

# Role of structural flexibility in fluorescence and photochromism of the salicylideneaniline: the ‘‘aldehyde’’ ring rotation

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## Abstract

X-ray analysis, absorption and luminescent steady-state spectroscopy as well as quantum-chemical calculations have been used for comparative investigations of salicylideneaniline (i) and the more rigid phenylimine of 7-hydroxyindanone-1 (ii) molecules.

In the latter the ‘‘aldehyde’’ ring A rotation is inhibited by inclusion of the saturated bridge fragment.

Fluorescence with anomalous Stokes shift (ASS fluorescence) is typical for both (i) (only in glassy solvent) and (ii) (in liquid or glassy solvent). The ASS fluorescence occurs only as the result of excited-state intramolecular proton transfer (ESIPT). In liquid solvents the ESIPT in (i) may be followed by twisted intramolecular charge transfer (TICT) formation via adiabatic 90° ring A twist around the C<sub>AR</sub>=C bond in the C=N bond (*Z*)-isomer of the zwitterion NH structure. The TICT state is one of the channels to quench the ASS fluorescence of (i) in the liquid solvent.

The compound (ii) is found to have no photochromism unlike (i). The photochromism of the latter is connected not only with ESIPT but also with ring A 60–80° twist about the C<sub>AR</sub>=C bond in the C=N (*E*)-isomer of the NH structure.

It is proposed that the photocolored form originates from the concerted diabatic process (ring A twist and (*Z*)-(*E*) isomerization) competing with ASS fluorescence and the formation of the ‘‘TICT-like’’ structure.

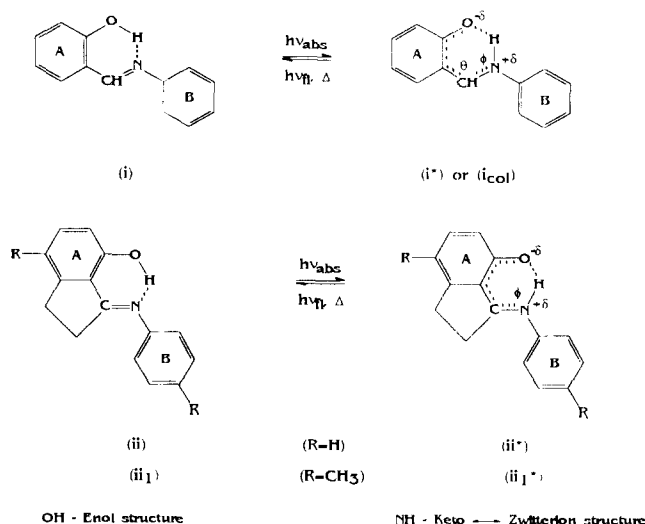
**Keywords:** Salicylideneaniline; Photochromism; Fluorescence; Anomalous Stokes shift; Excited-state intramolecular proton transfer; Twisted intramolecular charge transfer

## 1. Introduction

Adiabatic excited-state intramolecular proton transfer (ESIPT) OH → NH in the S<sub>1</sub> state is known to be a primary step only in the complex processes of photocoloration and in the origin of the fluorescence with anomalous Stokes shift (ASS fluorescence) for salicylideneaniline (i) and related molecules [1–7].

With steady-state excitation, ASS fluorescence and photocoloration may occur only in rigid matrices, especially in a glassy solvent at 77 K as well as in crystals [1–5].

Thus the molecular structure changes causing the ASS fluorescence quenching and the colored form decay are inhibited by viscous media (‘‘viscosity barrier’’).



The assumption was made that the necessary step of photocoloration may be connected with the NH...O bond disruption due to the ring A twist around the C=C bond in the

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Table 1  
The main comparative X-ray data for (i) and (ii)<sup>a</sup> (for the basic bond length and angles, see Fig. 1)

Fragment	Bond lengths (Å)			Angles (°)		
	Type	(i)	(ii <sub>1</sub> )	Type	(i)	(ii <sub>1</sub> )
A ring <sup>b</sup>	C–C	1.384	1.387	C–C–C	120.0	120.0
B ring <sup>b</sup>	C–C	1.382	1.390	C–C–C	120.0	120.0
Bridge group	C(1)–C(7)	1.453	1.435	C(1)–C(7)–N	121.9	120.8
	C(7)–N	1.294	1.293	C(7)–N–C(1')	121.2	121.8
	N–C(1')	1.419	1.412	$\theta$	0	0
	C(7)–C(8)	–	1.518	$\phi$	0	0
	C(8)–C(9)	–	1.558	$\psi$	49.0	50.7
	C(9)–C(6)	–	1.517			
H bond group	C(2)–O	1.347	1.349	C(2)–O–H	118.7	119.0
	O–H	0.89	0.84	O–H...N	148.2	125.0
	N...H	1.81	2.18			

<sup>a</sup> Detailed data have been given in Ref. [14].

