

ULTRAVIOLET ABSORPTION BANDS AND ELECTRONIC CHARGE TRANSFERS OF SALICYLIDENEANILINES IN SINGLET EXCITED STATES*

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ABSTRACT

Salicylideneaniline presents an electronic absorption band spectrum of complex patterns between 200 and 450 nm. However, we have successfully developed the electronic transition assignments of this molecular compound and its derivative species, substituted on the aniline ring of the salicylideneaniline structure. Thus, we have analyzed the substituent effect of the electron-acceptor groups such as $-\text{CN}$, $-\text{COCH}_3$, and $-\text{NO}_2$, as well as the electron-donor groups such as $-\text{CH}_3$, $-\text{OCH}_3$, and $-\text{N}(\text{CH}_3)_2$ on the electronic transition energies of the main absorption spectral region. From a theoretical point of view, we have characterized the orbital nature of the electronic transition energies and the

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net charge transfer in excited electronic states by means of molecular orbital theory calculations in the AM1 and ZINDO/S-CIS semiempirical frameworks. Our present study has permitted us to determine the three main electronic transitions localized under the broad absorption spectral band in the spectral region between 250 and 450 nm. Furthermore, we have experimentally characterized the effect of the substituents on the first three excited electronic states for every substituted salicylideneaniline compound.

Key Words: Salicylideneanilines; Electronic absorption bands; ZINDO/S-CIS calculations and electronic charge transfer transitions

INTRODUCTION

Recently we have reported the salicylideneaniline systems (*ortho*-OH-Ph-CH=N-Ph) as particular types of solar molecular screens due to their high protection factor and photostability to ultraviolet solar radiation (1,2). However, these molecular systems present a singular case of long distance intramolecular charge transfer when the aniline ring is substituted by an electron-acceptor group at the *para*-position.

Intramolecular electronic charge transfer (IECT) studies of polar aromatic compounds have been the subject of our program of research during the last few years (3-6). Therefore, our interest has been focused toward the molecular systems of the D-B-A type, defined by an electron-donor group (D), an electron-acceptor group (A), and a conductor bridge structure (B). Thus, these salicylideneanilines emerge as a singular case of D-B-A compounds, where the -C=N- molecular bridge determines the nature of the photoinduced charge transfer process (4).

In the present work, we have carried out a spectral assignment of the electronic absorption bands of the salicylideneaniline series by means of the substituent effect on the electronic structure. We have experimentally characterized the UV electronic absorption bands when the substituent is localized at the *para*-position of the aniline ring of the salicylideneaniline. Thus, we have synthesized substituted salicylideneanilines by an electron-acceptor group such as -CN, -COCH₃, and -NO₂, or by an electron-donor group such as -CH₃, -OCH₃, and -N(CH₃)₂. On the other hand, from a theoretical point of view, we have analyzed the electronic transition energies and the electronic charge distributions in excited states by means of semiempirical molecular orbital theory calculations, in the ZINDO/S-CIS framework (7).

MATERIALS AND METHODS

Salicylideneanilines (Fig. 1) were synthesized by a Schiff's base condensation procedure stirring equimolar quantities of salicylaldehydes and aniline in methanol solution (8). The synthesized compounds were salicylideneaniline (Anil-H), salicylidene-*p*-cianoaniline (Anil-CN), *p*-methoxysalicylidene-*p*-cianoaniline (MeO-Anil-CN), salicylidene-*p*-acetoaniline (Anil-COMe), *p*-methoxysalicylidene-*p*-acetoaniline (MeO-Anil-COMe), salicylidene-*p*-nitroaniline (Anil-NO₂), *p*-methoxysalicylidene-*p*-nitroaniline (MeO-Anil-NO₂), salicylidene-*p*-methylaniline (Anil-Me), salicylidene-*p*-methoxyaniline (Anil-MeO), and salicylidene-*p*-dimethylaminoaniline (Anil-NMe₂).

