J. Korean Chem. Soc., **15**, 293 (1971).

(3) F. H. Ree, T. Ree and H. Eyring, *J. Eng. Mech. Div. Proc. Am. Soc. Civ. Engr.,* **EM1,** 41 (1960); C. H. Kim and T. Ree, *J. Korean Chem. Soc.* **23**, 217.

(4) C. D. Han, *J. Appl. Polym. Sci.,* **18**, 481 (1974).

(5) C. D. Han and Y. W. Kim, *J. Appl. Polym. Sci.,* **19**, 2831 (1975).

(6) S. Krause, *J. Macromol. Sci. Revs. Macromol. Chem.,* **C7**, 251 (1972).

(7) H. Eyring, *J. Chem. Phys.,* **4**, 283 (1936).

The Linear Free Energy Relationship in Cinnamonitrile Derivatives

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Chemical shift differences of vinyl protons of *cis*- and *trans*-cinnamonitrile derivatives are very well correlated with (σ_I, σ_R^0), σ_P^+, and (F, R) $(r=0.9996-0.8946)$, much better correlation than the case of methyl cinnamates. *para*-Substituted and *trans*-cinnamonitrile derivatives have larger resonance contribution than *meta*-substituted and *cis*-derivatives.

Introduction

In our previous paper[1], we reported the linear free energy relationship (LFER) in methyl cinnamates studied by ^{1}H-NMR spectrometry. The chemical shift differences of α-vinyl protons of *trans*- and *cis*-methyl cinnamates are well correlated with Hammett substituent constant σ, (σ_I, σ_R^0)[2] and Swain and Lupton constant[3] $(F\&R)$ $(r=0.999-0.879)$. The resonance contribution is larger in *trans*- and *para*-substituted cinnamates than in *cis*- and *meta*-substituted cinnamates. One of the interesting observations is that the correlation is much better in *cis*-cinnamates than *trans*-cinnamates. It is suspected that the bulky alkoxycarbonyl group (-COOR) may have something to do with this phenomenon. For example, the bulky ester group will diminish the resonance effect substantially in *cis*-cinnamates by causing the nonplanarity of the compounds and the inductive effect will play the dominant role in *cis*-cinnamates as observed.

Therefore, we applied the same methodology to cinnamonitriles to test these kinds of effects. The linear and much smaller cyano group in cinnamonitrile compared to nonlinear, bulkier ester group in cinnamates will maintain the coplanarity even in *cis*-cinnamonitrile derivatives in contrast to cinnamates.

The chemical shift of α-vinyl protons of cinnamonitriles is measured and correlated with LFER parameters such as Hammett substituent constant (σ), Brown and Okamoto constant (σ_P^+), and Swain and Lupton constant $(F\&R)$. The same Hammett equation and its variations[4~6] used for cinnamates as shown below are applied.

$$\delta H_{\alpha, x} = \rho\sigma + \delta H_{\alpha, 0} \tag{eq. 1}$$

$$\delta H_{\alpha, x} = \rho_I \sigma_I + \rho_R \sigma_R + H_{\alpha, 0} \tag{eq. 2}$$

$$\delta H_{\alpha, x} = fF + rR + H_{\alpha, 0} \tag{eq. 3}$$

$$\lambda_p = (\rho_R/\rho_I)_p \tag{eq. 4}$$

$$\lambda'_p = (r/f)_p \tag{eq. 5}$$

$$\lambda_m = (\rho_R/\rho_I)_m \tag{eq. 6}$$

$$\lambda'_m = (r/f)_m \tag{eq. 7}$$

$$N_p = (\lambda_p)_{trans}/(\lambda_p)_{cis} \tag{eq. 8}$$

$$N_p' = (\lambda_p')_{trans}/(\lambda_p')_{cis} \tag{eq. 9}$$

$$N_m = (\lambda_m)_{trans}/(\lambda_m)_{cis} \tag{eq. 10}$$

$$N_m' = (\lambda_m')_{trans}/(\lambda_m')_{cis} \tag{eq. 11}$$

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

Materials. Cinnamonitrile derivatives were synthesized from the corresponding cinnamic acids by the standard method[7,8] as described below. Thionyl chloride was added to cinnamic acid and the mixture was refluxed with stirring for 5-8 hours. Excess thionyl chloride was removed by evaporation and precooled ammonium hydroxide was added dropwise to the residue and stirred with magnetic bar for 5 hours at room temperature to get amide crystals. The amide was filtered with suction, washed with distilled water and dried in vacuo. The dry and finely powdered amide and thionyl chloride mixture was placed in a round bottomed flask and refluxed for 4-7 hours with stirring. The solvent was evaporated off and methylene chloride was added to the reaction mixture. The solution was washed with distilled water, aqueous sodium bicarbonate, and with distilled water.

