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The substituent effects on the ^{13}C chemical shifts of the azomethine carbon atom of *N*-(substituted phenyl)salicylaldimines

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Abstract: Hammett correlations between the ^{13}C-NMR chemical shifts of the azomethine carbon atom and the corresponding substituent constants were established for thirteen Schiff bases. The successful correlation of the chemical shifts with the electrophilic substituent constants σ^+ indicate a significant resonance interaction of the substituents on the aniline ring with the azomethine carbon atom in the examined series of imines. The demand for electrons in the investigated compounds was compared to that of the *N*-benzylideneanilines and *N*-(substituted phenyl)pyridinealdimines. The manner of transmission of the substituent effects is discussed and they were separated into resonance and inductive effects. The inductive effects prevail over the resonance effects.

Keywords: ^{13}C-NMR chemical shifts; Hammett Equation; substituent constants; *N*-(substituted phenyl)salicylaldimines.

INTRODUCTION

N-(Substituted phenyl)pyridine aldimines have been in the field of interest for years.[1,2] They are important intermediates for the synthesis of aminoalkylpyridines[3] and pharmacologically active triazoles and triazolines.[4,5] In this latter context, it has also been established that substituents both from the aniline ring and from the aryl group at the azomethine carbon can influence the yields of the triazole products.[4]

Schiff bases of salicylaldehydes with anilines, aminopyridines and benzylamines were also investigated because of their photochromic and thermochromic

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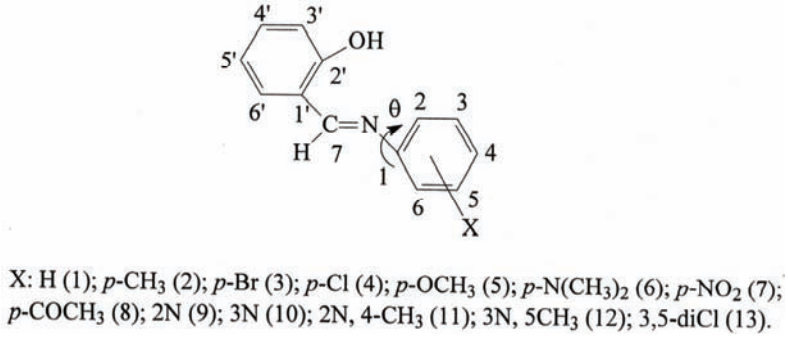
properties,[6] as well as the role they play in biological systems,[7] in addition to some other applications.[8]

Numerous previous investigations of the molecular structures of *N*-benzylideneanilines,[9–11] showed that the substituents in the aniline ring have a significant influence on the deflection of the angle θ between the rings by their electronic and/or steric effects (the general formula is given in Fig. 1) and consequently determine the conformation of the corresponding molecules.

The general formula of the investigated *N*-(substituted phenyl)salicylaldimines is shown in Fig. 1.



X: H (1); *p*-CH_3 (2); *p*-Br (3); *p*-Cl (4); *p*-OCH_3 (5); *p*-$N(CH_3)_2$ (6); *p*-NO_2 (7); *p*-$COCH_3$ (8); 2N (9); 3N (10); 2N, 4-CH_3 (11); 3N, 5CH_3 (12); 3,5-diCl (13).

Fig 1. The general formula of *N*-(substituted phenyl)salicylaldimines.

The intention of the present investigation was to study the effects of the substituents at the aniline ring and of the 2′-hydroxyphenyl group present on the azomethine carbon (C-7) on the ^{13}C-NMR chemical shifts of the azomethine carbon, as a continuation of previous studies of 2-, 3- and 4-*N*-(substituted phenyl)pyridine aldimines.[1,2] Based on the studied effects, it was possible to draw conclusions about the conformations of the investigated molecules.

