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Electronic effects on ^{13}C NMR chemical shifts of substituted 1,3,4-thiadiazolium salts

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A series of 3- and 4-X-cinnamoyl-1,3,4-thiadiazolium-2-phenylamine chlorides were prepared and fully characterized by spectroscopic techniques. The ^{13}C NMR chemical shifts of the α and β side-chain carbons were compared with those of the corresponding cinnamic acid precursors and more significant transmission electronic effects were observed for mesoionic compounds. The ratio ρ_R/ρ_I for the α and β side-chain carbons in mesoionic derivatives reflects a more important inductive contribution whereas the value of ρ_R/ρ_I for the β side-chain carbons indicates a higher resonance contribution. The chemical shifts of C-2 and C-5 of the heterocyclic ring were correlated with substituent constants and showed that the more extensive conjugation of the side-chain with an exocyclic moiety is favoured by electron-withdrawing groups. The correlation analysis of chemical shifts with dual parameters indicated a significant contribution of a resonance effect for C-2 ($\rho_R/\rho_I = 1.70$) when compared with C-5 ($\rho_R/\rho_I = 1.03$). Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{13}C NMR; 1,3,4-thiadiazolium salts; mesoionic compounds; electronic effects

INTRODUCTION

Mesoionic compounds have received much attention and have been extensively studied because of their unique structures, reaction behaviour and pharmaceutical activities.[1,2] Mesoionic compounds can be represented by the general formula **1**, where a–f are suitably substituted carbons or heteroatoms (Scheme 1). The general structure affords several different classes of heterocyclic mesoionics. The 1,3,4-thiadiazolium-2-aminide class has shown particular interest and their rearrangement isomers have been studied structurally using multinuclear NMR techniques in the solid state or in solution.[3–5] We have previously studied the S_NAr reactivity,[6,7] structural and chemical properties[5,8,9] and biological activity[10,11] of several mesoionic compounds of the 1,3,4-thiadiazolium-2-aminide class.

Linear free energy relationships have been of great importance to physical organic chemists in the description and rationalization of structural effects on chemical reactivity and physical properties. They are now investigating their use to predict biological activity. The treatment of substituent parameters resulting from the separation of electrical effects into field and/or inductive and resonance contributions gives the best results.[12]

The interesting and promising results[11] of antitumor activity obtained with a few hydrochlorides of the 1,3,4-thiadiazolium-2-aminide 5-cinnamoyl derivatives led us to synthesize and carefully study this series to collect data for future studies of structure–activity relationships (SAR).

In the present work, we synthesized eight 4-phenyl-5-(4-X-cinnamoyl)- and three 4-phenyl-5-(3-X-cinnamoyl)-1,3,4-thiadiazolium-2-phenylamine chlorides (**7**), where X = H, 4-OCH_3, 4-CH_3, 4-Cl, 4-F, 4-CN, 4-NO_2, 4-OH, 3-NO_2, 3-OH, 3-OCH_3 (Scheme 1), and we studied the linear free energy relationships to examine the transmission of electronic effects involving the ^{13}C NMR chemical shift values against Hammett constants and dual electronic parameters.

RESULTS AND DISCUSSION

The use of NMR chemical shifts in examining electronic substituent effects has been particularly used in studying less common molecules, and has contributed to the best understanding in recent years of several more important modes of transmission of substituent effects.[13,14] We synthesized **7a–k** (where **7c–f**, **i–k** are new compounds) by the dehydroacylation reaction between thiosemicarbazide (**6**) and appropriate 4- or 3-substituted cinnamoyl chlorides (**5**) (Scheme 2). The ^{13}C NMR data for the mesoionic salts **7a–k** and precursor cinnamic acids **4a–k** are summarized in Table 1.

The assignments of the carbon NMR signals were made using similar arguments to those used in earlier work[3,5,15] for the C-2 and C-5 carbons in the heterocyclic ring. These carbons appear at high frequencies compared with signals from other carbon atoms (with the exception of C-13 and C-12

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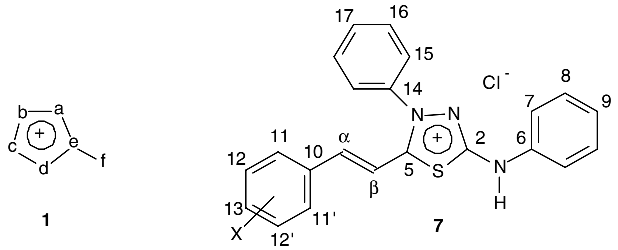


H (**7a**), 4-OCH$_3$ (**7b**), 4-CH$_3$ (**7c**), 4-Cl (**7d**)

4-F (**7e**), 4-CN (**7f**), 4-NO$_2$ (**7g**), 4-OH (**7h**),

3-NO$_2$ (**7i**), 3-OH (**7j**) and 3-OCH$_3$ (**7k**)

Scheme 1. Compounds studied.

for **7b**, **e**, **h** and **7i**, **j**, **k**, respectively, *ipso* to the substituent). We found δ157.97–159.40 for C-2 and δ160.65–162.58 for C-5, which are also consistent with the results of x-ray diffraction, theoretical studies[8] and ^{15}N NMR experiments[3] for other derivatives.