The organic layer was dried with magnesium sulfate and the solvent was evaporated off to get cinnamonitrile crystals or oil. Thus obtained cinnamonitriles were purified by column chromatography (Wakogel C–200) eluting with *n*-hexane and dichloromethane.

cis-Cinnamonitriles were prepared from the corresponding *trans*-cinnamonitriles photochemically. *trans*-Cinnamonitriles were dissolved in chloroform and placed in a Pyrex cell and irradiated with 300 nm UV light in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Co., Model RPR–208 and RPR–100) for a day to get *cis* isomers.

trans-Cinnamonitrile (97%, Aldrich); UV λ_{max}^{abs}(methanol): 272 nm, λ_{max}^{abs} (chloroform): 272 nm; NMR(chloroform-*d*) 5.83(d, 1H, AB, J=16.6Hz), 7.36(*d*, 1H, AB, *J*=16.6 Hz), 7.42(*s*, 5H): IR(NaCl) ν_{CN}=2215 cm^{-1}, $\nu_{C=C}$=1638 cm^{-1}.

trans-m-Chlorocinnamonitrile is obtained from the corresponding acid (Aldrich,), and recrystallized from dichloromethane and hexane. White crystal; m.p 54–55°C; UV λ_{max}^{abs} (methanol): 268 nm, λ_{max}^{abs} (chloroform): 272 nm; NMR(chloroform-*d*) 5.87(*d*, 1H, AB, *J*=16.8Hz), 7.34(*d*, 1H, AB, *J*=16.8 Hz), 7.28–7.40(*m*, 4H); IR(NaCl) ν_{CN}=2220 cm^{-1}, $\nu_{C=C}$=1640, 965 cm^{-1}.

trans-p-Chlorocinnamonitrile (Aldrich) is recrystallized from methanol. White crystal; m.p 84–84.5° C; UV λ_{max}^{abs} (methanol): 280 nm, λ_{max}^{abs} (chloroform): 283 nm; NMR (chloroform-*d*) 5.84 (*d*, 1H, AB, *J*=16.6 Hz), 7.36 (*d*, 1H, AB, *J*=16.6Hz), 7.40 (*s*, 4H); IR(KBr) ν_{CN}=2220 cm^{-1}, $\nu_{C=C}$=1644 965 cm^{-1}.

trans-m-Methoxycinnamonitrile is obtained from the corresponding acid (97 %, Aldrich). Liquid at room temperature; UV λ_{max}^{abs}(methanol): 274 nm, λ_{max}^{abs} (chloroform): 276 nm; NMR(chloroform-*d*) 5.75(*d*, 1H, AB, *J*=16.6Hz), 7.23(*d*, 1H, AB, *J*=16.6Hz), 6.80–7.30(*m*, 4H), 3.87 (*s*, 3H); IR(NaCl) ν_{CN}=2225 cm^{-1}, $\nu_{C=C}$=1645, 967 cm^{-1}.

trans-p-Methoxycinnamonitrile (98%, Aldrich) is separated from *cis-trans* mixture. White crystal; m.p 54–55°C; UV λ_{max}^{abs} (methanol): 305 nm, λ_{max}^{abs} (chloroform): 308 nm; NMR 5.68 (*d*, 1H, AB, 16.8Hz), 7.37 (*d*, 1H, AB, *J*=16.8Hz), 6.85, 7.00, 7.36, 7.51(*dd*, 4H, AA'BB'), 3.82(*s*, 3H); IR (KBr) ν_{CN}=2215cm^{-1}, $\nu_{C=C}$=1600cm^{-1}.

trans-m-Nitrocinnamonitrile is synthesized from the corresponding acid (99 %, Aldrich), and recrystallized from

dichloromethane. White crystal; m.p 157–157.5 °C; UV λ_{max}^{abs} (methanol) 258 nm, λ_{max}^{abs} (chloroform): 272 nm; NMR (chloroform-*d*) 6.06(*d*, 1H, AB, *J*=16.8Hz), 7.51(*d*, 1H, AB, *J*=16.8 Hz), 7.60–8.40(*m*, 4H): IR(KBr) ν_{CN}=2222 cm^{-1}, $\nu_{C=C}$=1645, 967 cm^{-1}.

