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## The Linear Free Energy Relationship in Cinnamionitrile Derivatives

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

### Introduction

In our previous paper<sup>1</sup>, we reported the linear free energy relationship (LFER) in methyl cinnamates studied by <sup>1</sup>H-NMR spectrometry. The chemical shift differences of  $\alpha$ -vinyl protons of *trans*- and *cis*-methyl cinnamates are well correlated with Hammett substituent constant  $\sigma$ ,  $(\sigma_I, \sigma_R^0)^2$  and Swain and Lupton constant<sup>3</sup> ( $F \& R$ ) ( $r=0.999-0.879$ ). 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 alkoxy carbonyl 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 cinnamionitriles to test these kinds of effects. The linear and much smaller cyano group in cinnamionitrile compared to nonlinear, bulkier ester group in cinnamates will maintain the coplanarity even in *cis*-cinnamionitrile derivatives in contrast to cinnamates.

The chemical shift of  $\alpha$ -vinyl protons of cinnamionitriles is measured and correlated with LFER parameters such as Hammett substituent constant ( $\sigma$ ), Brown and Okamoto constant ( $\sigma_p^+$ ), and Swain and Lupton constant ( $F \& R$ ). The same Hammett equation and its variations<sup>4-6</sup> used for cinnamates as shown below are applied.

$$\delta H_{\alpha,x} = \rho\sigma + \delta H_{\alpha,0} \quad (\text{eq. 1})$$

$$\delta H_{\alpha,x} = \rho_I\sigma_I + \rho_R\sigma_R + H_{\alpha,0} \quad (\text{eq. 2})$$

$$\delta H_{\alpha,x} = fF + rR + H_{\alpha,0} \quad (\text{eq. 3})$$

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

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

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

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

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

$$N'_p = (\lambda'_p)_{trans}/(\lambda'_p)_{cis} \quad (\text{eq. 9})$$

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

$$N'_m = (\lambda'_m)_{trans}/(\lambda'_m)_{cis} \quad (\text{eq. 11})$$

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  $\lambda$ .

### Experimental

**Materials.** Cinnamionitrile derivatives were synthesized from the corresponding cinnamic acids by the standard method<sup>7,8</sup> 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 cinnamionitrile crystals or oil. Thus obtained cinnamionitriles were purified by column chromatography (Wakogel C-200) eluting with *n*-hexane and dichloromethane.

*cis*-Cinnamionitriles were prepared from the corresponding *trans*-cinnamionitriles photochemically. *trans*-Cinnamionitriles 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*-Cinnamionitrile (97%, Aldrich); UV  $\lambda_{max}^{abs}$  (methanol): 272 nm,  $\lambda_{max}^{abs}$  (chloroform): 272 nm; NMR(chloroform-*d*) 5.83(*d*, 1H, AB,  $J=16.6$ Hz), 7.36(*d*, 1H, AB,  $J=16.6$  Hz), 7.42(*s*, 5H); IR(NaCl)  $\nu_{CN}=2215$  cm<sup>-1</sup>,  $\nu_{C=C}=1638$  cm<sup>-1</sup>.

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

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

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

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

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

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

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

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

*trans-p*-Methylcinnamionitrile is obtained from the corresponding acid (99%, Aldrich), and recrystallized from methanol. White crystal; m.p 68°C; UV  $\lambda_{max}^{abs}$  (methanol): 285 nm,  $\lambda_{max}^{abs}$  (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)  $\nu_{CN}=2220$  cm<sup>-1</sup>  $\nu_{C=C}=1640$ , 960 cm<sup>-1</sup>.

**Spectral Data.** <sup>1</sup>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  $\alpha$ -( $\delta H_\alpha$ ) and  $\beta$ -vinyl protons ( $\delta H_\beta$ ) of *cis*- and *trans*-cinnamionitriles 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  $\sigma$ ,  $\sigma_m$ ,  $\sigma_p$ ,  $\sigma_p^+$ ,  $\sigma_I$  &  $\sigma_R^0$  and *F* & *R* and are shown in Figure 1–7 and Tables 2–5. All these results are simultaneously optimized by multiple linear regression algorithm.