EXPERIMENTAL

The *N*-(substituted phenyl)salicylaldimines used in this study were synthesized by procedures described in the literature.[4,5,12,13] Equimolar amounts of salicylaldehyde and substituted anilines in ethanol were heated to 60–70 °C under constant stirring for 2–3 h. The products were recrystallized from analytical grade ethanol to constant melting point. The purity of the obtained compounds was confirmed by their melting points, elemental analyses and NMR spectra, which were in agreement with literature data.[4,5,12,13]

The ^{13}C-NMR chemical shifts data of the investigated compound were obtained using a Bruker AC 250 spectrometer at 62.896 MHz. The spectra were recorded at room temperature in deuterated dimethyl sulfoxide (DMSO-d_6) in 5 mm tubes. The chemical shifts are expressed in ppm values referenced to the residual solvent signal at 39.5 ppm.

RESULTS AND DISCUSSION

The ^{13}C-NMR chemical shifts of the azomethine carbon atom (δ_C) in the solvent DMSO-d_6 and the differences in the chemical shifts ($\Delta\delta_C$) together with

the corresponding σ[14] and σ^+[15] constants for substituents in the *m*- and *p*-position of the aniline ring are given in Table I.

TABLE I. ^{13}C-NMR chemical shifts of the azomethine carbon atoms of *N*-(substituted phenyl)salicylaldimines in DMSO-d_6 solution and the corresponding substituent constants

Substituent	X	$\delta_{C\text{-}7}$ / ppm	$\Delta\delta_{C\text{-}7}$ / ppm	σ_m or σ_p	σ_m^+ or σ_p^+
(1)	H	162.60	0.00	0.00	0.00
(2)	*p*-CH_3	161.66	–0.94	–0.17	–0.31
(3)	*p*-Br	162.98	0.37	0.23	0.15
(4)	*p*-Cl	162.93	0.32	0.23	0.11
(5)	*p*-OCH_3	160.43	–2.17	–0.27	–0.78
(6)	*p*-$N(CH_3)_2$	157.55	–5.05	–0.83	–1.70
(7)	*p*-NO_2	165.35	2.75	0.78	0.79
(8)	*p*-$COCH_3$	164.18	1.52	0.50	0.50
(9)	2N	164.72	2.13	0.73	0.72
(10)	3N	164.55	1.94	0.62	0.78
(11)	2N, 4CH_3	163.71	1.11	0.56[a]	0.41[a]
(12)	3N, 5CH_3	164.54	1.93	0.67[a]	0.65[a]
(13)	3,5-diCl	164.59	1.98	0.74[b]	0.78[b]

[a]σ and σ+ values were calculated as the sum of the σ or σ^+ substituent constants of a methyl group in the *m*- or *p*-position and the corresponding constant for the aza-substituent; [b]σ and σ^+ values were calculated as double values of the σ or σ^+ constants of a chlorine atom in the *m*- position.

The values of $\Delta\delta_C$ are the differences between the ^{13}C-NMR chemical shifts of the substituted imines and the ^{13}C-NMR chemical shift of the unsubstituted imine:

$$\Delta\delta_C = \delta_{C(subst.)} - \delta_{C(unsubst.)} \quad (1)$$

The general conclusion derived from the data in Table I is that all the substituents on the aniline ring of the imine influence *via* their electronic effects the value of the ^{13}C-NMR chemical shifts of the azomethine carbon atom. For electron donor substituents, these were upfield shifts, while downfield shifts were registered for electron acceptor substituents.

For a quantitative assessment of the effects of substituents on the ^{13}C-NMR chemical shifts, the Hammett Equation of the type:

$$\Delta\delta_C = \rho\sigma \quad (2)$$

was applied, where ρ is the reaction constant reflecting the sensitivity of the ^{13}C--NMR chemical shift to the substituent effects.

Using the data from Table I, the following correlation equation for *N*-(substituted phenyl) salicylaldimines was obtained:

$$\Delta\delta_{C\text{-}7} = (4.31 \pm 0.26)\sigma_{m/p} - 0.47 \quad (3)$$
$$(r = 0.981;\ s = 0.44;\ n = 13)$$

where r is the correlation coefficient, s the standard deviation and n the number of data included in the correlation.

