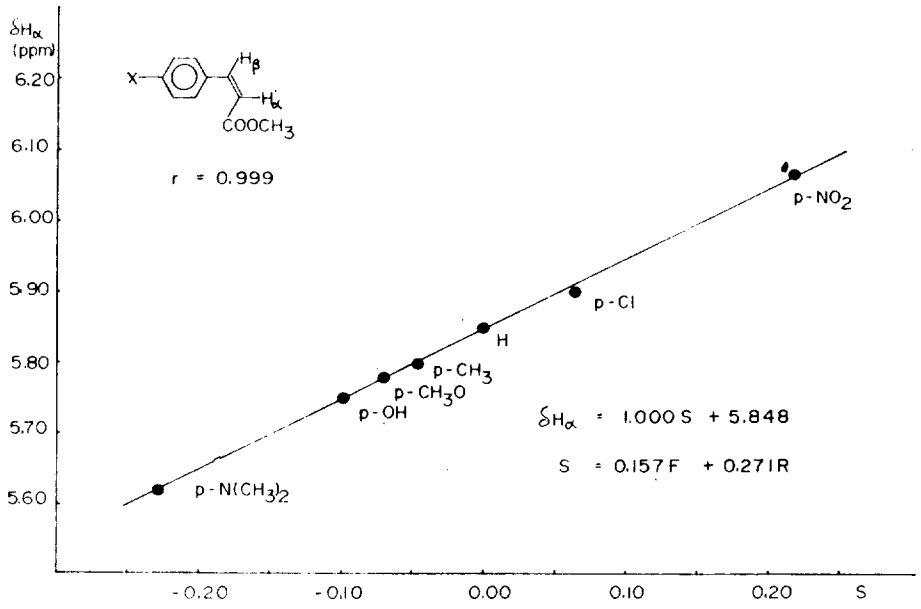

Figure 8. δH_α *vs. (F, R)* for *cis para* substituted methyl cinnamates.

λ_m' =0.93, r=0.879

for only the *cis meta* substituted methyl cinnamates,

$\delta H_\alpha = 0.287\sigma_I + 0.081\sigma_R^\circ + 5.848$
λ_m =0.28, r=0.949
$\delta H_\alpha = 0.184F + 0.045R + 5.846$
λ_m' =0.24, r=0.963

When δH_α values are represented by σ value, *cis*-methyl cinnamates have better correlation with σ than *trans*-methyl cinnamates. When these are correlated with σ_I and, σ_R°, inductive and resonance contribution respectively, both show a good correlationship. When δH_α values are expressed by F and R, as in the case of σ representation, *cis* derivatives have better correlation with F and R than *trans* derivatives. A remarkable result is that variance of δH_α value *versus* change of substituents in *trans* derivatives is similar to that of *cis* derivatives (the slope is 0.296 for *trans* derivatives and 0.284 for *cis* derivatives). The resonance contribution in *trans* derivatives is larger than that in *cis* derivatives (N_p=2.70, N_p'=2.11, N_m=3.39, N_m'=3.88) since coplanarity loss in *cis* derivatives will diminish the resonance contribution. From these interesting results, it is evident that the inductive contribution in *cis* derivatives is larger than that of *trans* derivatives. The resonance contribution in *meta* substituted derivatives is smaller than that of *para* substituted derivatives as expected (λ_p=4.00, λ_p'=3.70, λ_m=0.95, λ_m'=0.93 for *trans* derivatives; λ_p=1.48, λ_p'=1.75, λ_m=0.28, λ_m'=0.24 for *cis* derivatives), and the resonance contribution in *cis p*-substituted derivatives is larger than that of *trans* m-substituted derivatives (λ_p=1.48, λ_p'=1.75; λ_m=0.95, λ_m'=0.93). The inductive effect is the predominant one in *cis m*-substituted derivatives (λ_m=0.28, λ_m'=0.24).

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