Reactive chemicals and solvents were purchased from Aldrich Chemical Co. Each one of the compounds under study were structurally characterized by infrared and ¹H NMR spectroscopy and physical properties were previously confirmed. Recrystallizations were done twice in methanol at low temperature and the compounds were purified by sublimation. The absorption spectra of fresh solutions in ethanol were prepared for spectral registration in a Perkin Elmer Lambda 11 UV-vis at 20°C, in quartz cells.

Furthermore, the molecular geometry of these salicylideneaniline molecules has been obtained by means of molecular orbital theory calculations in the semiempirical AM1 approach (9), under complete relaxation of the bond lengths and bond angles reaching the lowest energy condition (grad 0.01).

Electronic transition energies and net charge density calculations of the atomic centers in the ground and excited states were obtained by means of the Zerner' standardized ZINDO/S-CIS molecular orbital calculations (9). These calculations take into account the first 625 monoexcited electronic configurations in the configuration interaction (CI) procedure. The electronic transition energies

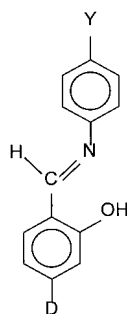


Figure 1. Salicylideneaniline series. D: -H, -OCH₃; Y: -H, acceptor groups (-CN, -COCH₃, -NO₂), or donor groups (-CH₃, -OCH₃, -N(CH₃)₂).

agree very well with the experimental spectral data. The computational work was done on a PC network station at our laboratory.

RESULTS AND DISCUSSION

Ultraviolet Absorption Bands

In Figures 2 and 3 we present the electronic absorption bands of these salicylideneanilines (1,2) in the UV-spectral region. These species present a complex pattern between 250 and 450 nm, but this spectral region can be well characterized by using three zones for the different compounds of the series under study. The first zone (band I) is characterized by a broad and intense spectral band between 330 and 450 nm; the second zone (band II) is defined by the intermediate spectral region between two main absorption band maxima where, in addition, this zone can be well characterized by fine spectral structure with two small absorption maxima between 290 and 330 nm; and finally, the third zone (band III) is

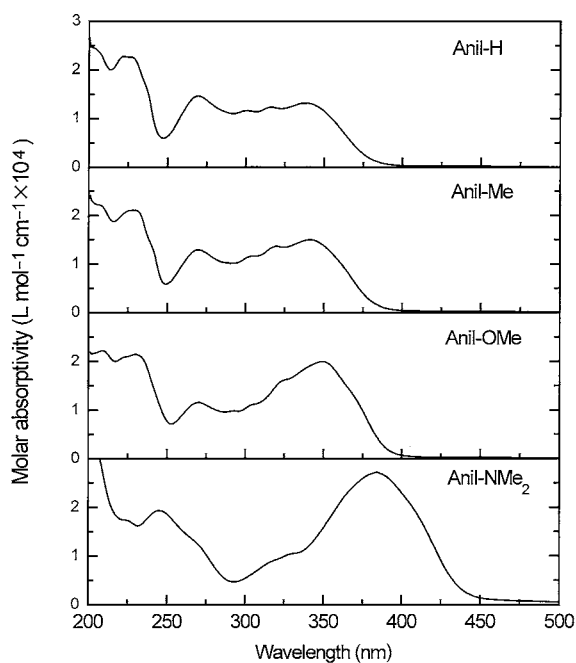


Figure 2. Electronic absorption spectra of salicylideneanilines substituted by electron-donor groups at the *para*-position of the aniline ring.

