Tetrahedron Letters No. 41, pp 3617 - 3620, 1974. Pergamon Press. Printed in Great Britain.

NOVEL SUBSTITUENT EFFECTS IN ^{1}H AND ^{13}C NMR SPECTRA OF 4- AND 4'-SUBSTITUTED N-BENZYLIDENEANILINES

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(Received in Japan 25 July 1974; received in UK for publication 29 August 1974)

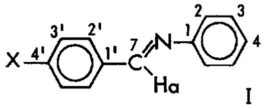
During the course of an investigation of benzylideneanilines,[1] *we have found that a series of substi*tution on the 4'-position (series I) and that on the 4-position (series II) show novel substituent effects in their NMR spectra.

The chemical shifts of imidoyl protons, $\delta_{H\alpha}$, and those of C-1, C-4, C-1', and C-4' atoms, δ_C, together with the ^{13}C-^{1}H coupling constants, J(^{13}C-Hα), for imidoyl groups in series I and II were determined in $CDCl_3$ and summarized in the Table. These values fit the Hammett relationship using Hammett's σ constants for each series; their ρ values are also listed in the Table.

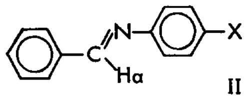
Hammett ρ for $\delta_{H\alpha}$ in series I (−0.162 ppm/σ) exhibits a negative sign as earlier reported by Tabei and Saitou.[2] On the contrary, $\rho_{H\alpha}$ for series II (0.042 ppm/σ) anomalously shows a positive sign (see FIG. 1) in contrast with reported results that ρ_H values have hitherto been observed only with a negative sign in $CDCl_3$ or CCl_4.[3] This is the first finding of a reverse of sign of ρ for ^{1}H chemical shifts measured in a solvent which does not exert any special solvent effect.

The $\rho_{J(^{13}C\text{-}H\alpha)}$ values for series I and II (4.45 and 1.99 Hz/σ, respectively) are fairly larger than those for methyl groups of side-chains in several series of substituted benzenes reported previously,[4,5] but smaller than that for the formyl proton in substituted benzaldehydes (ρ_J = 7.21 Hz/σ).[5] These two differences may result respectively from that between sp^3- and sp^2-hybridization of the carbon atoms of

Table. Chemical shifts ($\delta_{H\alpha}$ and δ_C)[a,b] and coupling constants (J in Hz)[a] observed in $CDCl_3$, and their Hammett relationships[c] for 4'- (series I) and 4-substituted N-benzylideneanilines (series II)



I



II

	No.	X	$\delta_{H\alpha}$	$J(^{13}C\text{-}H\alpha)$	$\delta_{C\text{-}4'}$	$\delta_{C\text{-}1'}$	$\delta_{C\text{-}7}$	$\delta_{C\text{-}1}$	$\delta_{C\text{-}4}$
	1	NO_2	8.56	161.0	149.40	141.78	157.38	151.06	127.26
	2	Cl	8.42	158.1	137.20	134.88	158.28	151.65	126.14
	3	H	8.47	157.3	131.24	136.48	160.01	152.18	125.94
	4	CH_3	8.41	156.5	141.58	134.02	159.87	152.45	125.73
I	5	OCH_3	8.38	156.1	162.39	129.52	159.41	152.58	125.60
	6	$N(CH_3)_2$	8.28	154.1	153.24	124.74	160.00	152.65	125.07
		ρ	-0.16_2	4.4_5	d	-10.47	1.74	1.09	-1.34
		r[e]	0.951	0.995		0.956	0.842	0.919	0.959
		ρ_q[f]	-6.05			-37.83	13.46	3.67	-4.19
		r[e]	0.980			0.951	0.988	0.962	0.981
	1	NO_2	8.43	158.6	132.56	135.68	162.79	158.08	145.69
	2	Cl	8.43	157.5	131.57	136.21	160.40	150.59	131.57
	3	H	8.47	157.3	131.24	136.48	160.01	152.18	125.94
	4	CH_3	8.45	156.5	130.91	136.61	158.81	149.53	135.41
II	5	OCH_3	8.48	156.6	131.04	136.81	157.95	144.96	158.55
		ρ	0.04_2	1.9_9	-1.56	1.05	-4.35	-10.45	d
		r[e]	0.834	0.980	0.968	0.966	0.982	0.915	
		ρ_q[f]	-3.53		-4.95	3.67	-18.98	-40.59	
		r[e]	0.993		0.990	0.943	0.998	0.958	