trans-p-Nitrocinnamonitrile is obtained from the corresponding acid (TCI), and recry stallized from dichloromethane. Yellow crystal; m.p 197–196°C; UV λ_{max}^{abs}(methanol) 288 nm, λ_{max}^{abs} (chloroform): 297 nm; NMR (chloroform-*d*) 6.03(*d*, 1H, AB, *J*=16.6 Hz), 7.46(*d*, 1H, AB, *J*=16.6Hz), 7.53, 7.68, 8.19, 8.34(*dd*, 4H, AA'BB'); IR(KBr) ν_{CN}= 2225 cm^{-1}, $\nu_{C=C}$=1638, 975 cm^{-1}.

trans-m-Bromocinnamonitrile is obtained from the corresponding acid (Aldrich), and recrystallized from hexane dichloromethane. Pale yellow crystal: m.p 57–58 °C; UV λ_{max}^{abs} (methanol): 270nm, λ_{max}^{abs} (chloroform): 272 nm; NMR (chloroform-*d*) 5.88(*d*, 1H, AB, *J*=16.6 Hz), 7.34(*d*, 1H AB, *J*=16.N Hz), 7.25–7.60(*m*, 4H); IR(KBr) ν_{CN}=2215 cm^{-1}, $\nu_{C=C}$=1645, 966 cm^{-1}.

trans-p-Methylcinnamonitrile is obtained from the corresponding acid (99 %, Aldrich), and recrystallized from methanol. White crystal; m.p 68°C; UV λ_{max}^{abs} (methanol): 285 nm, λ_{max}^{abs} (chloroform): 285 nm: NMR(chloroform-*d*) 5.80(*d*, 1H, AB, *J*=16.8 Hz), 7.38(*d*, 1H, AB, *J*=16.8 Hz), 7.13, 7.27, 7.32, 7.42(*dd*, 4H, AA'BB'), 2.37(*s*, 3H); IR(KBr) ν_{CN}=2220 cm^{-1} $\nu_{C=C}$=1640, 960 cm^{-1}.

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 or sodium chloride cell and Ultraviolet–visible spectra were recorded on a Cary–17 spectrophotometer.

Results

The chemical shifts of α-(δH_α) and β-vinyl protons (δH_β) of *cis*- and *trans*-cinnamonitriles in chloroform-*d* are tabulated in Table 1 along with the values of various substituent constants. These chemical shift values are correlated with the substituent constants σ, σ_m, σ_p, σ_p^+, σ_I & σ_R^0 and *F* & *R* and are shown in Figure 1–7 and Tables 2–5. All these results are simultaneously optimized by multiple linear regression algolism.

TABLE 1: Chemical Shifts of α- and β-Vinyl Protons of Cinnamonitrile Deverivatives and Values of Substituent Constants

Substituent	δH_α(ppm)		δH_β(ppm)	F^a	R^a	σ^a	σ_p^{+a}	σ^b_I	σ_R^b
	trans	*cis*	*trans*						
p-CH₃O	5.69	5.33	7.37	0.413	−0.500	−0.268	−0.648	0.26	−0.41
p-CH₃	5.80	5.37	7.38	−0.052	−0.141	−0.170	−0.256	−0.05	−0.10
H	5.83	5.42	7.36	0.000	0.000	0.000	0.000	0.00	0.00
m-CH₃O	5.75	5.33	7.23	0.413	−0.500	0.115		0.26	−0.41
p-Cl	5.84	5.48	7.36	0.690	−0.161	0.227	0.035	0.47	0.20
m-Cl	5.87	5.52	7.34	0.690	−0.161	0.373		0.47	−0.20
m-Br	5.88	5.52	7.34	0.727	−0.176	0.391		0.45	0.16
m-NO₂	6.06	5.69	7.51	1.109	0.155	0.710		0.64	0.19
p-NO₂	6.03	5.69	7.47	1.109	0.155	0.778	0.740	0.64	0.19