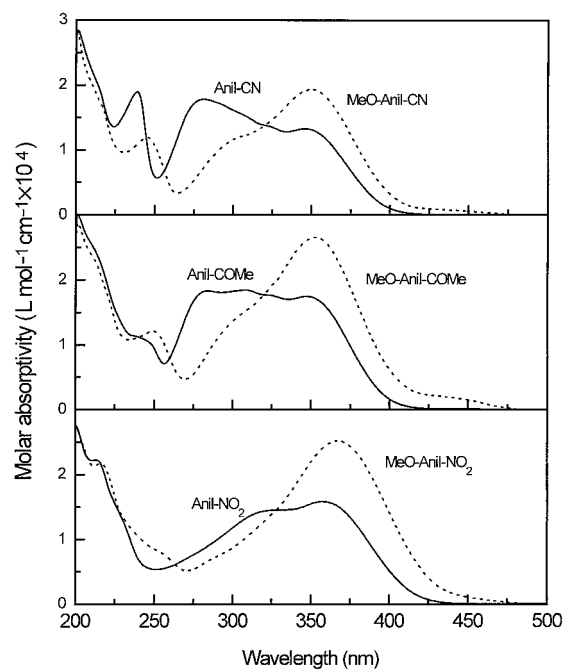


Figure 3. Electronic absorption spectra of salicylideneanilines substituted by electron-acceptor groups at the *para*-position of the aniline ring (—), and salicylideneanilines substituted by electron-acceptor groups at the *para*-position of the aniline ring and a methoxy group at the *para*-position of the salicylidene ring (---).

characterized by a broad and intense band, similar to the first one, between 250 and 290 nm.

However, these three spectral zones exhibit different behaviors according to the nature of the substituents on the molecular structure of the salicylideneaniline compounds. Thus, we have observed two main effects according to the electron-donor and electron-acceptor roles of the substituent.

Electron-Donor Substituent on the Aniline Structure

We have chosen three electron-donor substituents of different strengths: $-\text{CH}_3$, $-\text{OCH}_3$, and $-\text{N}(\text{CH}_3)_2$ groups. In Figure 2 we can appreciate how band I is shifted to the red while bands II and III practically remain in the same spectral region. Furthermore, the substituent effect increases the intensity of band I, while the other two bands keep almost the same intensity. It is interesting to note that

in the salicylidene-*p*-dimethylaminoaniline system a fourth band located under 250 nm is shifted to the red and emerges as a shoulder on band III (see the spectral region at 250 and 275 nm). The first conclusion of this study is related to the dependence of band I to the electron-donor character of the substituent, that is, band I is associated to an electronic transition mainly located in the aniline structure of the salicylideneaniline. On the other hand, since bands II and III are not shifted by the same substituents, we can conclude that these electronic transitions must be preferentially localized in the salicylidene structure of the salicylideneaniline.

Electron-Acceptor Substituent on the Aniline Structure

In this case we have chosen three electron-acceptor substituents of different strengths: $-\text{CN}$, $-\text{COCH}_3$, and $-\text{NO}_2$ groups. In Figure 3 we show these spectra and can appreciate the spectral differences with respect to the same substituted *p*-methoxysalicylideneaniline. From these spectra, we can appreciate how the band I remains practically without change in the same spectral region, while bands II and III are shifted to the red. Furthermore, it can be observed that the intensity of these last bands increases according to the electron-acceptor strength of the substituent group. However, while the ciano and carbonyl salicylideneaniline compounds present the three spectral zones previously identified, the strength of the nitro acceptor group in the third compound permits a shift of spectral band III over band II, over a wider range than band I. This last phenomenon is a typical effect of the charge transfer bands observed earlier in benzylideneanilines (10). Therefore, the spectral band III is a well-established photoinduced charge transfer transition involving the salicylidene and the aniline rings.

Electron-Donor Substituent on the Salicylidene Structure

In order to emphasize the effect of the substituents observed in the electron-acceptor groups, we have incorporated the methoxy substituent, as an intermediate electron-donor, on the salicylidene ring at the *para*-position. This substituent reinforces the same effect produced by the OH group at *ortho*-position, as a similar mild electron-donor. Thus, in Figure 3 we can see the spectral shift of band III, while band I remains in the same place. Furthermore, we can compare how the intensity of the first zone increases due to the superposition of both bands (i.e., bands I and III). This new effect permits us to confirm the nature of band III as a typical charge transfer transition from the salicylidene ring toward the aniline ring, that is, a photoinduced charge transfer between the electron-donor groups ($-\text{OCH}_3$ and $-\text{OH}$) and the electron-acceptor group, through the $-\text{C}=\text{N}-$ bridge.

