Transmission of substituent effects through extended systems—II. Substituted cis and trans cinnamonitriles

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Abstract—Infrared data and ¹³C chemical shifts are reported for a series of p-substituted *cis* and *m*-substituted *trans* cinnamonitriles. The i.r. values include intensities for the benzene, ethylene and cyanide vibrations which allow an estimation of resonance effects, These results are compared with those previously reported for *p*-substituted *trans* cinnamonitriles and discussed in terms of the relative importance of the various mechanisms of transmission of electronic effects. In particular, it is shown that the transmission of resonance effects through *cis* and *trans* ethylenic linkages is virtually identical.

INTRODUCTION

The transmission of substituent effects through unsaturated systems has attracted much interest and the various possible mechanisms of such transmissions are now broadly understood [1, 2, 3]. The mechanisms depend on the polar or the resonance properties of the substituent and their relative importance may differ considerably from one series of molecules to another. Hence, a good fit can often be found to equation (1) for a change in property (P) from that in the unsubstituted parent (P°).

$$P - P^0 = \rho_I \sigma_I + \rho_R \bar{\sigma}_R. \tag{1}$$

In this dual substituent parameter equation [4], σ_I is a measure of the polar character of a substituent, while the resonance parameter $\bar{\sigma}_R$ may take the various values σ_R^- , σ_R^0 , σ_R^{BA} , σ_R^+ depending on the demand for conjugative interaction.

The aim of the present investigation is to compare the efficiency of the varying modes of transmission over extended conjugated systems. We earlier reported [1] results for a series of *p*-substituted *trans* cinnamonitriles (IA) and here extend the work to *m*-substituted cinnamonitriles (IB) and *p*-substituted *cis* cinnamonitriles (II). The results for these compounds can also be compared to i.r. and ¹³C shift studies on di-substituted benzenes [5] including *p*-substituted styrenes [6, 7], *m*- and *p*substituted benzonitriles [8, 9] and on 1,2-di



Scheme 1.

substituted ethylenes [10]. These results should allow considerable insight into the differential transmission of resonance and polar effects. This is of particular interest in that some authors [11, 12] have suggested that there is a constant balance of the two effects in related systems.

Substituent effect studies need to be based on a sufficient number and variety of substituents. Recent work [4,13] suggests that two strong π -electron donors, H, Me, F, Cl or Br, and two suitable π -electron withdrawers provide a good basis set.

EXPERIMENTAL AND RESULTS

The purity of each compound was confirmed by proton NMR, i.r. and ¹³C NMR. In many cases, preparative thin layer chromatography or column chromatography was required for complete separation of the isomers. In these cases preprepared Merck Silica-gel 60 F-254 plates were used. Eluants were all pre-dried and pre-distilled by procedures recommended in the literature.

Preparation of cis-cinnamonitriles

The p-nitro cis cinnamonitrile was prepared by the Knoevenagel condensation [14] using pyridinepiperidine (method A) as a solvent-catalyst mixture. The procedure was described earlier [1]. The crude product was a 60/40 mixture of *trans* and *cis* isomers. The filtrate from this recrystallization was concentrated to give an 80/20 mixture of the *cis* and *trans* isomers. The pure *cis* isomer was then obtained by recrystallization.

The general method of obtaining the pure *cis* cinnamonitriles was a stepwise Knoevenagel condensation (method B) in which the intermediate beta-cyanocinnamic acid [15] was isolated and subsequently decarboxylated [16]. The following procedure was used.

Cyanoacetic acid (0.1 mol) was dissolved in an

aqueous potassium hydroxide solution (0.2 mol per 80 ml), and to this was added the substituted aldehyde (0.1 mol). The reaction mixture was heated on a water bath to approximately 40° and then allowed to come to room temperature over 1 h. The precipitated sodium salt was acidified with concentrated hydrochloric acid and allow to stand for a further hour. This was filtered, washed with cold water, dried, then washed with benzene and again allowed to dry. No further purification was required but a proton NMR was run to check that any unreacted starting materials had been removed. Yields of up to 90% of the cyanocinnamic acid were obtained.