^{a} From ref. 3, ^{b} From ref. 5.
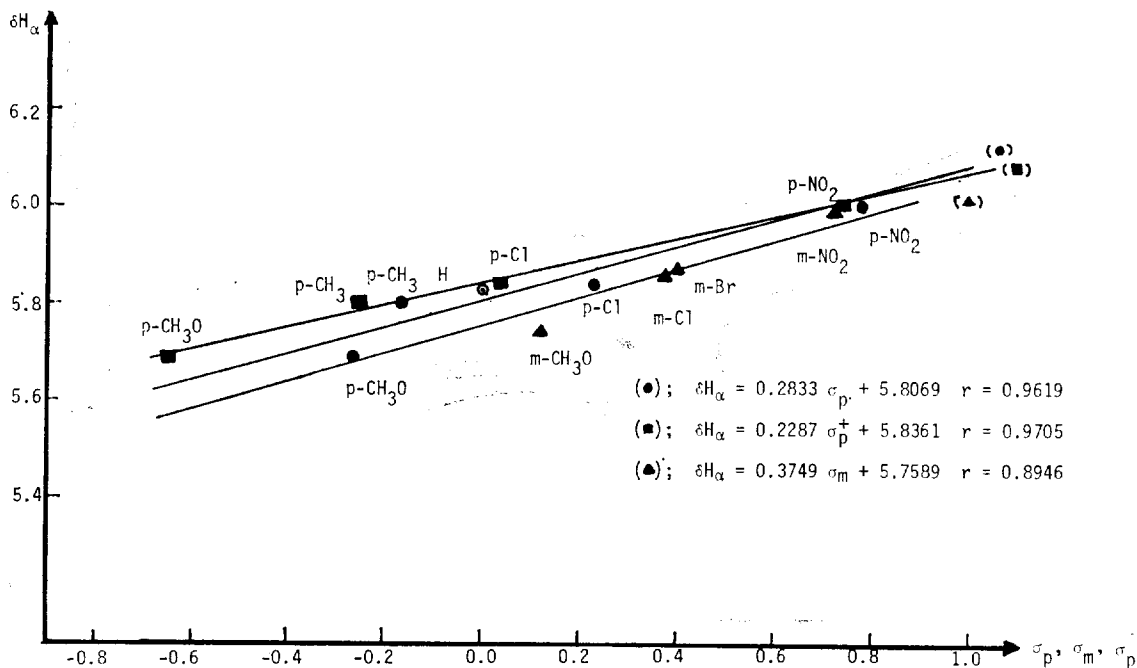
Figure 1. δH_α vs. σ_p, σ_m, and σ_p^+ for *trans*-cinnamonitrile derivatives.

$(\bullet)$; $\delta H_\alpha = 0.2833\ \sigma_p + 5.8069$ $r = 0.9619$

$(\blacksquare)$; $\delta H_\alpha = 0.2287\ \sigma_p^+ + 5.8361$ $r = 0.9705$

$(\blacktriangle)$; $\delta H_\alpha = 0.3749\ \sigma_m + 5.7589$ $r = 0.8946$
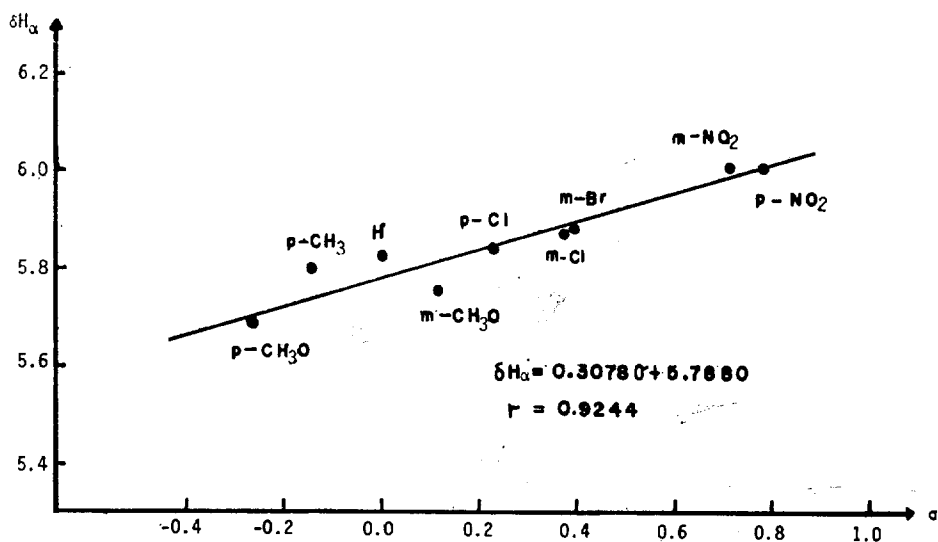
Discussion