TABLE 1: Chemical Shifts of  $\alpha$ - and  $\beta$ -Vinyl Protons of Cinnamionitrile Deverivatives and Values of Substituent Constants

Substituent	$\delta H_\alpha$ (ppm)		$\delta H_\beta$ (ppm)	<i>F</i> <sup>a</sup>	<i>R</i> <sup>a</sup>	$\sigma^a$	$\sigma_p^+$	$\sigma_I$	$\sigma_R^b$
	<i>trans</i>	<i>cis</i>	<i>trans</i>						
<i>p</i> -CH <sub>3</sub> O	5.69	5.33	7.37	0.413	-0.500	-0.268	-0.648	0.26	-0.41
<i>p</i> -CH <sub>3</sub>	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
<i>m</i> -CH <sub>3</sub> O	5.75	5.33	7.23	0.413	-0.500	0.115		0.26	-0.41
<i>p</i> -Cl	5.84	5.48	7.36	0.690	-0.161	0.227	0.035	0.47	0.20
<i>m</i> -Cl	5.87	5.52	7.34	0.690	-0.161	0.373		0.47	-0.20
<i>m</i> -Br	5.88	5.52	7.34	0.727	-0.176	0.391		0.45	0.16
<i>m</i> -NO <sub>2</sub>	6.06	5.69	7.51	1.109	0.155	0.710		0.64	0.19
<i>p</i> -NO <sub>2</sub>	6.03	5.69	7.47	1.109	0.155	0.778	0.740	0.64	0.19

<sup>a</sup> From ref. 3, <sup>b</sup> From ref. 5.

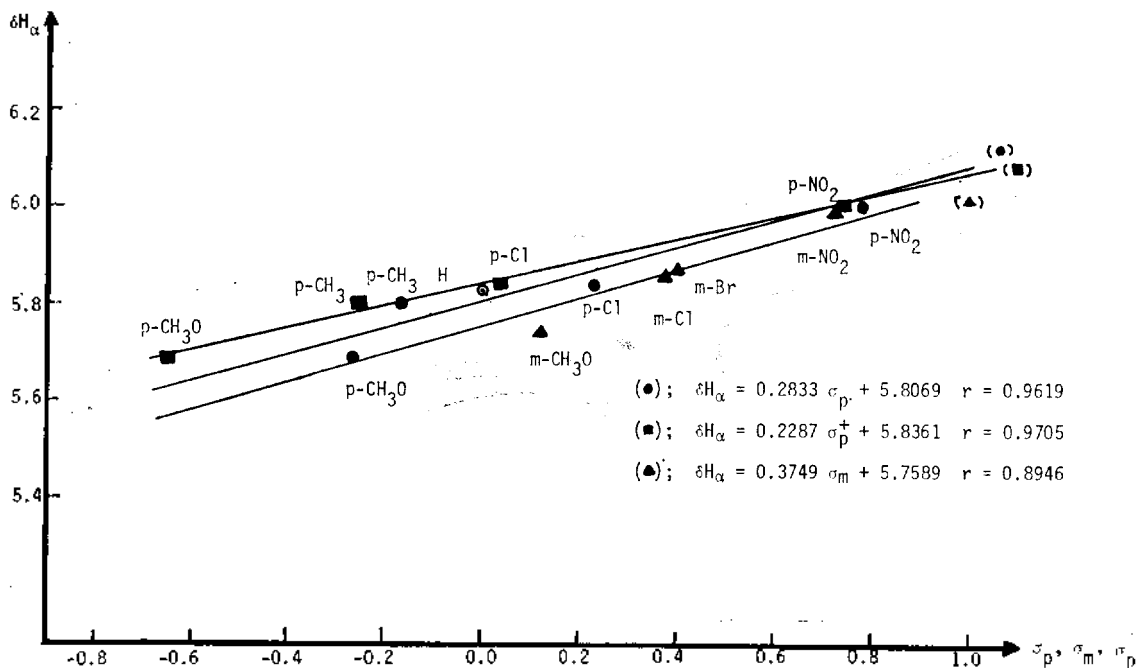


Figure 1.  $\delta H_\alpha$  vs.  $\sigma_p$ ,  $\sigma_m$ , and  $\sigma_p^+$  for *trans*-cinnamionitrile derivatives.