The decarboxylation [16] was carried out by heating the substituted cinnamic acid (2.5 g) and cuprous oxide (0.1 g) with a bunsen flame under a vacuum of about 5 mm or less. If the *cis* cinnamonitrile did not readily distill, the crude product was extracted from the reaction mixture with chloroform. The pure *cis* isomer was obtained by either crystallization or chromatographic techniques.

The para substituted cis cinnamonitriles prepared were (*p*-substituent, method of preparation, melting or boiling point, literature value or elementary analysis): NMe₂, B, 60-61°, 63° [17], OMe, B, $125-127^{\circ}/2$ mm, (calculate for C₁₀H₉NO: C, 75.44; H, 5.70; N, 8.80. Found: C, 75.06; H, 5.76; N, 8.90%); F, B, 40-42°, (calculate for C₉H₆FN: C, 73.44; H, 4.12; N, 9.52. Found: C, 73.27; H, 4.56; N, 9.92%); Cl, B, 62-63°, 66.5-67.5°, [16]; Br, B, 65-66°, 69-69.5°, [16]; CH₃, B, 136-138°/27 mm, (calculate for C₁₀H₉N: C, 83.87; H, 6.34; N, 9.78. Found: C, 83.78; H, 6.38; N, 9.86%); H, B, 127-130°/25 mm, 105-106°/10 mm, [16]; CN, B, 126-128°; (calculate for C₁₀H₆N₂: C, 77.91; H, 3.92; N, 18.18. Found: C, 77.76; H, 4.19; N, 18.12%); NO₂, A, 110-112°, 107°, [18].

Preparation of the meta trans cinnamonitriles

All of the *meta trans* cinnamonitriles, except the *meta*-amino cinnamonitrile, were prepared by the Meerwein arylation (method C) [19, 20] as described earlier [1].

The *meta*-amino cinnamonitrile was prepared by reduction of the *meta*-nitro cinnamonitrile with 10% palladium on charcoal with hydrazine hydrate in ethanol (method D). The pure amino compound was obtained after chromatography on a silica-gel column and eluting with ethyl acetate.

The meta-substituted trans cinnamonitriles prepared were (*m*-substituent, method of preparation, melting or boiling point, literature value or elementary analysis): NH₂, D, 78–79°, (calculate for C₉H₈N₂: C, 74.97; H, 5.60; N, 19.43. Found: C, 75.12; H, 5.54; N, 19.30%); OMe, C, 185– 190°/28 mm; (calculate for C₁₀H₉NO: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.40; H, 5.85; N, 8.62%); F, C, 58–60°, (calculate for C₉H₆FN: C, 73.44; H, 4.12; N, 9.52. Found: C, 73.64; H, 4.31; N, 9.46%); Br, C, 62–64°, (calculate for C_9H_6BrN : C, 51.94; H, 2.91: N, 6.73. Found: C, 51.70; H, 3.06; N, 6.68%); Me, C, 160–165°/25 mm, (calculate for $C_{10}H_9N$: C, 83.87; H, 6.34; N, 9.78. Found: C, 83.35; H, 6.40; N, 9.69%); COCH₃, 88–90°, (calculate for $C_{11}H_9NO$: C, 77.19; H, 5.30; N, 8.18. Found: C, 76.77; H, 5.30; N, 7.85%); CF₃, 140–142°/27 mm, (calculate for $C_{10}H_6F_3N$: (C, 60.90; H, 3.07; N, 7.10. Found: C, 61.26; H, 3.21; N, 7.12%); CN, 129–130°, (calculate for $C_{10}H_6N_2$: C, 77.90; H, 3.93; N 18.18. Found: C, 77.23; H, 4.18; N, 17.90% NO₂, 150–152°, 159°, [21].

Treatment of i.r. spectra

The i.r. frequencies and intensities were measured on a Perkin-Elmer 225 Grating Spectrometer using spectroscopic grade carbon tetrachloride or chloroform (dried over molecular sieves) as solvents. Potassium bromide cells were used, the fixed cell having a path length of 0.00898 cm. The cell path length was calculated using the standard interference method. For each compound, solutions of approximately 0.04, 0.03 and 0.01 M were prepared in duplicate. The intensity and frequency of the peak at infinite dilution was then determined by fitting the results to the line of best fit as determined by a least squares calculation.