The correlation between the chemical shifts of α- and β-vinyl protons of *cis*- and *trans*-cinnamonitriles and various substituent constants is very good in all cases (r =0.9996–0.8946), much better than the case of methyl cinnamates as expected. The differences in correlation between *cis*-and *trans* cinnamonitriles are much smaller than those of cinnamates probably because the coplanarity is maintained even in *cis*-cinnamonitriles in contrast to *cis*-cinnamates.
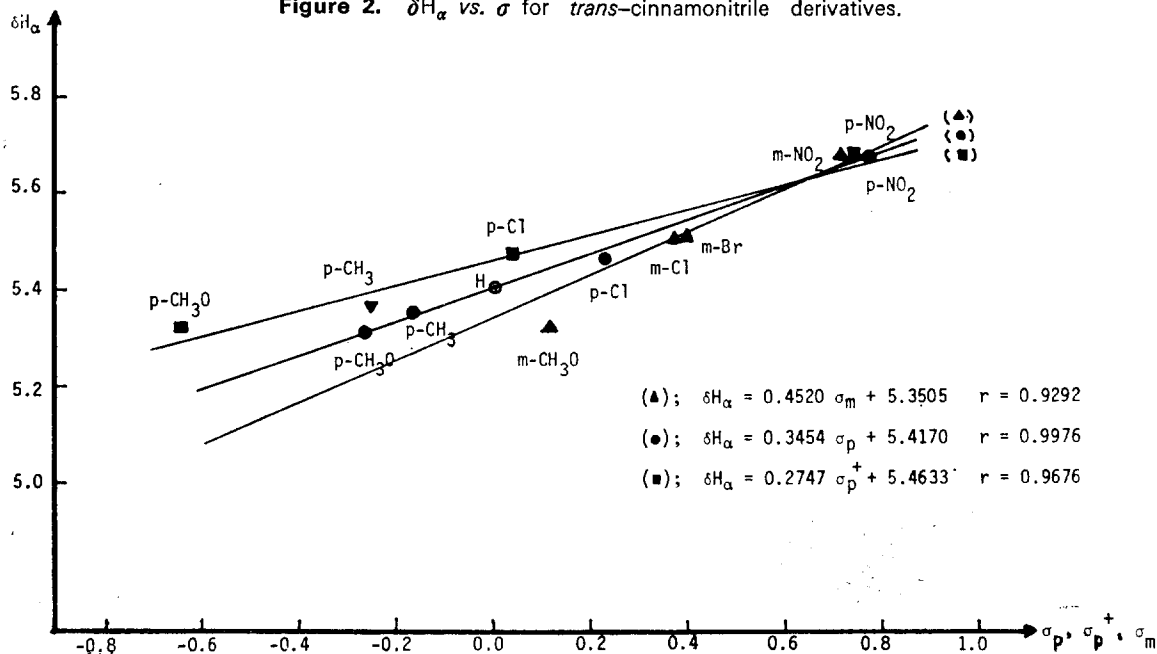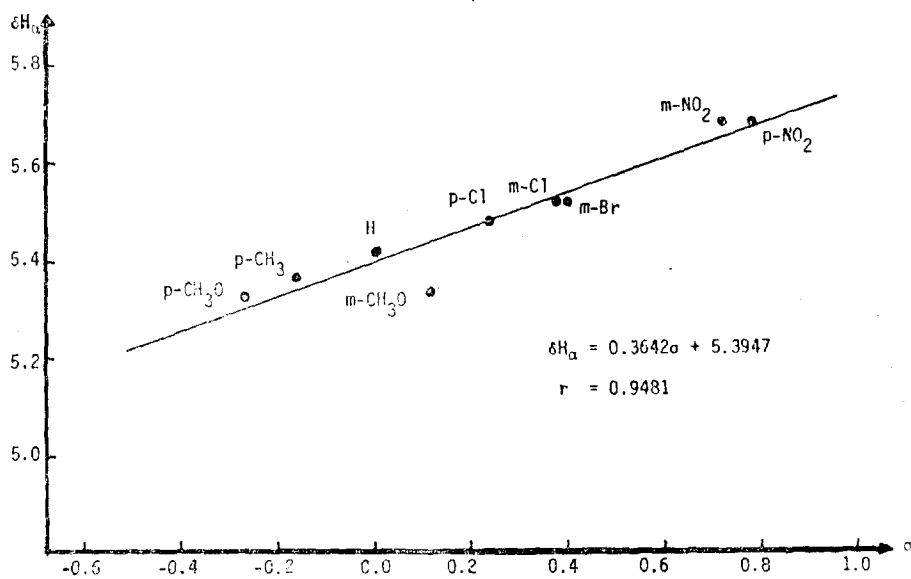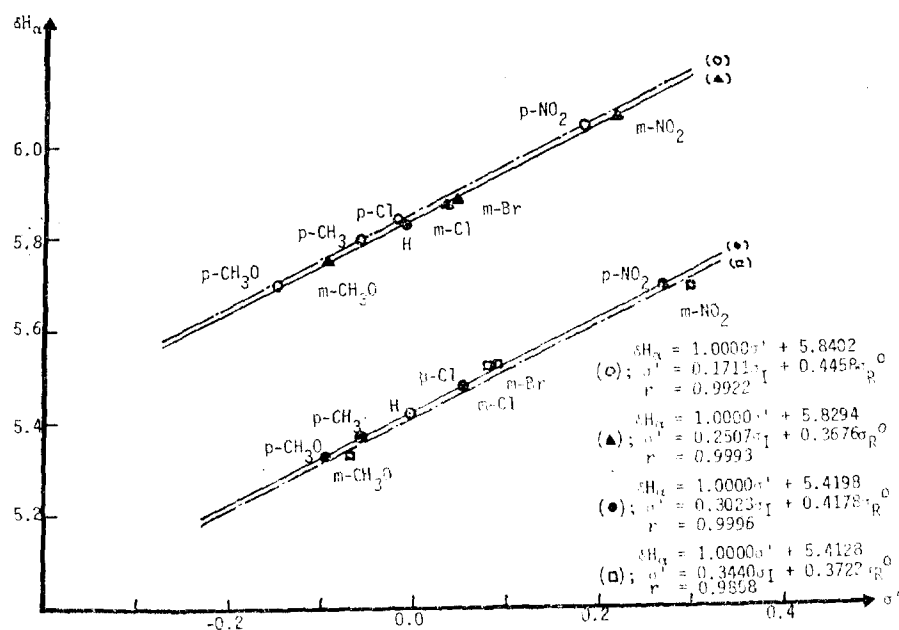