<sup>b</sup> The mean values for C–C bonds and C–C–C angles of the rings are given.

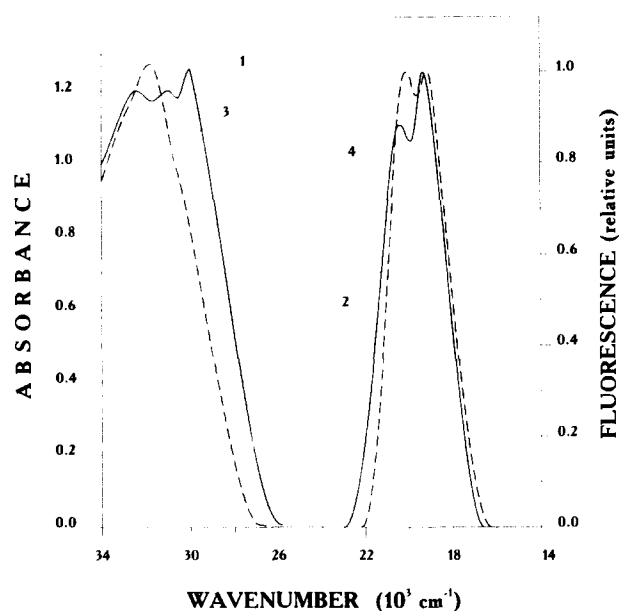


Fig. 2. Absorption and fluorescence spectra of the studied compound (i) and the model compound (ii) (solvent, glassy 4:1 (v/v) isopentane: isopropanol mixture; concentration,  $2 \times 10^{-4}$  M and  $2 \times 10^{-6}$  M for absorption and fluorescent measurements respectively with thickness of the cuvette 1.0 cm; excitation of the fluorescence, 365 nm): curves 1 and 2, absorption and fluorescence spectra respectively of (i); curves 3 and 4, absorption and fluorescence spectra respectively of (ii).

duced electron density redistribution in  $S_1$  state the increase in the OH acidity and C=N basicity can lead to ESIPT in both structures. As a result of this electronic transition (excitation in the long-wavelength band,  $\lambda_{Hg} = 365$  nm) the ASS fluorescence arises owing to ESIPT. The emission excitation and absorption spectra coincide well, as shown in Fig. 3. The emission has a rather high quantum yield in the liquid and glassy solutions of (ii) (Table 2) unlike (i) which fluoresces feebly in the rigid glassy solution only.

An increase in the viscosity of the polar solvent (in the temperature region 293–77 K) results in a blue shift of the

emission band of (ii) (Table 2). This blue shift is observed as a result of the inhibition of the orientation relaxation of the polar solvent molecules in the case of a decrease in the solute molecule electric dipole moment from  $|\mu_c|$  (in the excited ASS fluorescent structure (ii\*)) to  $|\mu_g|$  (in the ground-state structure (ii)) [15], i.e.  $|\mu_c| > |\mu_g|$ .

The emission bands (at 77 K) of both molecules are highly similar, having a typical fine vibronic structure (Fig. 2 and Table 2). It therefore follows from the above comparative findings that in (i) (as well as in the rigid model structure

Table 2  
The absorption and fluorescence characteristics of the compounds studied in a 4:1 (v/v) in isopentane:isopropanol mixture

Compound	$\nu_{\max}^{\text{abs}}$ ( $\text{cm}^{-1}$ )	$\nu_{\max}^{\text{fl}}$ ( $\text{cm}^{-1}$ )	Stokes shift ( $\text{cm}^{-1}$ )	$\phi^{\text{fl}}$
(i)	30000	– (19500, 18850) <sup>a</sup>	10500 <sup>b</sup>	$\approx 0.001$ <sup>a</sup>
(ii)	31600	19000, 18580 (19400, 18800) <sup>a</sup>	12600	0.044
(ii <sub>1</sub> )	31250	18380, 17690 (18790, 17950) <sup>a</sup>	12870	0.041

<sup>a</sup> At  $T = 77$  K.

<sup>b</sup> The difference between the maxima of the room-temperature absorption and low temperature (77 K) emission bands.

Table 3  
Characteristics of the  $S_1$  state of the enol structure

Energy (eV)		$\Delta q^a$			
Calculation	Experiment <sup>b</sup>	A ring	OH group	C=N group	B ring
3.69	3.72 (3.87)	+0.075	+0.031	–0.140	+0.034

<sup>a</sup> Change in the charge when excited in the  $S_1$  state.