The spectra were integrated using the Bandfit program of FRASER and SUZUKI [22] where a blend of Gaussian and Lorentzian peaks are fitted to complement the experimental spectrum.

The results for the *m*-substituted trans cinnamonitriles are given in Table 1 and for the *p*-substituted cis cinnamonitriles in Table 2.

¹³C NMR spectra

Spectra were recorded at 25 MHz on a Jeol JNM-PFT-100 PFT spectrometer with an EC-100 computer operating in a single pulsed Fourier transform mode with proton noise decoupling. Deuterochloroform was used as an internal reference. Samples were prepared in deuterochloroform to a concentration of approximately 75 mg/1.4 ml. Substituent chemical shifts were obtained by referencing the substituted compound to the parent number. Positive shifts are taken as downfield from the internal standard deuterochloroform.

The results for the *m*-substituted *trans* cinnamonitriles are given in Table 3 and for the *p*-substituted *cis* cinnamonitriles in Table 4.

DISCUSSION

In our earlier publication [1], we analysed the transmission of substituent electronic effects in *para*-substituted *trans* cinnamonitriles. In particular, we estimated the reduction in π -transfer between the cyano group and the benzene ring caused by the interposition of the ethylene bridge, the magnitude of polarization of the C-C and

Substance	$\nu_{\rm B}$ (benzene) A	v ₂ (ethylene) A	ν	ν _{CN} Α
NH ₂	2511	5791	2219.2	2082
OMe	4579	1100	2222.5	2610
F	2996	1135	2222.9	2241
Br	1468	1085	2222.6	2117
CH ₁	1354	1456	2219.3	1363
Н	416	2016	2220.9	1358
CF ₃	133	1242	2223.0	1469
CŃ	200	808	2224.3	*
NO ₂	301	699	2223.5	886

Table 1. Infrared data for *m*-substituted *trans* cinnamonitriles (ν in cm⁻¹, A in 1 mol⁻¹ cm⁻²)

*Intensities for the two cyano vibrations could not be separated.

Table 2. Infrared data for *p*-substituted *cis* cinnamonitriles (ν in cm⁻¹, A in 1 mol⁻¹ cm⁻²)

Substance	ν_8 (benzene) A	v ₂ (ethylene) A	ν _{CN} ν	A
NMe ₂	19824*		2210.5	3691
OMe	7550	702	2212.5	2188
F	3722	330	2216.0	1207
Cl	1366	1617	2217.9	1536
Br	1284	832	2217.3	1497
CH	2971*		2218.7	1843
Н	316	2118	2220.6	1443
CN	272	582	2220.4	1111
NO ₂	3064*		2220.8	848

* ν_8 and ν_2 not able to be separated.

Table 3. ¹³C chemical shifts (ppm for *trans* cinnamonitrile*, negative shifts denote upfield shifts) for *meta*-substituted *trans* cinnamonitriles

Substance	C-1	С-а	С- β	C-(CN)
NH ₂	1.21	0.51	- 0.19	0.39
OMe	1.41	0.15	0.44	0.09
F	2.04	- 1.06	1.75	-0.44
Br	2.23	- 1.50	1.99	-0.54
CH ₃	0.05	0.44	- 0.24	0.29
H	0.00	0.00	0.00	0.00
CF ₁	0.88	- 1.45	2.53	- 0.49
COCH	0.58	-0.87	1.75	- 0.29
CN	1.21	- 2.42	3.25	-0.78
NO ₂	1.70	-2.42	3.89	- 0.88

*Shifts in *trans* cinnamonitrile in ppm from the centre line of CDCl₃ are C-1, 56.30; C- α , 73.19; C- β , 19.12; C-(CN), 40.87.

cyano unsaturated linkages, the amount of π -electron transfer caused by substituent field effects, and also showed that canonical form III was an important contribution to the overall structure.