The chemical shifts of the ethylenic carbons linked to C-5 were assigned on the basis of the data for their corresponding cinnamic acids,[16,17] showing lower frequencies for C-β, due to the greater electron-withdrawing and anisotropic effects (±20 ppm) caused by the heterocyclic ring ($\sigma = 0.71$,[7] whereas $\sigma = 0.45$ for the COOH moiety). The remaining aromatic carbons in the rings attached to N-4 and *N*-exocyclic were assigned using aniline and anilinium groups as models.[17]

Ring styrene substituted derivatives have probably been involved in more studies of side-chain chemical shifts than any other class of compounds.[18–21] Happer and co-workers[16,22–24] investigated the range of styrene derivatives, including cinnamic acids, involving the measurement and analysis of side-chain substituent data for a wide range of *meta*- and *para*-substituted derivatives. Unfortunately, they did not include π-acceptor substituents in their data set for the DSP analysis[25–27] and the correlations with C-β chemical shift values indicated a strong dependence on the vinyl substituent groups, that is, when they are electron acceptors the best correlation is with σ_R^+ whereas if they are relatively neutral the correlation is with σ_R.

Table 1. ^{13}C NMR data (δ, ppm) for the C-α and C-β of the mesoionic salts **7a–k** and cinnamic acids **4a–k** (in CDCl$_3$)

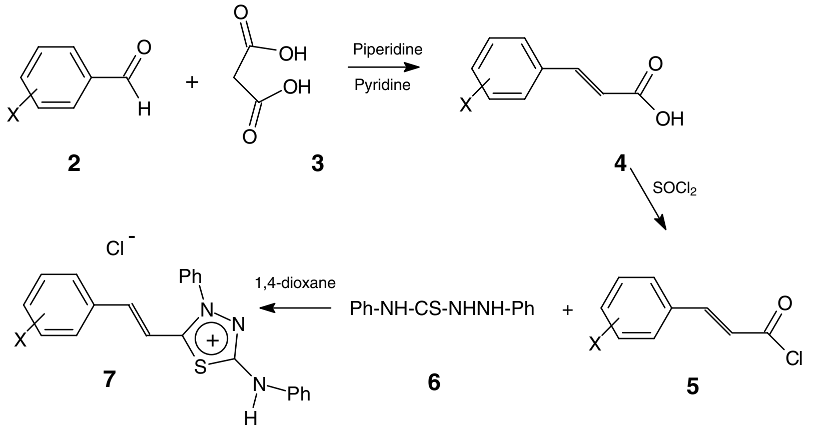
	Cinnamic acids		Mesoionic salts			
X	δ(C-α)	δ(C-β)	δ(C-α)	δ(C-β)	δ(C-2)	δ(C-5)
4-OH	—	—	148.93	105.86	157.94	162.58
4-OCH$_3$	143.89	116.59	149.00	107.12	157.97	162.03
4-CH$_3$	140.20	118.70	149.24	108.63	158.36	162.02
H	144.02	119.29	149.10	109.86	158.62	161.73
4-Cl	142.56	120.06	147.25	110.48	158.75	161.38
4-F	142.85	119.22	147.56	109.85	158.50	161.65
4-CN	142.02	122.91	145.38	113.16	n.o.[a]	161.00
4-NO$_2$	141.36	123.64	145.32	113.87	159.40	160.65
3-OH	144.17	118.91	149.35	109.83	158.67	162.31
3-OCH$_3$	143.99	116.27	148.98	110.23	158.60	161.63
3-NO$_2$	141.53	124.42	145.17	112.80	n.o.	n.o.

[a] n.o., peak was not observed.

