

^{13}C and ^1H NMR Study of *N*-5'-Methylsalicylideneanilines

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The ^{13}C and ^1H NMR spectra of six *N*-5'-methylsalicylideneanilines have been studied. Correlations of the chemical shifts of C- α (azomethine carbon) and C-4' with the σ , F , R , σ_1 and σ_R^0 parameters have been examined for *N*-5'-methylsalicylideneanilines, and also for *N*-benzylideneanilines and *N*-salicylideneanilines. The results suggest that the first compounds have a nearly planar conformation whereas the second and third type of derivatives have a twisted conformation.

KEY WORDS ^{13}C and ^1H NMR *N*-5'-methylsalicylideneanilines σ , F and R , σ_1 and σ_R^0 Conformation.

INTRODUCTION

The molecular conformation of *N*-benzylideneanilines and their derivatives, which is sensitive to the substituents on the ring, has been investigated by different methods, especially by electronic spectroscopy and measurement of dipole moments.^{1,2} During our studies of the reactions of metal ions with *N*-5'-methylsalicylideneanilines, it was desirable to have information on the molecular conformation of these molecules. *N*-Salicylideneanilines are known to exhibit interesting conformation-dependent properties, such as thermochromism.³ However, to our knowledge, no conformational analysis of these molecules is available in the literature. The ^{13}C NMR data of a few *N*-salicylideneanilines have been published.⁴ Correlations of ^{13}C chemical shifts with Hammett constants and Swain-Lupton-Hansch F and R parameters have been reported⁵ and shown to be suggestive of the molecular conformation in some *N*-benzylideneaniline derivatives. In the literature,^{1,2} generally only one twist angle is considered for *N*-benzylideneanilines, although it is normally necessary to consider two twist angles, θ_N and θ_C (Fig. 1). However, for *N*-5'-methylsalicylideneanilines, only θ_N need be considered, for reasons given later. A study of the ^{13}C and ^1H NMR spectra of six *N*-5'-methylsalicylideneanilines (1-6, Fig. 1) is described in this paper. Correlations of the chemical

shifts of C- α and C-4' with σ and F and R parameters⁶ are made for *N*-salicylideneanilines and *N*-benzylideneanilines.⁷ Further, dual substituent parameter (DSP) analysis (both linear and non-linear) has also been performed using the σ_1 and σ_R^0 parameters of Bromilow *et al.*⁸ The results show that the correlations are apparently indicative of the molecular conformation of *N*-salicylideneanilines.

EXPERIMENTAL

Compounds 1-6 were prepared by a known procedure⁹ and were purified by repeated crystallization from methanol. Compounds 4 (m.p. 174 °C) and 5 (m.p. 184 °C) are new and were analysed by mass spectrometry. The mean masses of 289.01 and 336.99 obtained for 4 and 5, respectively, are in agreement with the expected molecular weights.

^{13}C NMR spectra of 0.5 M solutions were recorded in CDCl_3 at ambient temperature on a Bruker WH 270 spectrometer operating at 67.89 MHz using TMS as internal standard. Spectra were acquired in 16K data blocks in the quadrature detection mode, using a pulse width of 30×10^{-6} s and an acquisition time of 1.0 s. ^1H NMR spectra of 0.05 M solutions in CDCl_3 were recorded at ambient temperature on the same instrument operating at 270 MHz. The experimental parameters were as follows: pulse width, 5×10^{-6} s; acquisition time, 3.0 s; and number of pulses, 20-30. TMS was used as an internal reference. The IR absorption spectra were obtained on a Perkin-Elmer 599 spectrometer and spectra of the solid samples were recorded as Nujol mulls. Molecular orbital calculations at the CNDO/2 level were performed using standard programs¹⁰ on a DEC 1090 computer system.

RESULTS AND DISCUSSION

The ^{13}C chemical shifts (δ , ppm) of 1-6 are listed in Table 1. Proton coupled spectra were utilized for the

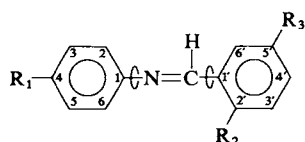


Figure 1. Conformation of *N*-benzylideneaniline and its derivatives. *N*-5'-Methylsalicylideneanilines (this work): $\text{R}_3 = \text{CH}_3$, $\text{R}_2 = \text{OH}$, $\text{R}_1 = \text{H}$ (1), OCH_3 (2), Cl (3), Br (4), I (5), NO_2 (6). *N*-Salicylideneanilines (*p*-substituted derivatives) (ref. 4): $\text{R}_3 = \text{H}$, $\text{R}_2 = \text{OH}$, $\text{R}_1 = \text{H}$, CH_3 , OCH_3 , Br , NO_2 , CN . *N*-Benzylideneanilines (4-substituted derivatives) (ref. 7): $\text{R}_3 = \text{R}_2 = \text{H}$, $\text{R}_1 = \text{H}$, CH_3 , OCH_3 , Cl , Br , I , COOH , COCH_3 , COOCH_3 , NO_2 .