[a] Values for $\delta_{H\alpha}$ (in ppm downfield from internal TMS) and $J(^{13}C\text{-}H)$ (in Hz) were determined with a Varian A-60A spectrometer; sample concentrations were about 30% (w/v) and the $\delta_{H\alpha}$ was extrapolated to an infinite dilution. Accuracies are about ±0.01 ppm for $\delta_{H\alpha}$ and about ±0.5 Hz for J. [b] The natural-abundance ^1H noise-decoupled ^{13}C FT NMR spectra were taken with a Varian NV-14 FT NMR spectrometer operating at 15.087 MHz. Sample concentrations were about 1 mol/l. Signals were assigned by known chemical shift rules[15] and single-frequency off-resonance decoupling techniques.[15] Accuracies of δ_C (in ppm downfield from internal TMS) are about ±0.07 ppm. [c] In accordance with the procedure of other related studies hitherto reported,[6] we use a negative sign for a downfield signal shift in this paper. [d] The chemical shift of this carbon atom does not follow the Hammett equation. [e] Correlation coefficients. [f] Obtained from relative electron densities, $\Delta q(H\alpha) \cdot (\times 10^3)$ and relative total electron densities, $\Delta q(C_{total}) \cdot (\times 10^3)$.

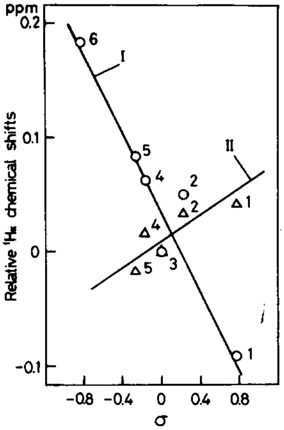


FIGURE 1. Plots of relative Hα chemical shifts for series I (o) and II (Δ) vs. Hammett's σ constants.

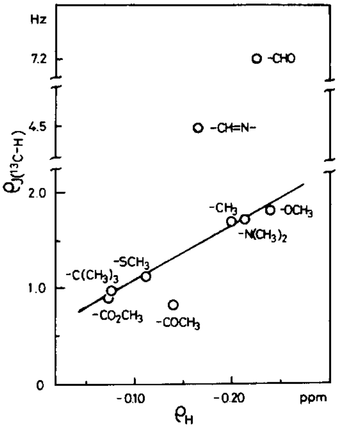


FIGURE 2. The ρ-ρ relationship between $\rho_{J(^{13}C-H)}$ and ρ_H for protons bonded to sp³- and sp²-carbons in aromatic side-chains.

interest as previously discussed[5] and from the electronegativity difference between the N and O atoms bonded to the carbons. The ρ_J value is larger in series I than in series II probably because of a closer distance between the substituted and imidoyl carbons in series I than in series II. Thus, in order to find out a general relationship between $\rho_{J(^{13}C-H)}$ and ρ_H values, the both values obtained here and reported for other series of substituted benzenes[4-12] were plotted against each other as shown in FIG. 2. It is evident from FIG. 2 that concerning methyl groups in substituted aromatic side-chains in substituted toluenes,[4,6,7] anisoles,[4,5,8] N,N-dimethylanilines,[4,9] thioanisoles,[5,6,10] t-butylbenzenes,[4] methyl benzoates,[5,11] and acetophenones,[5-7] the ρ_J values are linearly increased with an increase in the ρ_H values. However, concerning protons attached to unsaturated carbons such as the imidoyl proton in series I and the formyl proton in benzaldehydes,[5,12] the ρ_J values deviate far from the above linear relationship for the methyl groups evidently.

The results obtained for ^{13}C chemical shifts indicate that the ρ_C values for each atom on the conjugated systems for each series appear to alternate in sign and tend to decrease absolutely on progressing from the substituted carbon atom along the conjugated framework. For example, in series I, the ρ_C values for C-1' and C-4 and those for C-7 and C-1 are respectively negative and positive decreasing their magnitudes in each order. Moreover, the ρ_C values are reverse in sign between series I and II for each carbon. The above sign alternation in these long conjugated systems provides a firm experimental proof for Pople and Gordon's prediction on the alternating induced charge effect.[13,14]

^{13}C chemical shifts are known to correlate with electron densities on the carbon atoms.[15] Thus, CNDO/2 calculations[16] were carried out on a geometric conformation reported for benzylideneaniline[17] to obtain electron densities of the respective carbons and the imidoyl hydrogen in each series. The calculated electron densities for the respective atoms were shown to correlate linearly with Hammett's σ constants for each series; the resulting ρ_q values are also included in the Table. Comparison of the observed ρ_C values with those of the calculated electron densities for each carbon shows that both values vary in a parallel manner for each series.

The signs of $\rho_{H\alpha}$ and ρ_q for the imidoyl proton in series II are opposite to each other, however. For each series, the observed $\rho_{H\alpha}$ value has an opposite sign to that of ρ_{C-7} , but this correlation may be occasional because ρ_H values for α- and β-protons in substituted styrenes are not reversed in sign to each other[18,19] contrary to ρ_C values for α- and β-carbons having opposite signs to each other.[19] Further detailed discussion will be given elsewhere, but it is worthwhile to mention here that a field effect[19,20] might be responsible for the anomalous substituent effect on the $\delta_{H\alpha}$ described above.

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