<sup>b</sup> Maximum of the absorption long-wavelength band in isopentane for (i) and (ii) (in parentheses).

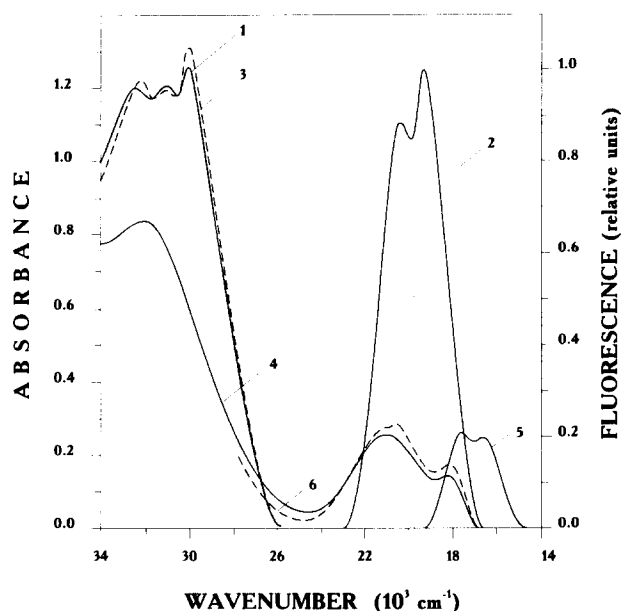
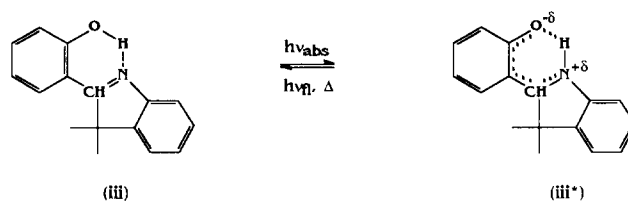


Fig. 3. Photocoloration of (i) (for measurement conditions see Fig. 2): curves 1, 2 and 3, absorption, ASS fluorescence emission and excitation spectra respectively of the initial form (i) (before irradiation); curves 4, 5 and 6, absorption, fluorescence emission and excitation spectra respectively of the colored form ( $i_{\text{col}}$ ) (after irradiation for 20 min at 365 nm).

(ii) the excited zwitterion *cis* (with respect to the C=C bond) NH structure ( $i^*$ ,  $\theta=0^\circ$ ) formed by ESIPT is responsible for ASS fluorescence.

These data also testify to the crucial role of ring A twist in the ASS fluorescence quenching. In fact, in (i) unlike (ii) the quenching "twisted intramolecular charge transfer (TICT)-like" NH structure with orthogonal ring A ( $i^*$ ,  $\theta=90^\circ$ ) may be formed adiabatically after ESIPT. This mechanism may be assumed by analogy with one suggested earlier [16–18]. In fact, the quantum-chemical data for the model structure ( $i_A$ ) (Table 4) obtained recently by us (semiempirical PM3 method) point clearly to the existence of the minimum on the potential surface of the  $S_1$  state with the polar structure ( $\mu_e = 12.5$  D) and a very small energy gap between excited ( $S_1$ ) and ground ( $S_0$ ) states ( $\Delta E = 0.63$  eV) at  $\theta=90^\circ$ . Thus the twist might result in quenching of the ASS fluorescence of (i) in liquid solutions. An increase in the solvent viscosity at low temperature arises in the hindrance of the ring A twist, increasing the fluorescence efficiency (Table 2).

According to experimental data there is, however, an additional emission quenching channel connected with the flexibility of the molecular structure (i). In fact the low fluorescence efficiency of (ii) with "frozen" ring A in the liquid solution (Table 2) may be indicative of ASS fluorescence quenching due to twist around the C=N bond in both (i) and (ii) by analogy with the C=C bond [16]. Following the preliminary examination undertaken on the model compound (iii) with inhibited twist around the C=N bond, it was found unlike (i) to be feebly fluorescent in the liquid solution ( $T = 293$  K) with ASS ( $\Delta\nu = 9000$   $\text{cm}^{-1}$ ) because of ESIPT ((iii)  $\rightarrow$  (iii\*)).



The well-known photochromism of (i) in rigid media and crystals (see Section 1) is connected with the photoinduced formation of the colored structure ( $i_{\text{col}}$ ) having the long-wavelength absorption band with maxima at about 480 and 540 nm (Fig. 3).

A significant experimental fact consists in the lack of photocoloration of (ii) under the same conditions in spite of the ESIPT reaction (see above). Hence the formation of a metastable photocolored structure by irradiation of the initial compound (i) must be connected not only with ESIPT but also with the ring A twist. Thus direct proof of the crucial role of the ring A twist in the photochromism of molecule (i) has been provided.