It is convenient to use the results for this system as a standard to estimate the relative effects of, firstly, *meta*-substituted *trans* cinnamonitriles and then of *para*-substituted *cis* cinnamonitriles.



Scheme 2.

Table 4. ¹³C chemical shifts (ppm from *cis* cinnamonitrile*, negative shifts denote upfield shifts) for *para*-substituted *cis* cinnamonitriles

Substance	C-1	<u>C</u> -α	С-в	C-(CN)
NMe ₂	- 11.94	- 0.39	-7.43	1.65
OMe	- 6.99	-0.63	- 3.16	0.64
F	- 3.79	- 1.36	- 0.44	- 0.09
Br	- 1.36	- 1.36	0.72	- 0.38
Cl	- 1.56	- 1.46	0.63	- 0.29
CH ₃	-2.62	-0.10	-1.41	0.29
Н	0.00	0.00	0.00	0.00
CN	3.78	-2.33	3.83	- 1.06
NO ₂	5.53	- 2.62	4.61	- 1.06

*Shifts in cis cinnamonitrile in ppm from centre line of CDCl3 are C-1, 56.50; C- α , 71.64; C- β , 18.01; C-(CN), 40.28.

Comparison of transmission between meta- and para-substituted trans cinnamonitriles

A comparison can best be made through the use of the dual substituent parameter equation for the appropriate property and position. Thus, for the ¹³C substituent chemical shifts (SCS), the relevant equations are (2-9). These employ the corresponding set of resonance parameters in each pair to facilitate comparison. [Slightly better fits were found in equation (2) to σ_R^0 and in equation (4) to σ_R^+ .] The normalized standard deviation [4] is shown in parentheses after each equation. The equation for the *meta* series is shown first in each pair.

Carbon-1 SCS:

$$2.9\sigma_I - 1.5\sigma_R^{BA} \quad (0.23) \tag{2}$$

$$5.0\sigma_I + 14.5\sigma_R^{BA} \quad (0.09) \tag{3}$$

Carbon- α SCS:

$$-3.4\sigma_I - 1.8\sigma_R^{0}$$
 (0.18) (4)

$$-3.3\sigma_I - 1.3\sigma_R^{0} \quad (0.14) \tag{5}$$

Carbon- β SCS:

$$5.4\sigma_I + 1.8\sigma_R^{BA} \quad (0.05) \tag{6}$$

$$6.0\sigma_I + 8.1\sigma_R^{BA} \quad (0.12) \tag{7}$$

Carbon-(CN) SCS:

$$-1.2\sigma_I - 0.4\sigma_R^+ \quad (0.18) \tag{8}$$

$$-1.2\sigma_I - 1.1\sigma_R^+$$
 (0.08). (9)

The inductive effect from the substituents is remarkably similar for the two series at distant $(C-\alpha, C-\beta, C-(CN))$ centres. The value at the ring carbon -1 also reflects π -polarization effects which lead to a greater value in the *para* series [23]. This is good evidence for the transmission of such effects by a field mechanism which, in energy terms, should be proportional to $(\mu \cos \theta)/Dr^2$, where μ is the substituent dipole, θ the angle subtended to the direction of that dipole by the line drawn to the distant centre, *r* the corresponding distance and *D* the effective dielectric constant. The distance *r* would be slightly less in the *meta* series than in the *para* series but the cos θ term would likewise be somewhat smaller. Apparently these two effects almost balance out.

The resonance effects are, as expected, of little significance in determining the SCS in the *meta*-substitution *trans* cinnamonitriles. An interesting feature is the similar magnitude, but opposite sign, for the equations describing the SCS of carbons α and β . This is clear evidence for the polarisation of this bond both by the field effect of the substituent and indirectly from the dipole created by the resonance interaction of the substituent with the benzene ring [24]. The somewhat larger value of the inductive transmission at the β -position may arise from contributions from canonical forms such as IV.