In order to examine the influence of the electron-donor and the electron-acceptor substituents, the obtained data were separated according to their electronic effects, as shown in Eqs. (4) and (5):

For electron-donors:

$$\Delta\delta_{C\text{-}7} = (6.05 \pm 0.56)\sigma_p - 0.12 \quad (4)$$
$$(r = 0.992;\ s = 0.35;\ n = 4)$$

For electron-acceptors:

$$\Delta\delta_{C\text{-}7} = (3.31 \pm 0.35)\sigma_{m/p} - 0.47 \quad (5)$$
$$(r = 0.961;\ s = 0.28;\ n = 10)$$

From these correlations, it could be noticed that the electron-donor substituents influence the shifts of the azomethine carbon atom more than electron-acceptor subsituents.

When σ^+, the value of the electrophilic substituent constants, are used instead of σ (Eq. (3)), an even more precise correlation for *N*-(substituted phenyl)-salicylaldimines was obtained:

$$\Delta\delta_{C\text{-}7} = (2.91 \pm 0.08)\sigma^+_{m/p} - 0.02 \quad (6)$$
$$(r = 0.996;\ s = 0.20;\ n = 13)$$

This correlation is presented in Fig. 2.

For electron-donor subsitutents, the following correlation equation was obtained:

$$\Delta\delta_{C\text{-}7} = (2.96 \pm 0.07)\sigma^+_p + 0.02 \quad (7)$$
$$(r = 0.999;\ s = 0.09;\ n = 4)$$

while for electron-acceptor subsitutents, the following was obtained:

$$\Delta\delta_{C\text{-}7} = (2.89 \pm 0.25)\sigma^+_{m/p} - 0.02 \quad (8)$$
$$(r = 0.971;\ s = 0.23;\ n = 10)$$

The better correlation coefficients obtained when the electrophilic substituent constant σ^+ was employed for both electron-acceptor and electron-donor substituents undoubtedly shows a considerable resonance interaction of the substituents on the aniline ring with the azomethine carbon atom.

Based on the obtained results and the correlation (6), it could be concluded that the electronic effect of substituents influence the ^{13}C chemical shifts of azomethine carbon atom, and that this influence depends on the position of the substituent in the aniline part of the molecule. The fact that the majority of substituted aldimine molecules are non-planar comes from the deviation of the phenyl ring from the molecular plane, which creates a special geometry of the molecule. The change of the angle between the rings (θ) is the consequence of the presence

of substituents. The electron-acceptor substituents cause an increase in the angle between the rings, while electron-donor substituents decrease this angle, tending to make the molecular structure more planar.