$\delta H_\alpha = 0.3078\ \sigma + 5.7880$

$r = 0.9244$

Figure 2. δH_α vs. σ for *trans*-cinnamonitrile derivatives.

$(\blacktriangle)$; $\delta H_\alpha = 0.4520\ \sigma_m + 5.3505$ $r = 0.9292$

$(\bullet)$; $\delta H_\alpha = 0.3454\ \sigma_p + 5.4170$ $r = 0.9976$

$(\blacksquare)$; $\delta H_\alpha = 0.2747\ \sigma_p^+ + 5.4633$ $r = 0.9676$

Figure 3. δH_α vs. σ, σ_{pm}, and σ_p^+ for *cis*-cinnamonitrile derivatives.

$\delta H_\alpha = 0.3642\sigma + 5.3947$

$r = 0.9481$

Figure 4. δH_α vs. σ for cis–cinnamonitrile derivatives.

Figure 5. δH_α vs. (σ_I, σ_R^0) for cinnamonitrile derivatives.
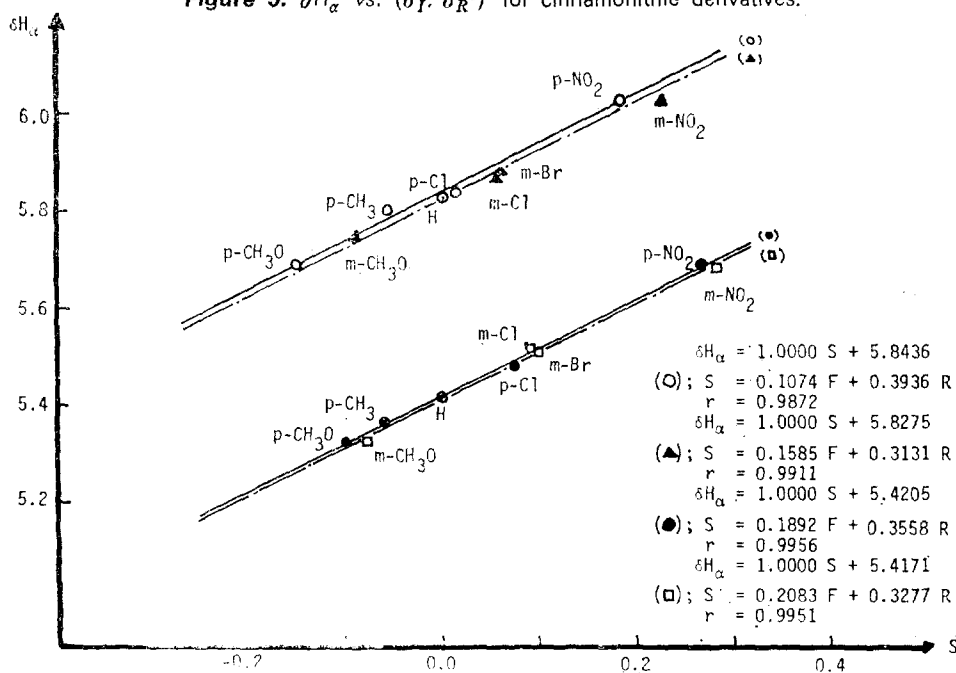
Figure 6. δH_α vs. (F,R) for cinnamonitrile derivatives.