$(\pi \rightarrow \pi^*)$ Singlet Electronic Transitions

Our electronic transition analysis has been done on the basis of ZINDO/S-CIS molecular orbital theory calculations (9). In this present work we have neglected the ($n \rightarrow \pi^*$) electronic transitions due to a low molar absorptivity of these absorption spectra with respect to the ($\pi \rightarrow \pi^*$) bands. On the other hand, we have focalized our analysis on the first four ($\pi \rightarrow \pi^*$) singlet electronic transitions that appear in the UV-spectral range, since the remainder computational transitions appear in the spectral range under 250 nm, and near to vacuum UV.

Table 1. ZINDO/S-CIS Electronic Transition Wavelengths (nm), Oscillator Strength (f_{osc}), Polarization's Axis of the Transition^a (X or Y), and Main Configuration Orbital Composition^b (%) of Salicylideneanilines Substituted by Electron-Donor Groups at the Aniline Ring

Compound	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$	$S_0 \rightarrow S_3$	$S_0 \rightarrow S_4$
Anil-H				
Wavelength (nm)	334	304	284	281
f_{osc}	0.193	0.374	0.404	0.008
Polarization	X	X	X	Y
Orbital configurations	H \rightarrow L 35% H-4 \rightarrow L 34%	H-1 \rightarrow L 35% H \rightarrow L 33%	H \rightarrow L 24% H-3 \rightarrow L 16% H-1 \rightarrow L 16%	H \rightarrow L + 2 46% H-2 \rightarrow L + 3 19% H-2 \rightarrow L 19%
Anil-Me				
Wavelength (nm)	338	304	289	286
f_{osc}	0.258	0.402	0.020	0.358
Polarization	X	X	Y	X
Orbital configurations	H \rightarrow L 43% H-4 \rightarrow L 33%	H-1 \rightarrow L 37% H \rightarrow L 27% H-4 \rightarrow L 12%	H \rightarrow L + 2 57% H-2 \rightarrow L + 3 16% H-2 \rightarrow L 15%	H \rightarrow L 21% H-3 \rightarrow L 18% H-1 \rightarrow L 14%
Anil-OMe				
Wavelength (nm)	339	305	293	288
f_{osc}	0.303	0.444	0.027	0.300
Polarization	X	X	Y	X
Orbital configurations	H \rightarrow L 46% H-4 \rightarrow L 33%	H-1 \rightarrow L 33% H \rightarrow L 28% H-4 \rightarrow L 17%	H \rightarrow L + 2 62% H-1 \rightarrow L + 3 14% H-2 \rightarrow L 12%	H \rightarrow L 17% H-3 \rightarrow L 14% H-1 \rightarrow L 18%
Anil-NMe₂				
Wavelength (nm)	351	313	308	293
f_{osc}	0.573	0.453	0.044	0.065
Polarization	X	X	Y	X
Orbital configurations	H \rightarrow L 64% H-4 \rightarrow L 18%	H-1 \rightarrow L 15% H \rightarrow L 20% H-4 \rightarrow L 30%	H \rightarrow L + 2 73% H-2 \rightarrow L + 3 8%	H \rightarrow L + 1 13% H-3 \rightarrow L 14% H-1 \rightarrow L 27%

^a X \perp Y.

^b HOMO: H; LUMO: L.

Table 2. ZINDO/S-CIS Electronic Transition Wavelengths (nm), Oscillator Strength (f_{osc}), Polarization's Axis of the Transition^a (X or Y), and Main Configuration Orbital Composition^b (%) of Salicylideneanilines Substituted by Electron-Acceptor Groups at the Aniline Ring