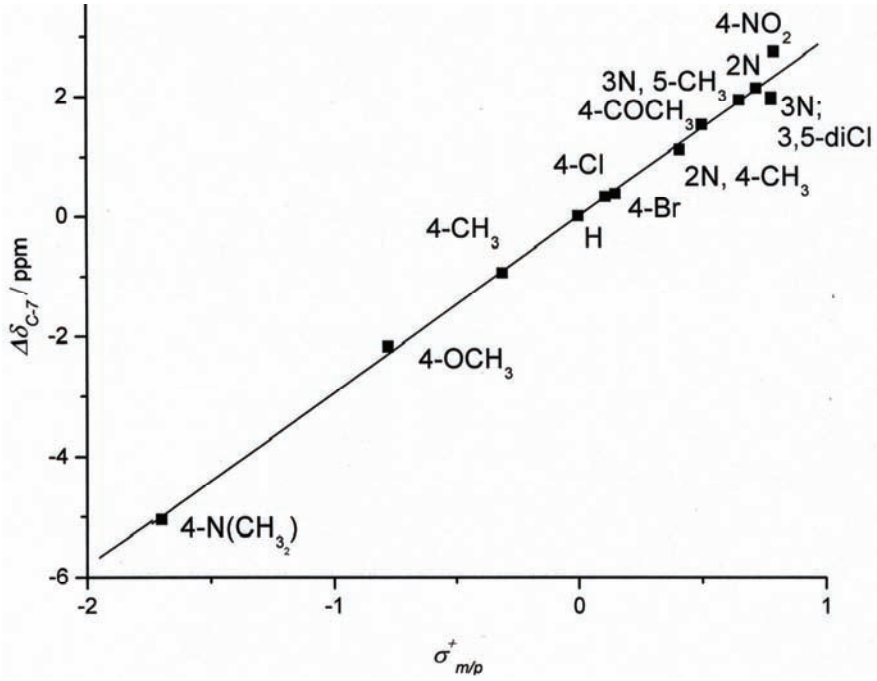


Fig. 2. $\Delta\delta_{C\text{-}7}$ as a function of the substituent constant σ^+.

It was deemed of interest to compare the obtained values of ρ^+ = 2.96, Eq. (7), for *N*-(substituted phenyl)salicylaldimines with those found for 2N, 3N, and 4N *N*-(substituted phenyl)pyridinealdimines, ρ^+ = 3.06, 3.01 and 3.40, respectively, and with that for substituted *N*-benzylidenanilines,[16] ρ^+ = 2.81 carrying the same substituents: H, *p*-CH_3, *p*-Cl, *p*-OCH_3 and *p*-$N(CH_3)_2$. In the case of both *N*-(substituted phenyl)salicylaldimines and the various *N*-(substituted phenyl)pyridinealdimines, there was an increased demand for the electrons of the azomethine carbon atom relative to the demand of the corresponding carbon in *N*-benzylideneanilines. Most probably, this could be attributed to the effect of the 2-hydroxyphenyl and the substituted pyridine groups bound to the azomethine carbon atom. It is evident that the electron donating effect of the substituents on the aniline ring of the azomethine carbon atom for *N*-(substituted phenyl)salicylaldimines lies between the same effect for the *N*-benzylideneanilines and the *N*-(substituted phenyl)pyridinealdimines.

In addition, it was considered very interesting to compare the values of the reaction constant ρ^+ for the series of substituted *N*-(substituted phenyl)salicylal-

dimines with those for *N*-benzylideneanilines and isomeric pyridinealdimines investigated in previous studies,[1,2] with electron donating substituents in the *p*-position of the aniline ring (*p*-CH_3, *p*-OCH_3 and *p*-$N(CH_3)_2$), where these substituents probably allow a nearly planar conformation of the investigated compounds. The calculated ρ^+ values for the previously examined compounds, with the same substituents, are as follow: 2.81 for *N*-benzylideneanilines;[1] 3.36 for 4-pyridinealdimines;[1] 3.05 for 2-pyridinealdimines and 2.92 for 3-pyridinealdimines[2] and 2.96 for the *N*-(substituted phenyl)salicylaldimines, giving the following order for ρ^+:

phenyl < 3-pyridine < 2-hydroxyphenyl < 2-pyridine < 4-pyridine.

According to this comparison, it could be concluded that the inductive and resonance effects of the nitrogen atom in the pyridine ring affect the degree of resonance interaction through the molecule as a whole.

When the literature values[1,16,17] of the ^{13}C-NMR chemical shifts of *N*-benzylideneanilines (H, 160.31; *p*-CH_3, 159.45; *p*-OCH_3, 158.36; *p*-NO_2, 162.59; *p*-$N(CH_3)_2$, 155.52 and *p*-Cl, 160.69) are correlated with the ^{13}C-NMR chemical shifts from both investigated series with the same substituents in the aniline ring, the following relationships were obtained:

$$\delta_{\text{C-7(2OH,X)}} = (1.09 \pm 0.03)\delta_{\text{C(H,X)}} - 12.51 \quad (9)$$
$$(r = 0.999;\ s = 0.153;\ n = 6)$$

The high correlation coefficient obtained, as well as those reported earlier for pyridinealdimines,[1,2] proved that the mechanism of transmission of polar substituent effects to the azomethine carbon atom is the same as in the case of the substituted *N*-benzylideneanilines. This also implies that the dihedral angle for these two cases is not significantly different. However, the above intercorrelation includes both electron acceptor and electron donor substituents.