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Table 1. ^{13}C and ^1H chemical shifts (δ , ppm) of *N*-5'-methylsalicylideneanilines

R_1	C- α	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C-1	C-2 C-6	C-3 C-5	C-4	H- α	2-OH
H	162.8	119.1	159.2	117.2	134.1	128.2	132.3	149.0	121.2	129.4	126.8	8.58	13.02
OCH ₃	160.3	119.3	159.1	117.1	133.3	128.1	132.0	141.9	122.3	114.9	—	8.57	13.17
Cl	163.2	118.9	159.2	117.3	134.5	128.4	132.4	147.6	122.6	129.6	132.6	8.55	12.81
Br	163.2	118.8	159.1	117.2	134.5	128.3	132.6	147.9	122.8	132.4	120.3	8.55	12.77
I	163.2	118.9	159.2	117.2	128.3	128.3	132.3	148.7	123.2	138.6	91.2	8.55	12.75
NO ₂	165.5	118.6	159.5	117.5	135.6	128.8	132.9	—	121.9	125.3	154.6	8.59	12.37

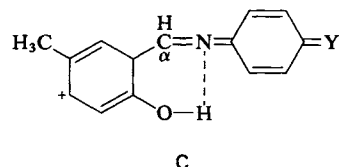
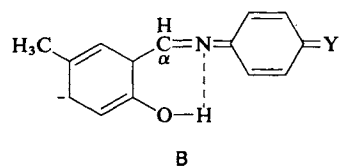
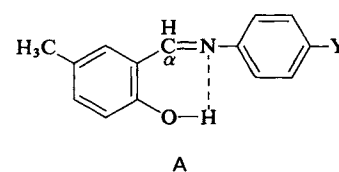
correct assignment of the chemical shifts. The signal due to C-4 in **2** and that due to C-1 in **6** was not observed. This can be attributed to either the inherent weakness of the signal or overlap with other signals occurring in this region. The H- α chemical shifts are also included in Table 1.

The pronounced downfield shift of the 2-OH protons (δ 12–13 ppm) in the ^1H NMR spectra of **1–6** (Table 1) clearly demonstrates the presence of strong internal O—H \cdots N hydrogen bonding. It was impossible however, to obtain evidence of intramolecular hydrogen bonding in **1–6** from the N-H stretching modes as they were not observed in the IR spectra. Percy and Thornton,¹¹ in a study of some salicylideneanilines, cited similar evidence for intramolecular hydrogen bonding. The formation of internal hydrogen bonding and the geometry of the CH=N grouping requires that the C-phenyl ring be coplanar with the HC=N skeleton, consequently increasing the conjugative interaction of the two phenyl rings (hence θ_C can be neglected). This is reflected in the significant downfield shift of the C- α signal in **1–6** compared with those in similar but non-hydrogen-bonded compounds.⁷

X-ray structure determinations have shown¹² *N*-5'-methylsalicylideneaniline (**1**) to be isostructural with *N*-5'-chlorosalicylideneaniline, which is planar.¹³ On the other hand, the parent *N*-salicylideneaniline takes a non-planar conformation and has a twist angle, θ_N , of 49°, as determined by x-ray crystallography.¹⁴ These facts demonstrating the importance of the 2-OH and 5'-methyl groups led us to postulate that **1–6** may be planar. The following important resonance forms contributing to bonding may be written for the planar molecules. The canonical form B contributes to a greater extent for an electron-donating Y substituent while form C is more dominant when the Y substituent is an electron-withdrawing group. This is consistent with the data in Table 1 and explains, for example, the upfield shift of C- α and C-4' for **2** and the downfield shift of C- α and C-4' for **6**.

Molecular orbital calculations were performed by the CNDO/2 method for the representative compound **1**. Geometrical parameters were transferred from the x-ray structural data of *N*-5'-chlorosalicylideneaniline.¹³ Bond distances and inter-bond angles were assumed to be unchanged during the internal rotations. The total energies calculated for different twist angles of θ_N at intervals of 20° ($\theta_C = 0^\circ$) showed only small differences between different conformations (approximately 2 kcal mol⁻¹), suggesting that all the conformations are equally accessible in the gaseous state.

