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Effect of substituents on the ^{13}C NMR chemical shifts of para-substituted α-phenyl-β-pyridylacrylic acids

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Abstract

The ^{13}C NMR spectra of para-substituted α-phenylcinnamic and 3- and 4-pyridylacrylic acids, with a wide range of substituents effects, were determined in deuterated dimethylsulfoxide (DMSO-d_6). The effect of substituents in both the α-phenyl and β-pyridine groups in these acids is investigated using linear free energy relationships and multiple regression analysis as applied to ^{13}C NMR chemical shifts of the C_α and C_β of the ethylenic bond and the carboxylic group carbon. Dissection of the α-phenyl substituent effects into the inductive and resonance components, using the dual substituent parameter (DSP) method, points to a blend of inductive and resonance effects in the π-electronic system. © 1997 Elsevier Science B.V.

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1. Introduction

In our previous paper [1] we presented the results of the investigation of the reactivities of *trans*-α-phenylcinnamic and substituted *trans*-α-phenyl 3- and 4-pyridylacrylic acids in order to study the transmission of substituents effects through the π-electronic system. The reaction employed was esterification with diazodiphenylmethane (DDM) in the solvent dimethylformamide, at 30°C, using the well-known spectrophotometric method for kinetic measurements. The Hammett equation in its original form was applied to the experimentally determined values of the reaction constants, using the sum of substituent constants from both aromatic nuclei, but the overall correlation was only fair. A better insight into the transmission of substituents effects was obtained using Taft's dual substituent parameter equation (DSP method) and it was possible to distinguish between the contribution from the inductive (ρ_I) and the resonance (ρ_R) effects of the substituents.

In the present work we investigated substituents effects in para-substituted α-phenylcinnamic and 3- and 4-pyridylacrylic acids on the ^{13}C NMR chemical shifts of the α- and β-carbon atoms of the ethylenic bonds, and also of the carboxylic group carbon. The simple Hammett equation and Taft's DSP equation are used to study the transmission of electronic effects through the delocalised π-electronic system, as in our earlier investigations [2–4] of *trans*-pyridylacrylic, substituted *trans*-cinnamic and meta-substituted *trans*-α-phenylpyridylacrylic acids.

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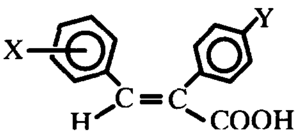
The structural formula of the acids investigated, all of E configuration, is as follows:



where X,Y: H,H (**I**); H,*p*-Cl (**II**); H,*p*-OCH_3 (**III**); H,*p*-NO_2 (**IV**); 3N,H (**V**); 3N,*p*-Cl (**VI**); 3N,*p*-Br (**VII**); 3N,*p*-CH_3 (**VIII**), 3N,*p*-OCH_3 (**IX**); 3N,*p*-NO_2 (**X**); 4N,H (**XI**); 4N,*p*-Cl (**XII**); 4N,*p*-Br (**XIII**); 4N,*p*-CH_3 (**XIV**), 4N,*p*-OCH_3 (**XV**); 4N,*p*-NO_2 (**XVI**).

2. Experimental

The acids investigated were prepared by Perkin condensation of the appropriate aldehyde with substituted phenylacetic acids in acetic anhydride following the procedure already described in our previous paper [1] and identified by m.p.s, microanalysis and MS data.

The ^{13}C NMR spectra of the compounds investigated were recorded in deuterated dimethylsulfoxide (DMSO-d_6) with tetramethylsilane (TMS) as internal reference standard using a Bruker AC 250E spectrometer (DEP; APT ^{13}C, ^{1}H-hetcor; ^{13}C, ^{1}H-coupled; ^{13}C{1H} NMR) operating at 62.9 MHz and room temperature.

Table 1
^{13}C NMR chemical shifts of para-substituted α-phenylcinnamic and α-phenyl 3- and 4-pyridylacrylic acids (SCS)[a]

Acid (X,Y)	C_α	C_β	$C_{C=O}$
I H,H	133.47	139.00	168.42
II H,*p*-Cl	132.37	139.44	168.12
III H,*p*-OCH_3	133.03	138.69	168.69
IV H,*p*-NO_2	131.77	140.34	167.40
V 3N,H	135.40	135.72	167.91
VI 3N,*p*-Cl	134.25	136.34	167.60
VII 3N,*p*-Br	134.24	136.27	167.49
VIII 3N,*p*-CH_3	135.40	135.43	168.11
IX 3N,*p*-OCH_3	135.10	135.27	168.21
X 3N,*p*-NO_2	133.70	137.32	167.03
XI 4N,H	137.60	136.26	167.79
XII 4N,*p*-Cl	136.30	136.87	167.44
XIII 4N,*p*-Br	136.30	136.80	167.35
XIV 4N,*p*-CH_3	137.50	135.89	167.93
XV 4N,*p*-OCH_3	137.20	135.72	168.07
XVI 4N,*p*-NO_2	135.88	137.70	166.88

[a] ^{13}C NMR chemical shifts caused by substituents are given in ppm relative to TMS.