In this work, to obtain a better comparison with mesoionic salts, we correlated the chemical shift values of C-α and C-β in cinnamic acids with σ_m, σ_p and σ_p^+ constants and dual parameters, σ_I and σ_R.[12] For *para*-substituted derivatives, the ratio ρ_R/ρ_I obtained with dual parameters suggest a more significant inductive effect for C-α chemical shift values (0.73) whereas for C-β chemical shifts ($\rho_R/\rho_I = 1.33$) the resonance effect has a more significant contribution. These results were consistent with Butt and Topsom's analysis.[27]

The correlation analysis for mesoionic salts was made with chemical shift for C-α, C-β and carbon atoms of the heterocyclic ring, C-2 and C-5 (Table 2). We had started studying the correlations of δC-α and C-β with Hammett constants, σ, σ_p and σ^+, and observed the best relationship for C-β against σ^{+28} ($\rho = 4.43$, sd $= 0.293$, correlation coefficient $= 0.994$, $F = 694$), in accordance with the study of styrene derivatives by Brownlee and Craik.[20]

Thus, the bilinear correlations between C-α, C-β chemical shifts with dual parameters[12] showed good results, indicating that the magnitude of the ρ_R component at C-β ($\rho_R/\rho_I = 1.29$) is greater than the corresponding at C-α ($\rho_R/\rho_I = 0.49$). The resonance effect reflects the electron demand placed on the C-β by the adjacent heterocyclic ring,



Scheme 2. Reaction sequence used in this work.

Table 2. Correlation analysis for ^{13}C NMR chemical shifts of C-α and C-β of the mesoionic salts against σ[12], σ^{+}[28] and dual parameters[12] (σ_I and σ_R)

Correlation[a]	ρ[b]	r[c]	Sd[d]	F[e]
δ(C-α) × σ	-3.90	0.905	0.772	40.8
δ(C-α) × σ^{+}	-2.49	0.855	0.949	21.7
δ(C-β) × σ	6.02	0.976	0.562	182
δ(C-β) × σ^{+}	4.43	0.994	0.293	694
δ(C-2) × σ	1.28	0.980	0.092	172
δ(C-2) × σ^{+}	0.852	0.990	0.070	303
δ(C-5) × σ	-1.42	0.950	0.183	74.8
δ(C-5) × σ^{+}	-0.969	0.962	0.167	87.3
δ(C-α) × σ_I and σ_R^{f}	$\rho_I^{g} = -5.31$ $\rho_R^{h} = -2.62$	0.977[i]	0.412	52.8
δ(C-β) × σ_I and σ_R	$\rho_I = 5.93$ $\rho_R = 7.66$	0.986[i]	0.548	84.8
δ(C-2) × σ_I and σ_R	$\rho_I = 1.03$ $\rho_R = 1.48$	0.996[i]	0.056	239
δ(C-5) × σ_I and σ_R	$\rho_I = -1.52$ $\rho_R = -1.56$	0.983[i]	0.133	71.8

[a] The general equations utilized in correlation analysis[12,17] were $\delta(\mathrm{C}) = a + \rho\sigma$ (or σ^{+}) and $\delta(\mathrm{C}) = a + \rho_I\sigma_I + \rho_R\sigma_R$.

[b] Transmission coefficient.

[c] Correlation coefficient.

[d] Standard deviation.

[e] F test for significance of correlation.

[f] Only *para*-substituted derivatives.

[g] The sensitivity of the substituent chemical shifts to resonance effects.

[h] The sensitivity of the substituent chemical shifts to inductive effects.

[i] Multiple correlation coefficient.

even though the ρ_I value at C-β (5.93) is slightly greater than, but with opposite sign to, the corresponding component at C-α (-5.31). This reflects some additional polarization of the C-β site above seen at C-α. This trend applies to the other styrene series and Butt and Topsom[27] rationalized it in terms of π-polarization of the vinyl group. In comparison with the cinnamic acid series, the ratio $\rho_R/\rho_I = 0.73$ for C-α against 0.49 for the mesoionic series reflected the higher efficiency in the transmission of resonance effect across the vinyl group into the heterocyclic moiety. Polar and resonance effects are largest at the C-β site. The preferred scale σ^{+} reflects the electron demand placed on this site by the adjacent heterocyclic group.

The chemical shifts of C-2 and C-5 were correlated against Hammett constants and showed better results for the σ^{+} parameter with C-2, indicating extensive conjugation of side-chain with the exocyclic moiety favoured by electronic-withdrawing groups (Table 2). The bilinear correlations between chemical shifts of C-2 and C-5 against resonance and inductive parameters separately presented good results, showing a more significant contribution of the resonance effect for C-2, $\rho_R/\rho_I = 1.70$, and for C-5, $\rho_R/\rho_I = 1.03$, suggesting that the π-polarization effects might therefore be transmitted via molecular lines of force, that is, we envisage that the dielectric properties of the molecular framework can modify the electric field transmission of polarization effects.