Compounds	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$	$S_0 \rightarrow S_3$	$S_0 \rightarrow S_4$
Anil-H				
Wavelength (nm)	334	304	284	281
f_{osc}	0.193	0.374	0.404	0.008
Polarization	X	X	X	Y
Orbital configurations	H \rightarrow L 35% H-4 \rightarrow L 34%	H-1 \rightarrow L 35% H \rightarrow L 33%	H \rightarrow L 24% H-3 \rightarrow L 16% H-1 \rightarrow L 16%	H \rightarrow L + 2 46% H-2 \rightarrow L + 3 19% H-2 \rightarrow L 19%
Anil-CN				
Wavelength (nm)	332	306	288	286
f_{osc}	0.326	0.439	0.012	0.473
Polarization	X	X	X, Y	X
Orbital configurations	H \rightarrow L 42% H-4 \rightarrow L 31%	H-1 \rightarrow L 31% H \rightarrow L 29%	H \rightarrow L + 3 45% H-2 \rightarrow L 15% H-3 \rightarrow L 11%	H \rightarrow L 19% H-3 \rightarrow L 8% H-1 \rightarrow L 17%
Anil-COMe				
Wavelength (nm)	332	307	289	287
f_{osc}	0.347	0.516	0.142	0.302
Polarization	X	X	X	X
Orbital configurations	H \rightarrow L 40% H-4 \rightarrow L 26%	H-1 \rightarrow L 20% H \rightarrow L 35%	H \rightarrow L + 3 19% H-1 \rightarrow L 11% H-2 \rightarrow L 27%	H \rightarrow L + 3 14% H \rightarrow L 11% H-1 \rightarrow L 13%
Anil-NO₂				
Wavelength (nm)	336	315	298	273
f_{osc}	0.737	0.279	0.038	0.148
Polarization	X	X	X, Y	X
Orbital configurations	H \rightarrow L 55% H-4 \rightarrow L + 1 16%	H-4 \rightarrow L + 1 18% H \rightarrow L 21%	H-1 \rightarrow L 22% H \rightarrow L + 1 22% H-1 \rightarrow L + 1 11%	H \rightarrow L + 1 44% H-1 \rightarrow L + 1 12% H \rightarrow L 11%

^a $X \perp Y$ in plane.

^bHOMO: H; LUMO: L.

In Tables 1 and 2 we present the energy and orbital configurations of the main electronic transitions for the acceptor and donor group series. In both molecular series we have found an electronic transition of very low intensity, below 0.04 oscillator strength (f_{osc}) units, except for the $-\text{COCH}_3$ species ($f_{\text{osc}} = 0.142$). However, the remaining three electronic transitions of similar orbital configurations present a high intensity and a main polarization through the principal long axis of the molecules (X). According to the experimental absorption bands, we have assigned band I to the first electronic transition, band II to the second electronic transition, and band III to the third electronic transition of salicylideneaniline, while this

same band III is assigned to the fourth electronic transition in the remainder of the substituted salicylideneaniline compounds, because of the low f_{osc} calculated in the third electronic transition (see Tabs. 1 and 2).

Charge Transfer in Excited States

From the molecular orbital analysis in the ground and excited states, we have determined the charge transfer distribution observed in both series of substituted salicylideneanilines. In order to compare every compound, we have fractionated the molecular structure into the following five fragments: the salicylidene ring

Table 3. ZINDO/S-CIS Electronic Charge Transfer in Excited States (ZDO in e.u.) by Fragments^a of the Molecular Structure and the Total Dipolar Moment (μ_T in Debyes) of Salicylideneanilines Substituted by Electron-Donor Groups at the Aniline Ring

Compounds	ΔPh_s	ΔOH	$\Delta(HC=N)$	ΔPh_a	ΔY	μ_T
Anil-H						
S ₀						3.75
S ₁	-0.158	0.026	-0.013	0.134		5.55
S ₂	-0.016	0.046	-0.160	0.127		2.03
S ₃	-0.113	0.027	-0.096	0.180		4.77
S ₄	0.030	0.014	0.008	-0.053		3.56
Anil-Me						
S ₀						2.27
S ₁	-0.220	0.024	-0.035	0.187	0.005	6.08
S ₂	-0.034	0.050	-0.145	0.115	0.010	0.96
S ₃	0.026	0.012	0.003	-0.081	0.013	2.24
S ₄	-0.119	0.026	-0.085	0.163	0.011	3.42
Anil-OMe						
S ₀						3.84
S ₁	-0.249	0.023	-0.004	0.184	0.036	6.75
S ₂	-0.061	0.047	-0.135	0.112	0.028	1.90
S ₃	0.055	0.012	0.014	-0.153	0.038	3.75
S ₄	-0.125	0.030	-0.096	0.124	0.031	5.07
Anil-NMe ₂						
S ₀						4.25
S ₁	-0.321	0.009	-0.160	0.253	0.216	10.8
S ₂	-0.203	0.028	-0.083	0.077	0.174	4.94
S ₃	0.037	0.006	0.048	-0.285	0.199	4.91
S ₄	-0.142	0.039	-0.124	0.119	0.120	4.85

^aSalicylidene ring (Ph_s), hydroxyl group of the salicylidene ring (OH), $-HC=N-$ bridge (HC=N), aniline ring (Ph_a), and the electron-donor substituent (Y).