3. Results and discussion

The ^{13}C chemical shifts of the C_α and C_β atoms of the ethylenic bond and the carboxylic group carbon are given in Table 1. σ_X substituent constants are from [4] and have the following values: $\sigma_{3N} = 0.74$ and $\sigma_{4N} = 1.105$. σ_Y [6] are as follows: $\sigma_{p\text{-Cl}} = 0.23$; $\sigma_{p\text{-Br}} = 0.23$, $\sigma_{p\text{-CH}_3} = -0.17$; $\sigma_{p\text{-OCH}_3} = -0.27$; $\sigma_{p\text{-NO}_2} = 0.78$. Inductive substituent constants (σ_{IY}) and resonance substituent constants (σ_{RY}) from [5] are as follows: *p*-Cl ($\sigma_I = 0.46$; $\sigma_R = -0.23$); *p*-Br (σ I$=0.44$, $\sigma_R = -0.19$) *p*-CH_3 ($\sigma_I = -0.04$, $\sigma_R = -0.11$); *p*-OCH_3 ($\sigma_I = 0.27$, $\sigma_R = -0.61$); *p*-NO_2 ($\sigma_I = 0.65$, $\sigma_R = 0.15$).

The simple Hammett correlation in the form of the equation

$$SCS = \rho(\sigma_X + \sigma_Y) \qquad (1)$$

was not possible for the ^{13}C chemical shifts of the C_α and C_β ethylenic bond and carboxylic group carbon, which showed that the effects of substituents from the α-phenyl nucleus and of the pyridine nitrogen on the C_α, C_β and carboxylic group carbon are too complex to be explained in this simple manner.

It is of particular interest to analyze the ^{13}C chemical shifts from Table 1 using Taft's DSP method in the form of the equation:

$$SCS = \rho_X\sigma_X + \rho_{IY}\sigma_{IY} + \rho_{RY}\sigma_{RY} \qquad (2)$$

because it is thus possible to separate the effects of the substituents from the α-phenyl nucleus into the inductive (σ_{IY}) and resonance (σ_{RY}) components while the total effects of the pyridine nitrogen (− I, − R effect) is encompassed in the corresponding σ_X constant.

The results obtained from eqn (2) for the α-phenylcinnamic acids, for the chemical shifts of the C_α, C_β and carboxylic group carbon, are as follows:

$$SCS_\alpha = -2.541\sigma_I - 0.387\sigma_R + 133.47$$
$$(r = 0.999;\ s = 0.025;\ n = 4) \qquad (3)$$

$$SCS_\beta = 1.721\sigma_I + 1.310\sigma_R + 139.00$$
$$(r=0.999;\ s=0.061;\ n=4) \qquad (4)$$

$$SCS_{C=O} = -1.288\sigma_I - 1.054\sigma_R + 168.42$$
$$(r=0.998;\ s=0.061;\ n=4) \qquad (5)$$

The results obtained from Eq. (2) for α-phenyl-3- and 4-pyridylacrylic acids for the chemical shifts of the C_α, C_β and carboxylic group carbon are as follows:

$$SCS_\alpha = 5.796\sigma_X - 2.494\sigma_I - 0.517\sigma_R + 131.05$$
$$(r=0.996;\ s=0.134;\ n=12) \qquad (6)$$

$$SCS_\beta = 1.279\sigma_X + 2.106\sigma_I 1.617\sigma_R + 134.75$$
$$(r=0.996;\ s=0.073;\ n=12) \qquad (7)$$

$$SCS_{C=O} = -0.406\sigma_X - 1.221\sigma_I - 0.959\sigma_R + 168.23$$
$$(r=0.995;\ s=0.048;\ n=12) \qquad (8)$$

It is evident from the above values for ρ_{IY} and ρ_{RY} that substituents from the α-phenyl nucleus, in addition to their expected inductive effect, influence the ^{13}C chemical shifts through their resonance effect. The identical conclusion has been reached on the grounds of the reactivity with DDM [1]. This is interesting because it is known that the α-phenyl ring is not coplanar with the rest of the molecule [6], but it appears that the degree of coplanarity is sufficient to permit a considerable transmission of the resonance effect of the substituents. The above DSP analysis indicates that the main effect through which these substituents influence the C_α ^{13}C NMR chemical shifts is the inductive effect (field effect) while the resonance effect is less pronounced; values of λ = ρ_R/ρ_I are 0.152 and 0.207 from Eqs. (3) and (6) respectively. The inductive effect of substituents from the α-phenyl nucleus is also present in the C_β chemical shifts but to a lesser extent, while the resonance effect is more intense (λ = 0.716 and 0.47 from Eqs. (4) and (7) respectively). The possibility of relay of the inductive effect from the α-phenyl ring to the C_β atom through a combination of localized (direct-field polarization) and extended polarization of the π-system has been discussed by Reynolds [7]. It is evident that substituents from the α-phenyl nucleus mainly affect the carboxylic group carbon through their inductive (field) effect and also through their resonance effect (λ = 0.820 and 0.785 from Eqs. (5) and (8) respectively).

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