When δH_α values are correlated with σ, cis–cinnamonitrile derivatives $(r=0.9481)$ show slightly better correlationship than *trans* derivatives $(r=0.9244)$. The best correlation is observed when δH_α is correlated with Brown and Okamoto constant σ_p^+ in *trans*-cinnamonitriles but σ_p gives the best correlation in *cis*–cinnamonitriles.

When $(\sigma_I,\ \sigma_R^0)$ and (F, R) are used, both *cis*- and *trans*-cinnamonitriles give good results where *cis* shows nearly equal or slightly better correlation than the *trans*-derivatives. However, the difference between *cis*- and *trans*-cinnamonitriles is again much smaller than that of cinnamates. From the correlation of δH_α and (σ_I, σ_R^0), the larger resonance contribution in *para*-substituted *trans*-cinnamonitriles $(\lambda_p=2.6213)$ is apparent compared to *cis*-derivatives $(\lambda_p=1.3821)$. The same results are obtained in *meta*-substituted cinnamonitriles except the smaller contribution of resonance effect in *meta* compared to *para*-substituted cinnamonitriles $(\lambda_{m,trans}=1.4663,\quad \lambda_{m,cis}=1.0820)$. When δH_α values are expressed by (F, R), the similar phenomena are observed $(\lambda'_{p,trans}=2.3100, \lambda'_{p,cis} =1.8805;\ \lambda'_{m,trans}=1.9754, \lambda'_{m,cis}= 1.5732)$. However, the differences of resonance contribution in *trans*- and *cis*–cinnamonitriles are much smaller than those of cinnamates which can be attributed to the coplanarity of *trans*- and *cis*-cinnamonitriles. From the comparison of the same resonance contribution to the inductive and field effect, the field effect is greater than the inductive effect in *trans*-cinnamonitriles $(\lambda_{p,trans}>\lambda'_{p,trans})$. However, the inductive effect contributes more than the field effect in *para*-substituted *cis*-cinnamonitriles and in both isomers of *meta*-substituted cinnamonitriles $(\lambda_{p,cis} <\lambda'_{p,cis};\ \lambda_{m,trans} < \lambda'_{m,trans};\ \lambda_{m,cis} < \lambda'_{m,cis})$. In methyl cinnamates, the inductive effect was greater than the field effect in all cases except the *para*-substituted *cis*-cinnamates
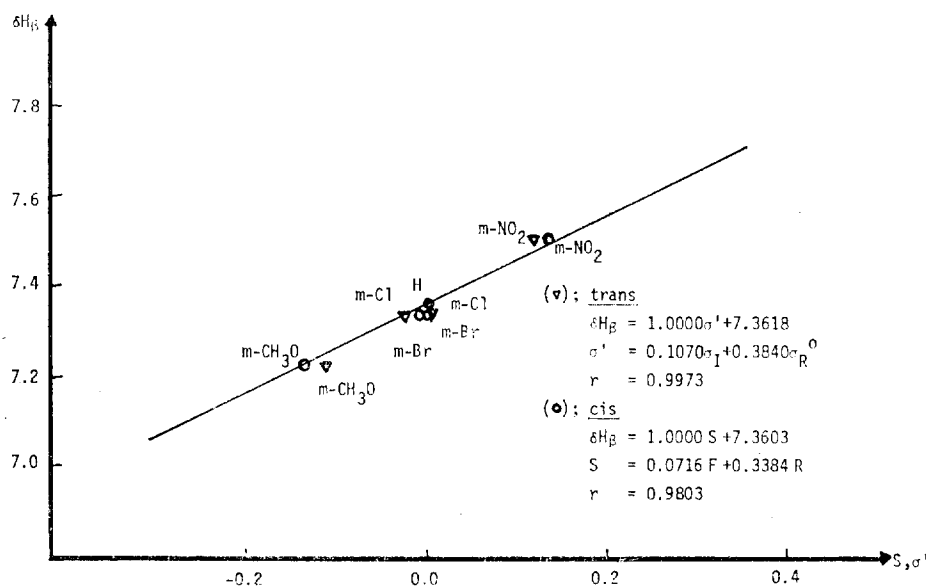
Figure 7. δH_β vs. (σ_I, σ_R^0) and (F,R) for *meta*-substituted cinnamonitrile derivatives.