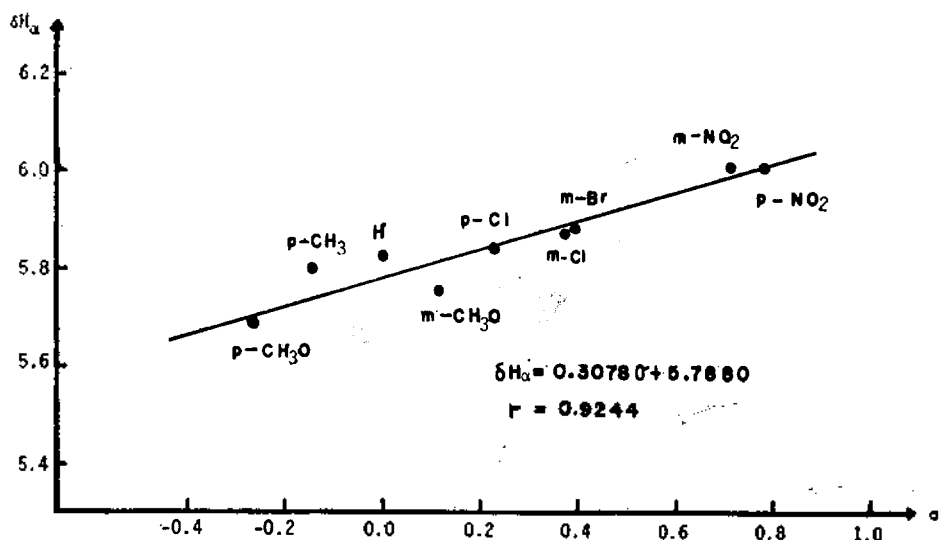


Figure 2.  $\delta H_\alpha$  vs.  $\sigma$  for *trans*-cinnamionitrile derivatives.

Discussion

The correlation between the chemical shifts of  $\alpha$ - and  $\beta$ -vinyl protons of *cis*- and *trans*-cinnamionitriles 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* cinnamionitriles are much smaller than those of cinnamates probably because the coplanarity is maintained even in *cis*-cinnamionitriles in contrast to *cis*-cinnamates.