Finally, the comparison between cinnamic acids and mesoionic salts showed that the better transmission of the electronic effects is more efficient when the heterocyclic ring is the substituent group in the vinyl moiety. This observation reflects the increase in the extended π-polarization favoured by the relative coplanarity of the rings and vinyl system in the mesoionic derivatives.

EXPERIMENTAL

Spectra

^{13}C NMR spectra were run on a Bruker AC-200 spectrometer operating at 50.3 MHz, with a 5 mm probe, using $CDCl_3$ as solvent, and their signals were employed as standards with TMS as internal standard. All ^{13}C spectra were taken with 16K data points and a digital resolution of 1.1 Hz for a concentration of ca 0.5 mmol ml^{-1} and a 90° pulse was used with no relaxation delay.

Compounds

General synthetic procedure

4- and 3-X-cinnamic acids, **4**: the preparation of compounds **4a–k** was carried out by published procedures.[29] The purity of the compounds was checked by TLC.

5-Phenyl-4-(4- or 3-X-cinnamoyl)-1,3,4-thiadiazolium-2-phenylamine chloride, **7a–k**: a solution of the freshly prepared[30] appropriately substituted cinnamoyl chloride (10 mmol) in 1,4-dioxane (5 ml) was added to a suspension of 1,4-diphenylthiosemicarbazide (10 mmol) in 1,4-dioxane (15 ml), and the mixture was stirred at room temperature until complete solubilization and a yellow solution was formed. The reaction mixture was left standing for 24–48 h to give a very bright yellow solid, which was filtered off and purified by recrystallization from dichoromethane–ethanol (1 : 1). The ^{13}C NMR data for all compounds are listed in Table 3.

Analytical data

Melting-points were determined with a Melt-Temp apparatus and are uncorrected. IR spectra were taken for KBr pellets with a Perkin-Elmer Model 1420 instrument. Elemental analyses were performed on a Perkin-Elmer Model 2400 instrument and mass spectra were obtained with a Hewlett-Packard Model 5987A spectrometer.

7a, X = H, yield 75%, m.p. 266–7 °C (lit.[11] 266–7 °C); $\nu_{\max}$ (cm^{-1}), 3430, 3064, 2680, 1605, 1570, 1510 and 965; m/z (%), $M^{+\bullet}$ 356 (17), 355 (64), 206 (10), 147 (100), 103 (12), 135 (7), 77 (46). **7b**, X = 4-OCH_3, yield 70%, m.p. 195–6 °C (lit.[11] 195 °C); $\nu_{\max}$ (cm^{-1}), 3410, 3020, 2920, 2690, 1600, 1570, 1512 and 1260; m/z (%), $M^{+\bullet}$ 386 (28), 385 (100), 236 (14), 177 (98), 134 (24), 135 (8), 77 (21). **7c**, X = 4-CH_3, yield 73%, m.p. 195–6 °C (Found: C, 68.1; H, 4.7; N, 10.1. $C_{23}H_{20}ClN_3S$ requires C, 68.0; H, 5.0; N, 10.4%); $\nu_{\max}$ (cm^{-1}), 3423, 3030, 2890, 2690, 1615, 1600, 1510, 1326 and 1175; m/z (%), $M^{+\bullet}$ 370 (21), 369 (80), 220 (10), 161 (100), 135 (5), 117 (10), 77 (61). **7d**, X = 4-Cl, yield 75%, m.p. 264–5 °C (Found: C, 61.9; H, 4.1; N, 9.6. $C_{22}H_{17}Cl_2N_3S$ requires C, 62.0; H, 4.0; N, 9.9%);