In order to separate the inductive and resonance effects of the substituents in the aniline ring and to observe their individual influence on the ^{13}C-NMR chemical shifts of the azomethine carbon atom, it is useful to apply the Taft equation in the form:

$$\Delta\delta_{\text{C-7}} = \rho_{\text{I}}\sigma_{\text{I}} + \rho_{\text{R}}{}^{+}\sigma_{\text{R}}{}^{+} \quad (10)$$

If the substituents on the aniline ring with dominantly electron-donor properties (*p*-CH_3, *p*-OCH_3 and *p*-$N(CH_3)_2$) are taken into consideration, using literature values[18] of σ_{I} and $\sigma_{\text{R}}{}^{+}$ (substituent constants describing the inductive and the positive resonance effects, respectively) for *N*-(substituted phenyl)salicylaldimines, the following correlation is obtained:

$$\Delta\delta_{\text{C-7}} = (3.51 \pm 0.01)\sigma_{\text{I}} + (3.00 \pm 0.03)\sigma_{\text{R}}{}^{+} - 0.03 \quad (11)$$
$$(r = 0.999;\ s = 0.04;\ n = 4)$$

Based on the obtained ratio ρ_R^+/ρ_I, which was 3.00/3.51=0.86 for the *N*-(substituted phenyl)salicylaldimines, it may be concluded that the inductive effect prevails over the positive resonance effect of the substituents. However, the same approach for the *N*-(substituted phenyl)pyridine-4-aldimines, with the same substituents on the aniline ring, gives the result ρ_R^+/ρ_I of 3.35/2.98 = 1.12,[1] meaning that the influence of the resonance effect was considerably higher for these previously examined compounds than for *N*-(substituted phenyl)salicylaldimines.

The observation that the positive resonance effect was less pronounced than the inductive on can be explained by the fact that the hydroxy group in position 2' decreases the possibility for any resonance interaction in the molecule. This is probably due to of the existence of a hydrogen bond between it and the nitrogen atom (Fig. 3), which causes an increase in the demand for electrons of the azomethine carbon atom. The lone electron pair on the nitrogen is blocked by the described hydrogen bond, which prevents the transmission of the resonance effect of the subsitutents to the aniline ring.

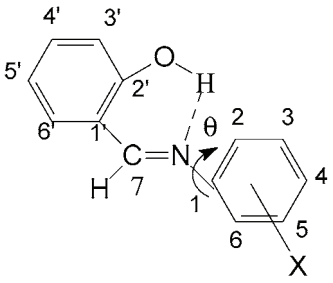


Fig 3. Hydrogen bond between the 2'-hydroxy group and nitrogen in the molecule of *N*-(substituted phenyl)salicylaldimine.

The observation that the 2'-hydroxy group causes a decrease in the positive resonance effects, compared to pyridinealdimines, can also be explained by the deflection from planarity of the molecule, caused by repulsion between the lone electron pair of the hydroxylic oxygen and the π-electrons from the azomethine bond.

CONCLUSIONS

It has been shown that linear free energy relationships can be applied to the study of the transmission of substituent effects in *N*-(substituted phenyl)salicylaldimines using the data from ^{13}C-NMR chemical shifts. It can be seen from the applied linear free energy relationships that both inductive and resonance effects influence the electron demand of the azomethine carbon.