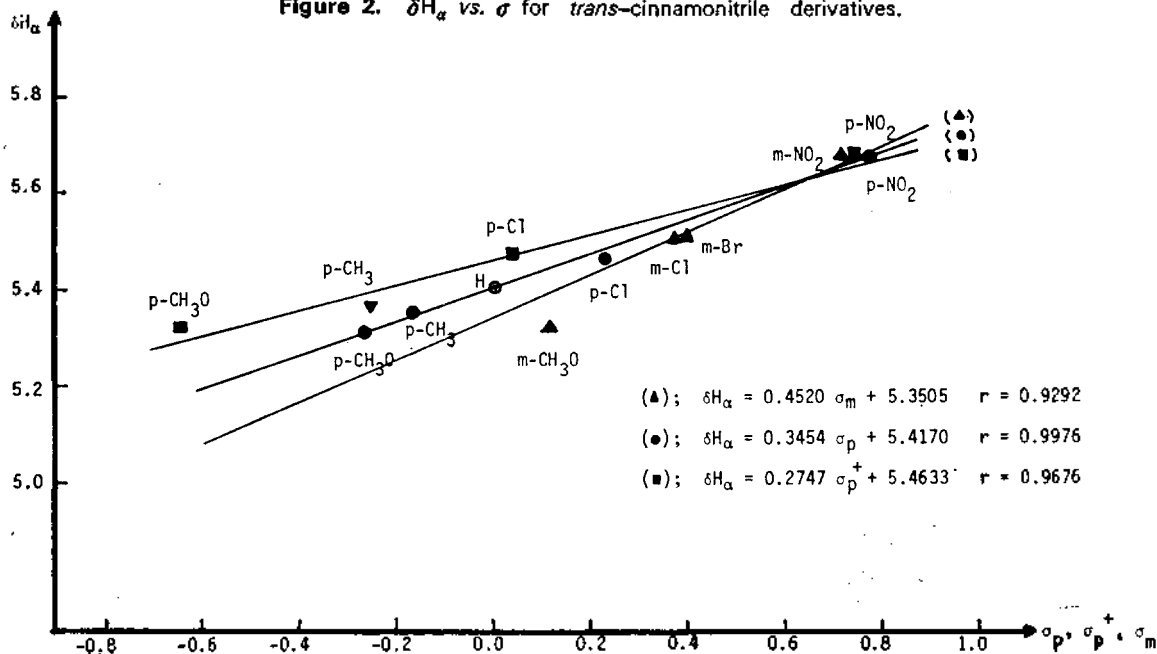
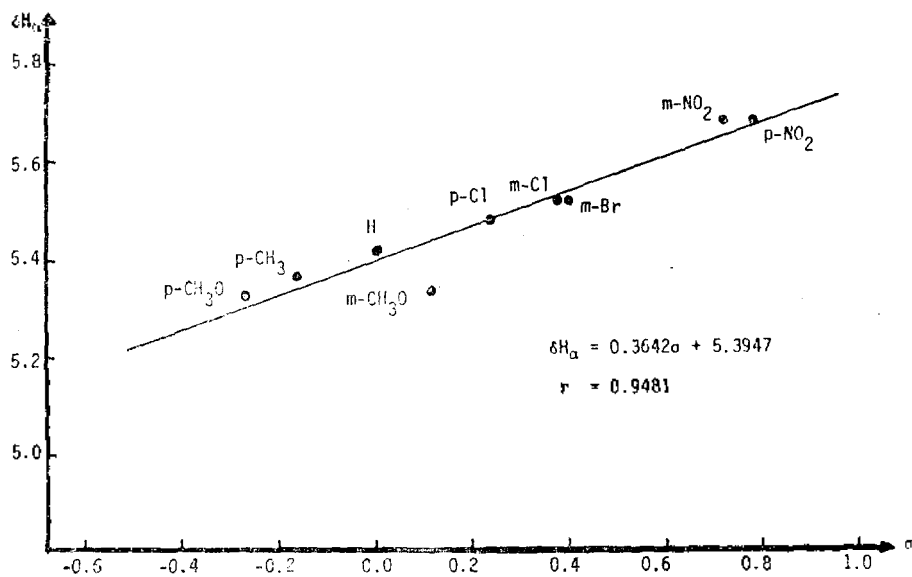
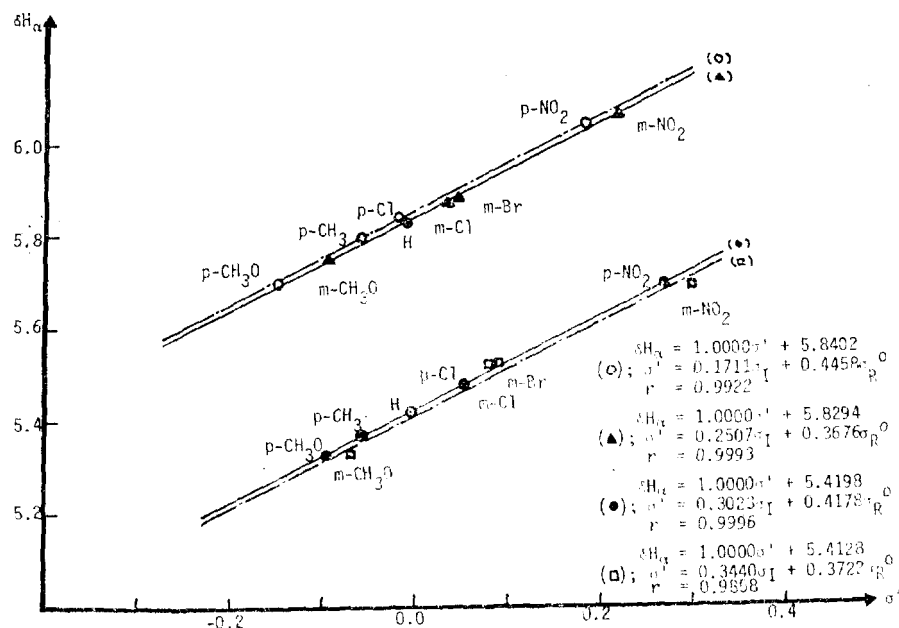
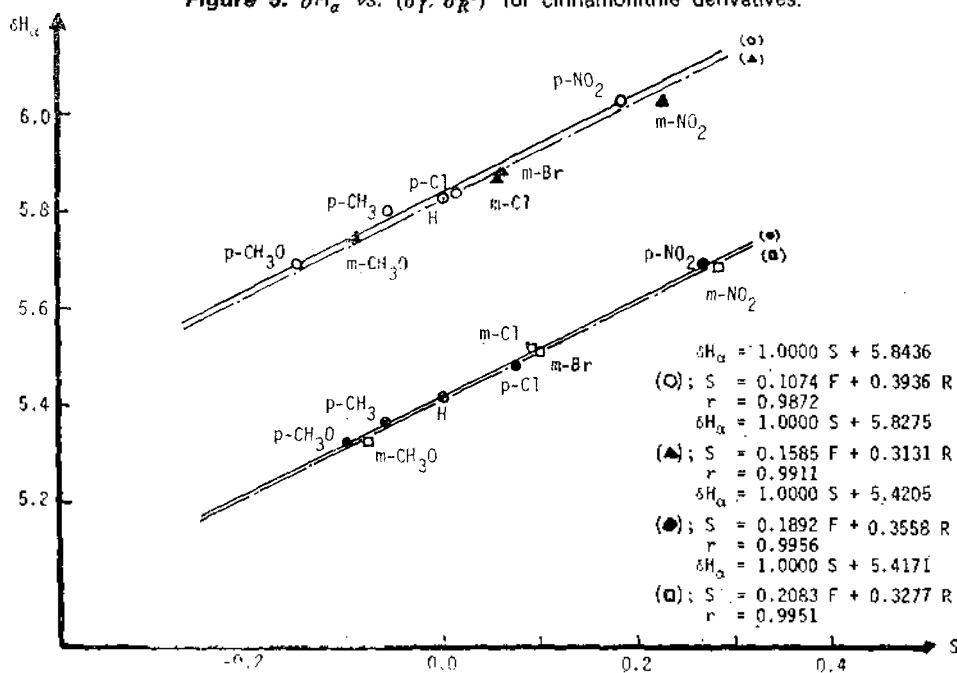