Table 3. ^{13}C NMR chemical shifts (δ, ppm) for **7a–k**

Carbon	**7a**	**7b**	**7c**	**7d**	**7e**	**7f**	**7g**	**7h**	**7i**	**7j**	**7k**
2	158.62	157.97	158.36	158.75	158.50	158.93	159.40	157.94	n.o.[a]	158.60	158.60
5	161.74	162.03	162.02	161.38	161.65	161.00	160.65	162.58	n.o.	161.63	161.63
6	137.82	137.99	137.73	138.33	137.79	137.34	137.62	139.49	137.40	137.80	n.o.
7	118.85	118.56	118.46	118.71	118.56	118.42	118.70	118.85	118.44	118.66	118.69
8	129.15	128.81	128.84	129.84	130.12	128.51	129.29	130.18	124.63	128.97	128.94
9	124.33	123.95	124.21	124.23	124.16	124.36	124.54	124.24	124.36	124.43	124.30
10	132.97	125.81	130.24	131.63	129.36	n.o.[a]	138.94	124.72	134.50	n.o.	134.94
11′	130.18	130.92	130.03	128.95	130.94	128.69	130.22	131.45	125.21	119.62	114.03
12′	128.92	114.70	129.76	129.45	116.47	132.94	124.06	116.42	n.o.	157.86	159.83
13	131.91	163.15	143.64	136.57	164.83	n.o.	148.86	159.00	122.70	115.00	117.84
14	136.45	136.15	136.33	137.94	136.43	137.00	136.38	138.07	136.30	125.24	136.39
15	125.33	125.35	125.18	125.45	125.30	124.92	125.33	125.42	124.96	130.12	125.35
16	128.85	130.09	128.66	130.21	128.65	129.61	128.97	129.00	128.69	131.85	130.21
17	132.36	131.61	131.73	131.91	131.85	131.54	132.15	132.67	131.58	n.o.	131.94
α	149.10	149.00	149.24	147.25	147.56	145.38	145.32	148.93	145.17	149.35	148.98
β	109.88	107.12	108.63	110.48	109.85	113.16	113.87	105.86	112.79	109.83	110.23
11									133.42	120.10	n.o.
12									129.75	n.o.	n.o.
OCH_3		55.32									55.34
CH_3			21.07								
CN						117.30					

[a] n.o., peak was not observed.

ν_{max} (cm^{-1}), 3423, 3040, 2650, 1625, 1600, 1570, 1510, 1450, and 1326; m/z (%), $M^{+\bullet}$ 390 (30), 389 (100), 240 (11), 181 (99), 134 (6), 135 (5), 77 (94). **7e**, X = 4-F, yield 77%, m.p. 252–3 °C (Found: C, 64.4; H, 4.1; N, 10.1. $C_{22}H_{17}ClFN_3S$ requires C, 64.5; H, 4.2; N, 10.3%); ν_{max} (cm^{-1}), 3442, 3007, 2669, 1618, 1570, 1512, 1448, 1315 and 1230; m/z (%), $M^{+\bullet}$ 374 (28), 373 (98), 224 (12), 165 (100), 121 (7), 77 (55, 51 (19). **7f**, X = 4-CN, yield 80%, m.p. 185 °C (Found: C, 66.3; H, 4.1; N, 13.1. $C_{23}H_{17}ClN_4S$ requires C, 66.3; H, 4.1; N, 13.4%); ν_{max} (cm^{-1}), 3404, 3060, 2740, 2220, 1610, 1570, 1500, 1420 and 1310; m/z (%), $M^{+\bullet}$ 381 (24), 380 (80), 231 (14), 17 (39), 135 (29), 128 (9), 77 (100), 51 (23). **7g**, X = 4-NO_2, yield 78%, m.p. 232–3 °C (lit.[11] 232–3 °C); ν_{max} (cm^{-1}), 3410, 3090, 1600, 1570 and 1380; m/z (%), $M^{+\bullet}$ 401 (12), 400 (48), 251 (10), 192 (5), 135 (81), 91 (40), 77 (100), 51 (17). **7h**, X = 4-OH, yield 65%, m.p. 282–4 °C (lit.[11] 282–3 °C); ν_{max} (cm^{-1}), 3425, 3050, 1600, 1570, 1500 and 1270. **7i**, X = 3-NO_2, yield 73%, m.p. 270–1 °C (Found: C, 60.5; H, 3.8; N, 12.5. $C_{22}H_{17}ClN_4O_2S$ requires C, 60.5; H, 3.9; N, 12.8%); ν_{max} (cm^{-1}), 3420, 3050, 1620, 1570 and 1335; m/z (%), $M^{+\bullet}$ 401 (16), 400 (57), 251 (13), 208 (14), 135 (63), 91 (42), 77 (100), 51 (30). **7j**, X = 3-OH, yield 58%, m.p. 284–5 °C (Found: C, 64.7; H, 4.5; N, 10.0. $C_{22}H_{18}ClN_3OS$ requires C, 64.8; H, 4.5; N, 10.3%); ν_{max} (cm^{-1}), 3410, 3050, 2285, 1615, 1595, 1570, 1495 and 1290; m/z (%), $M^{+\bullet}$ 372 (19), 371 (48), 354 (23), 353 (18), 222 (16), 163 (39), 135 (45), 118 (32), 91 (66), 77 (100), 65 (32), 51 (46). **7k**, X = 3-OCH_3, yield 62%, m.p. 243–5 °C (Found: C, 65.4; H, 4.7; N, 9.7. $C_{23}H_{20}ClN_3OS$ requires C, 65.5; H, 4.8; N, 10.0%); ν_{max} (cm^{-1}), 3411, 3060, 2600, 1620, 1490.

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