The i.r. data support these calculations. The relevant equations are as follows, again with the *meta* series recorded first

 v_2 (ethylene)

$$A^{1/2} - A^{1/2}_{0} = -29.3\sigma_I - 0.7\sigma_R^0 \quad (0.24) \quad (10)$$

$$A^{1/2} - A^{1/2} = -29.4\sigma_I - 10.4\sigma_R^0 \quad (0.26) \quad (11)$$

 $v_{\rm CN}$

$$\nu - \nu_0 = 4.6\sigma_I + 1.3\sigma_R^+$$
 (0.17) (12)

$$v - v_0 = 4.9\sigma_I + 5.3\sigma_R^+$$
 (0.08). (13)

The inductive transmissions are remarkably similar in each case and the resonance effect is not significant in the *meta* series. These results also show the wide range of relative resonance and inductive transmissions to various centres in the molecule showing the inappropriateness of a single sigma parameter, combining both inductive and resonance effects.

Comparison of the transmission of substituent effects in cis and trans cinnamonitriles

The para-substituted series were chosen for this comparison because of the important resonance transmission here compared to the corresponding meta compounds. The relevant dual substituent parameter equations for the SCS of the para-substituted cis cinnamonitriles are (14)-(17)which can be compared with the corresponding equations (3), (5), (7), (9), for the trans series.

Carbon-1

$$4.4\sigma_{\rm I} + 14.3\sigma_{\rm R}^{BA} \quad (0.11) \tag{14}$$

Carbon-a

$$-3.5\delta_I + -0.6\sigma_R^{-}(0.14) \tag{15}$$

Carbon $-\beta$

$$5.5\sigma_I + 8.5\sigma_R^{BA}$$
 (0.13) (16)

Carbon-CN

$$-1.5\sigma_I + -1.0\sigma_R^+ \quad (0.07). \tag{17}$$

We note the close similarity of the results between the *cis* and *trans* series, in all positions. The results clearly show almost equal resonance transmission in the two systems. The SCS at the carbon- β are slightly better (nsd = 0.09) fitted to the σ_{R}^+ scale for the *cis* but not for the *trans* series; the reason for this is discussed below. The reversal of the signs of the inductive effect at C- α and C-(CN) is again explicable in terms of the polarisation of the unsaturated linkage by the substituent dipole.

The i.r. results support the finding that the resonance transmission is equal in the *cis* and *trans* ethylene bridges. Thus, the intensities of the v_{CN} vibrations are represented by equations (18) and (19) for the *cis* and *trans* cinnamonitriles respectively

$$A^{1/2} - A_0^{1/2} = -8.4\sigma_I - 12.7\sigma_R^+ \quad (0.14) \quad (18)$$

$$A^{1/2} - A_0^{1/2} = -8.1\sigma_I - 12.6\sigma_R^+ \quad (0.08). \quad (19)$$

Since these intensities reflect the changing ability of the cyano triple bond to interact with the π systems of neighbouring groups, it is clear that the resonance transmissions are effectively identical. The inductive terms reflect a π -polarization of the phenyl and ethylene systems leading to a changing interaction with the cyano π -system.

By contrast, the corresponding equations for the frequencies show differing inductive dependencies

$$\nu - \nu_0 = -1.9\sigma_I + 6.2\sigma_R^+ \quad (0.14) \tag{20}$$

$$\nu - \nu_0 = 4.9\sigma_I + 5.3\sigma_R^+ \quad (0.08), \tag{21}$$

This is expected, since the frequencies depend on the immediate electronic environment of the cyano group. The relative geometry of the cyano group to the substituent in the *cis* series (VI) mean that it is polarized in the opposite direction to that in the *trans* series (V).



CONCLUSION

A considerable number of investigations [25] have appeared concerning transmission through ethylene bonds including series $XC_6H_4CH = CYZ$. Nevertheless, the relative effectiveness of inductive and resonance transmissions through *cis* and *trans* ethylenic linkages was not clear. We have now clearly shown that resonance effects are transmitted effectively equally in the two geometrical arrangements. Inductive transmission depends on the relative geometry. It is clearly inappropriate therefore to use a single substituent parameter to correlate effects, for example in the ν_{CN} substituent induced frequency changes.

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