(▼): trans
$$\delta H_\beta = 1.0000\sigma'+7.3618$$
$$\sigma' = 0.1070\sigma_I+0.3840\sigma_R^0$$
$$r = 0.9973$$

(○): cis
$$\delta H_\beta = 1.0000\,S +7.3603$$
$$S = 0.0716\,F +0.3384\,R$$
$$r = 0.9803$$

TABLE 2: Correlation of δH_α with Substituent Constants in *trans*-Cinnamonitrile Derivatives

Substituent constant	$^\sigma H_{\alpha,0}$	ρ	r
σ_p	5.8069	0.2833	0.9619
σ	5.7880	0.3078	0.9244
σ_m	5.7589	0.3749	0.8946
σ^+_p	5.8361	0.2287	0.9705

TABLE 3: Correlation of δH_α with Substituent Constants in *cis*-Cinnamonitrile Derivatives

Substituent Constant	$\delta H_{\alpha,0}$	ρ	r
σ_p	5.4170	0.3454	0.9976
σ	5.3947	0.3642	0.9481
σ_m	5.3505	0.4540	0.9292
σ_p^+	5.4633	0.2747	0.9676

TABLE 4: Correlation of δH_α with Substituent Constants in *para*-Substituted Cinnamonitrile Derivatives

Substituent constant		$\delta H_{\alpha,0}$	$\rho_I(f)$	$\rho_R(\gamma')$	r
$\sigma_I\&\sigma_R^0$ vs. δH_α	trans	5.8402	0.1711	0.4458	0.9922
	cis	5.4198	0.3023	0.4178	0.9996
$F\,\&\,R$ vs. δH_α	trans	5.8436	0.1074	0.3936	0.9872
	cis	5.4205	0.1892	0.3558	0.9956

TABLE 5: Correlation of δH_α with Substituent Constants in *meta*-Substituted Cinnamonitrile Derivatives

Constant		$\delta H_{\alpha,0}$	$\rho_I(f)$	$\rho_R(\gamma')$	r
$\sigma_I\&\sigma_R^0$ vs. δH	trans-H_α	5.8294	0.2507	0.3676	0.9993
	trans-H_β	7.3618	0.1070	0.3840	0.9973
	cis-H_α	5.4128	0.3440	0.3722	0.9858
$F\,\&\,R$ vs. δH	trans-H_α	5.8275	0.1585	0.3131	0.9911
	trans-H_β	7.3603	0.0716	0.3384	0.9803
	cis-H_α	5.4171	0.2083	0.3277	0.9951

$(\lambda_{p,cis}=1.48, \lambda'_{p,cis}=1.75)$.

The ratio of λ values are calculated by the equations 4-11 and are shown below. The ratio is much smaller than that of methyl cinnamates

	N_p	N_p'	N_m	N_m'
Cinnamonitriles	1.90	1.23	1.36	1.23
Methyl cinnamates	2.70	2.11	3.39	3.88

again substantiating the explanation by the coplanarity of *cis*-cinnamonitriles. The resonance contribution is still greater in *para*-substituted *trans*-cinnamonitriles than in *cis*- and *meta*-substituted cinnamonitriles.

References

(1) S. C. Shim and J. W. Park, *Bull. Kor. Chem. Soc.,* **2**, 29 (1981).

(2) N. B. Chapman and J. Shorter, "Correlation Analysis Chemistry", Chap 4, Chap 8, Plenum Press., New York, N. Y., 1978.

(3) C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.,* **90**, 4328 (1968).

(4) L. P. Hammett, "Physical Organic Chemistry," 2nd Ed., p. 347, McGraw-Hill, Tokyo, 1970.

(5) P. R. Wells, S. Ehrenson and R. W. Taft, *Progr. Phys. Org. Chem.,* **6**, 147 (1968).

(6) S. G. Williams and F. E. Norrington, *J. Amer. Chem. Soc.,* **98**, 508 (1976).

(7) E. C. Horning Ed., "Organic Syntheses," Coll. Vol. 3, p. 491, 714, John Wiley & Sons. Inc., New York, 1955.

(8) N. Rabjohn Ed., "Organic Syntheses," Coll. Vol. 4, p. 436, John Wiley & Sons. Inc., New York, 1963.