Reliable correlations with the Hammett σ constants for *N*-(substituted phenyl)salicylaldimines, and the excellent correlation coefficients obtained with σ^+ and σ_R^+ for predominantly electron donating substituents in the aniline ring, indicate extensive delocalization and significant resonance interactions in these

systems. Therefore, it is probably true that as long as electron-donating substituents are present in the aniline ring, there is a substantial decrease in the θ angle, so the molecule attains nearly planar conformation and the resonance interaction increases. This is in accordance with the conclusions reported in the literature that in special cases, strong electron donor substituents present in the aniline ring and strong electron acceptor substituents on the benzylildene ring can cause near-planar conformation of the corresponding molecules due to the complete delocalization through the whole molecule.[16,17] Considering the ρ_R^+/ρ_I ratio, it is seen that the positive resonance effect decreases in the presence of the 2'-hydroxy group in the molecule of *N*-(substituted phenyl)salicylaldimine in comparison to the *N*-(substituted phenyl)pyridine-4-aldimine. This fact could be tentatively explained by the formation of a hydrogen bond between the 2'-hydroxy group and the nitrogen or by the repulsion of the electrons of the azomethine bond and the hydroxylic oxygen. Both factors could increase the angle (θ) between the phenyl rings, thereby decreasing the planarity of the molecule and the resonance effects of the substituents on the aniline ring on the azomethine carbon atom.

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И З В О Д

ЕФЕКАТ СУПСТИТУЕНАТА НА ^{13}C ХЕМИЈСКА ПОМЕРАЊА АЗОМЕТИНСКОГ УГЉЕНИКА *N*-(СУПСТИТУИСАНИ ФЕНИЛ)САЛИЦИЛАДИМИНА

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^{13}C-NMR хемијска померања 13 Шифових база корелисана су са константама супституената коришћењем Хаметове једначине. Добра корелација хемијских померања азометинског угљеника са електрофилним константама супституената (σ^+) показује да постоји изражена резонантна интеракција супституената на анилинском прстену са азометинским угљеником. Испитиван је пренос електронских ефеката супституената и они су раздвојени на индуктивне и резонантне ефекте, а показано је да преовлађују индуктивни ефекти.

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REFERENCES

1. B. Ž. Jovanović, M. Mišić-Vuković, A. D. Marinković, V. Vajs, *J. Mol. Struct.* **482** (1999) 375
2. B. Ž. Jovanović, M. Mišić-Vuković, A. D. Marinković, V. Vajs, *J. Mol. Struct.* **642** (2002) 113
3. J. E. Robertson, H. J. Biel, T. F. Mitchell, *J. Med. Chem.* **6** (1963) 805
4. P. K. Kabada, *J. Heterocycl. Chem.* **12** (1975) 143

5. P. K. Kabada, *J. Med. Chem.* **31** (1998) 196
6. E. Hadjoudis, M. Vittorakis, I. Moustakali-Mavridis, *Tetrahedron* **43** (1987) 1345
7. R. J. Johnson, C. M. Metzler, *J. Am. Chem. Soc.* **102** (1980) 6075
8. B. L. Feringa, W. F. Jager, B. de Lange, *Tetrahedron* **49** (1993) 8267
9. R. Akaba, K. Tokumaru, T. Kobayashi, *Bull. Chem. Soc. Jpn.* **53** (1980) 1993
10. R. Akaba, K. Tokumaru, T. Kobayashi, C. Utsunomiya, *Bull. Chem. Soc. Jpn*. **53** (1980) 2002
11. P. Skrabal, J. Steiger, H. Zollinger, *Helv. Chim. Acta* **58** (1975) 800
12. C. T. Bahner, R. Neely, *J. Org. Chem.* **22** (1957) 1109
13. G. E. Matsubayashi, M. Okunaka, T. Tanaka, *J. Organomet. Chem.* **56** (1973) 215
14. D. H. McDaniel, H. C. Brown, *J. Org. Chem.* **23** (1958) 420
15. H. C. Brown, Y. Okamoto, *J. Am. Chem. Soc.* **80** (1958) 4979
16. A. Kawasaki, *J. Chem. Soc., Perkin Trans 2* (1990) 223
17. R. Akaba, H. Sakuragi, K. Tokumaru, *Bull. Chem. Soc. Jpn.* **58** (1985) 1186
18. S. Ehrenson, R. T. C. Brownlee, R. W. Taft, *Prog. Phys. Org. Chem.* **10** (1973) 13.