Figure 3.  $\delta H_\alpha$  vs.  $\sigma$ ,  $\sigma_p$ ,  $\sigma_m$ , and  $\sigma_p^+$  for *cis*-cinnamionitrile derivatives.

Figure 4.  $\delta H_\alpha$  vs.  $\sigma$  for *cis*-cinnamitrile derivatives.Figure 5.  $\delta H_\alpha$  vs.  $(\sigma'_I, \sigma'_R)$  for cinnamitrile derivatives.Figure 6.  $\delta H_\alpha$  vs.  $(F, R)$  for cinnamitrile derivatives.

When  $\delta H_\alpha$  values are correlated with  $\sigma$ , *cis*-cinnamitrile derivatives ( $r=0.9481$ ) show slightly better correlation than *trans* derivatives ( $r=0.9244$ ). The best correlation is observed when  $\delta H_\alpha$  is correlated with Brown and Okamoto constant  $\sigma_p^+$  in *trans*-cinnamitriles but  $\sigma_p$  gives the best correlation in *cis*-cinnamitriles.

When  $(\sigma_I, \sigma_R^0)$  and  $(F, R)$  are used, both *cis*- and *trans*-cinnamitriles give good results where *cis* shows nearly equal or slightly better correlation than the *trans*-derivatives. However, the difference between *cis*- and *trans*-cinnamitriles is again much smaller than that of cinnamates. From the correlation of  $\delta H_\alpha$  and  $(\sigma_I, \sigma_R^0)$ , the larger resonance contribution in *para*-substituted *trans*-cinnamitriles ( $\lambda_p=2.6213$ ) is apparent compared to *cis*-derivatives ( $\lambda_p=1.3821$ ). The same results are obtained in *meta*-substituted cinnamitriles except the smaller contribution of resonance effect in *meta* compared to *para*-substituted cinnamitriles ( $\lambda_{m,trans}=1.4663$ ,  $\lambda_{m,cis}=1.0820$ ). When  $\delta H_\alpha$  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*-cinnamitriles are much smaller than those of cinnamates which can be attributed to the coplanarity of *trans*- and *cis*-cinnamitriles. 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*-cinnamitriles ( $\lambda_{p,trans} > \lambda'_{p,trans}$ ). However, the inductive effect contributes more than the field effect in *para*-substituted *cis*-cinnamitriles and in both isomers of *meta*-substituted cinnamitriles ( $\lambda_{p,cis} < \lambda'_{p,cis}$ ;  $\lambda_{m,trans} < \lambda'_{m,trans}$ ;  $\lambda_{m,cis} < \lambda'_{m,cis}$ ). In methyl cinnamates, the inductive effect was greater than the field effect in all cases except the *para*-substituted *cis*-cinnamates