In Table 2, the correlations of the chemical shifts of C-4' and C- α with different parameters are shown for



1–6, and also for 4-substituted *N*-salicylideneanilines and *N*-benzylideneanilines, with the data for the latter two sets of derivatives taken from the literature.^{4,7} For **1–6** the chemical shifts of C-4' and C- α show good correlations with σ as well as the *F* and *R* parameters. For determining whether the inductive effect or the resonance effect dominates in the substituent-induced chemical shift (SCS) correlations, Charton¹⁵ has shown that the DSP approach using the σ_1 and σ_R^0 parameters is more helpful than the *F* and *R* parameters. It can be seen from Table 2 that the correlations of C-4' and C- α with the σ_1 and σ_R^0 values are reasonably good ($f < 0.2$).¹⁶ Further, for **1–6** acceptable DSP-NLR correlations ($f \leq 0.06$) are obtained for the C-4' and C- α SCS values. The analysis reveals that the resonance effect is predominant, the inference being consistent with the result from the *F* and *R* analysis. Although the ratio B_3/B_2 is not much greater than 1 in both analyses, it is significant enough to show the predominance of the resonance contribution even at the distant C-4'; this indicates the nearly planar conformation for these molecules. For *N*-benzylideneanilines, on the other hand, C-4' does not correlate with σ or the *F* and *R* parameters and *f* does not converge to an acceptable limit by the DSP-NLR treatment (Table 2). However, the correlation of the C-4' chemical shifts with *F* alone is excellent. These observations are in accord with the known non-planarity of *N*-benzylideneanilines.^{1,17}

An analysis of the ^{13}C NMR data for 4-substituted *N*-salicylideneanilines by Salman *et al.*⁴ showed exactly the same trends as for *N*-benzylideneanilines (Table 2),

Table 2. Correlations^a of ¹³C chemical shifts

Compound	Carbon	Parameters	Coefficients			
			B ₁	B ₂	B ₃	r
N-5'-Methylsalicylideneanilines (this work)	C-4'	σ	134.0	2.13	—	0.992
		F, R	134.1	1.75	2.34	0.995
		F	No correlation (r < 0.8)			
		R	134.8	2.87	—	0.861
		σ ₁ , σ _R ⁰	ε = 0	1.77	2.82	0.094 ^b
	C-α	σ ₁ , σ _R ⁰	ε = -0.7	1.84	2.19	0.010 ^b
		σ	162.1	4.62	—	0.967
		F, R	162.8	2.86	5.96	0.990
		σ ₁ , σ _R ⁰	ε = 0	2.92	7.06	0.156 ^b
		σ ₁ , σ _R ⁰	ε = -0.9	3.13	4.96	0.015 ^b
N-Salicylideneanilines (Ref. 4)	C-4'	σ	133.4	1.69	—	0.845
		F, R	133.1	2.40	0.69	0.902
		F	133.0	2.64	—	0.881
		R	No correlation (r < 0.8)			
		σ ₁ , σ _R ⁰	ε = 0	3.29	0.03	0.32 ^c
	C-α	σ	163.2	4.34	—	0.904
		F, R	163.1	5.12	4.37	0.936
		σ ₁ , σ _R ⁰	ε = 0	6.22	2.92	0.351 ^c
N-Benzylideneanilines ^d (Ref. 7)	C-4'	σ	No correlation (r < 0.8)			
		F, R	No correlation (r < 0.8)			
		F ^e	130.9	4.10	—	0.997
N-Benzylideneanilines	C-4'	R	No correlation (r < 0.8)			
		σ ₁ , σ _R ⁰	ε = 0	2.84	-1.24	0.787 ^c
	C-α	σ	—	4.88 ^f	—	0.973 ^f
		F, R	159.7	3.53	5.37	0.984
		σ ₁ , σ _R ⁰	ε = 0	4.06	6.82	0.197 ^c

^a B₁, B₂ and B₃ are coefficients of the correlations $\delta = B_1 + B_2\sigma$ or $\delta = B_1 + B_2F + B_3R$ or $\delta = B_1 + B_2F$ or $\delta = B_1 + B_2R$ or SCS = $B_2F + B_3R$; r is the correlation coefficient.

^b f values.

^c Non-convergent f values.

^d p-COOH derivative is excluded.

^e p-H derivative is excluded.

^f Ref.7.

and suggests a non-planar conformation for these molecules.

The azomethine proton shows an upfield shift of 0.03 ppm for 5-nitro-N-salicylideneaniline relative to the unsubstituted derivative.¹⁸ This may be explained on the basis of a twisted conformation for this molecule.¹⁹ The range of the H-α chemical shifts (Table 1) for the compounds studied in this paper is too small to attempt any correlations but no anomalous substituent effect is

observed, consistent with the expected planar conformation for 1-6.

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