Table 4. ZINDO/S-CIS Electronic Charge Transfer in Excited States (ZDO in e.u.) by Fragments^a of the Molecular Structure and the Total Dipolar Moment (μ_T in Debyes) of Salicylideneanilines Substituted by Electron-Acceptor Groups at the Aniline Ring

Compounds	ΔPh_s	ΔOH	$\Delta(HC=N)$	ΔPh_a	ΔY	μ_T
Anil-H						
S ₀						3.75
S ₁	-0.158	0.026	-0.013	0.134		5.55
S ₂	-0.016	0.046	-0.160	0.127		2.03
S ₃	-0.113	0.027	-0.096	0.180		4.77
S ₄	0.030	0.014	0.008	-0.053		3.56
Anil-CN						
S ₀						5.99
S ₁	-0.154	0.028	0.016	0.100	0.002	1.02
S ₂	-0.034	0.049	-0.118	0.040	-0.007	7.20
S ₃	0.167	0.015	0.010	-0.199	0.006	5.95
S ₄	-0.089	0.029	-0.090	0.152	-0.003	6.75
Anil-COMe						
S ₀						7.78
S ₁	-0.031	0.029	0.073	0.029	-0.105	4.76
S ₂	0.096	0.044	-0.050	0.019	-0.109	8.02
S ₃	0.022	0.021	-0.077	0.123	-0.088	8.27
S ₄	0.045	0.027	-0.040	0.046	-0.082	8.50
Anil-NO ₂						
S ₀						7.57
S ₁	0.192	0.036	0.066	0.107	-0.405	9.32
S ₂	0.033	0.034	0.046	0.133	-0.253	9.16
S ₃	0.148	0.049	-0.080	0.133	-0.250	11.9
S ₄	0.009	0.030	-0.076	0.257	-0.222	11.2

^aSalicylidene ring (Ph_s), hydroxyl group of the salicylidene ring (OH), $-HC=N-$ bridge (HC=N), aniline ring (Ph_a), and the electron-acceptor substituent (Y).

(Ph_s), the hydroxyl group of the salicylidene ring (OH), the $-HC=N-$ bridge (HC=N), the aniline ring (Ph_a), and the electron-acceptor or electron-donor substituent (Y). In Table 2 we present the charge transfer distribution and the total dipolar moment (μ_T) in the ground and singlet excited electronic states. It is interesting to see how the theoretical dipolar moment in the first excited state increases according to the strength of the donor substituent, while the same condition is not observed by the acceptor substituents. Thus, the charge transfer goes from the donor to the salicylidene structure (see Tab. 3). This theoretical result is completely coherent to the experimental results previously discussed in the Introduction.

Another singular case is constituted by the fourth electronic transition in the acceptor series. In these species, the dipolar moment increases in proportion to the strength of the acceptor groups, and the charge transfer goes through the Ph_s ring to the acceptor group (see Tab. 4). A similar trend is observed in the second transition. These results coincide with the experimental data discussed earlier in this section. However, when we compare both of these charge transfer electronic transitions (i.e., the second and the fourth), the last one is the greatest, similar in experimental results when we compare bands III and II.

Finally, from the present spectral assignments, we would like to emphasize the characterization of band III as the band associated to the third (1) ($\pi \rightarrow \pi^*$) excited state of the salicylideneaniline. This is the main charge transfer excited state involving all the molecular structure from the electron-donor to the electron-acceptor group, while in the remainder electron-acceptor substituted species, this state corresponds to the fourth excited state.

Other similar D–B–A molecular systems with B as $(-\text{HC}=\text{N}-)_n$ and $n = 2$ and 3, are being subjects of new theoretical and experimental studies in our group.

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