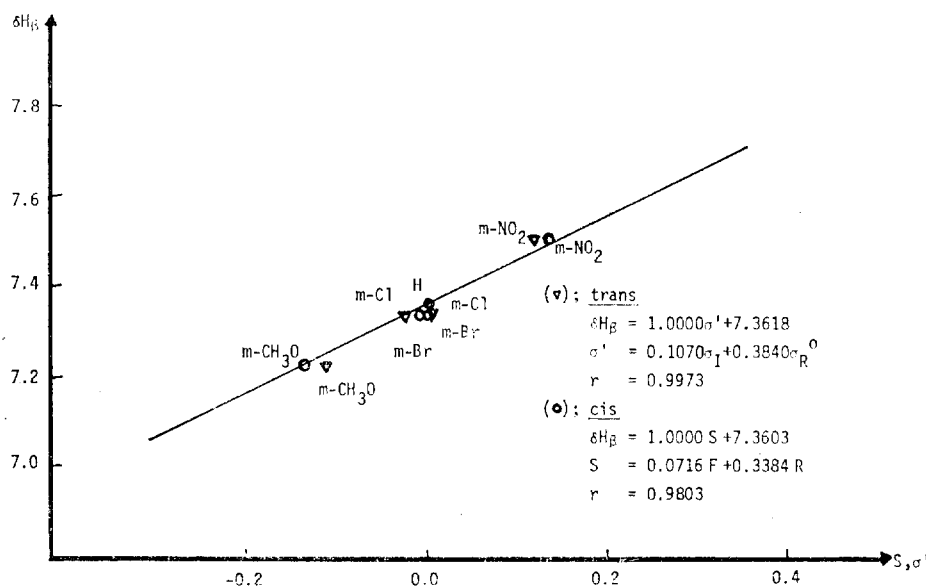


Figure 7.  $\delta H_{\beta}$  vs.  $(\sigma_I, \sigma_R^0)$  and  $(F, R)$  for *meta*-substituted cinnamitrilo derivatives.

TABLE 2: Correlation of  $\delta H_{\alpha}$  with Substituent Constants in *trans*-Cinnamitrilo Derivatives

Substituent constant	$\sigma_{H_{\alpha,0}}$	$\rho$	$\gamma$
$\sigma_p$	5.8069	0.2833	0.9619
$\sigma$	5.7880	0.3078	0.9244
$\sigma_m$	5.7589	0.3749	0.8946
$\sigma_p^+$	5.8361	0.2287	0.9705

TABLE 3: Correlation of  $\delta H_{\alpha}$  with Substituent Constants in *cis*-Cinnamitrilo Derivatives

Substituent Constant	$\delta H_{\alpha,0}$	$\rho$	$\gamma$
$\sigma_p$	5.4170	0.3454	0.9976
$\sigma$	5.3947	0.3642	0.9481
$\sigma_m$	5.3505	0.4540	0.9292
$\sigma_p^+$	5.4633	0.2747	0.9676

TABLE 4: Correlation of  $\delta H_{\alpha}$  with Substituent Constants in *para*-Substituted Cinnamitrilo Derivatives

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

TABLE 5: Correlation of  $\delta H_{\alpha}$  with Substituent Constants in *meta*-Substituted Cinnamitrilo Derivatives

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

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

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

	$N_p$	$N_p'$	$N_m$	$N_m'$
Cinnamitriles	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*-cinnamitriles. The resonance contribution is still greater in *para*-substituted *trans*-cinnamitriles than in *cis*- and *meta*-substituted cinnamitriles.

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