The concrete structure of the NH colored form with twisted ring A ( $i_{\text{col}}$ ) (the value of the angle  $\theta$ ) is the next essential problem which has been examined by quantum-chemical calculations.

As follows from the data presented (Table 4) the first ( $S_0$ – $S_1$ ) electron transition in the NH structure of (i) is connected essentially with charge transfer from the keto ring A to the C=N group as well as in the model structure ( $i_A$ ) having no ring B. Therefore it is expected that characteristics of the transition depend strongly on the ring A twist.

The transition energy falls (the wavelength of the absorption band maximum shifts to red) on an increase in the ring A acoplanarity with the extremum of  $90^\circ$  ( $E_{\text{min}} = 1.92$  eV;  $\lambda = 645$  nm) (Table 5). According to the data of both the CNDO/S and PPP methods of quantum-chemical calculations the planar *trans* ( $\theta = 180^\circ$ ) as well as *cis* ( $\theta = 0^\circ$ ) structures ( $i_{\text{col}}$ ) cannot be responsible for the observed absorption bands of the colored form ( $\lambda_{\text{max}} = 480$  and 540 nm (Fig. 2)). A conformity of the experimental and calculated band positions is observed at  $\theta = 60$ – $80^\circ$  with a small oscillator strength of the transition (Table 5). For the same angles, a strong charge separation occurs between ring A and the C=N bond in the non-planar NH structure (Table 6).

In other words the weakly absorbing NH acoplanar (but not *trans*!) zwitterionic structure is responsible for the photochromism of the salicylideneaniline molecule.

Table 4  
Redistribution of the charge  $\Delta q$  in the NH structure ( $\theta=0^\circ$ ) on excitation ( $S_0 \rightarrow S_1$ ) in the studied and model molecules

Compound	$\Delta q$			
	O atom	A ring	C=N group	B ring
(i), (ii)	+0.019	+0.090	–0.128	+0.019
( $i_A$ ) <sup>a</sup>	+0.023	+0.073	–0.096	–

<sup>a</sup> Model structure without B ring:  $A^- - C=N^+ H_2$ .

Table 5  
Dependence of the energy  $E$  (wavelength  $\lambda$ ) and oscillator strength  $f$  of the lowest electron transition ( $S_0 \rightarrow S_1$ ) on A ring twist  $\theta$  in the NH structure <sup>a</sup>

$\theta$ (°)	$E$ (eV)	$\lambda$ (nm)	$f10^2$
0	<u>2.87</u> (2.76)	432 (449)	<u>22.6</u> (54.0)
30	<u>2.84</u>	436	<u>6.9</u>
40	2.71	457	
50	2.57	482	
60	<u>2.43</u>	510	<u>0.7</u>
70	2.26	548	
80	<u>2.09</u>	593	<u>0.8</u>
85	<u>2.01</u>	617	
90	<u>1.92</u>	645	<u>0.9</u>
95	<u>2.01</u>	617	
100	<u>2.10</u>	590	
110	2.28	544	
120	<u>2.47</u>	502	<u>0.3</u>
130	2.64	470	
140	2.82	440	
150	<u>2.99</u>	415	<u>0.1</u>
180	<u>2.99</u> (2.82)	414 (440)	<u>43.1</u> (73.0)

<sup>a</sup> The underlined values and values in parentheses (for flat structures) were calculated by CNDO/S and PPP methods respectively. The others are obtained by linear interpolation.

The above structure of the colored form allows us to understand why the activation energy of the dark bleaching reaction ( $30 \text{ kJ mol}^{-1}$  [8,19]) for (i) was found to be much less than that of the *trans-cis* isomerization about the C=C bond ( $160\text{--}170 \text{ kJ mol}^{-1}$  [8]). As this metastable structure has a very short lifetime in the liquid solvents,  $10^{-6}\text{--}10^{-7} \text{ s}$  [19], it is stabilized by rigid media, especially in the glassy solvent at 77 K. In these conditions the fluorescence corresponding to the absorption band of the colored form was observed (Fig. 3).

According to experimental data, this emission is not excited in the long-wavelength absorption band of the initial form (i) and differs strongly from the ASS fluorescence (Fig. 3). Hence the photocolored structure originates in the ground state from the excited state directly, i.e. the photocoloration is the diabatic ('non-adiabatic') process.

However, the mechanism and energetics of such an unusual twisted structure are not sufficiently clear and further studies of this problem are necessary. Possible mechanisms may be considered. The twist around the C=N bond in the NH structure is also assumed to be responsible for diabatic

formation of the colored structure with twisted ring A. In fact, (iii) with the inhibited rotation around the C=N bond is not found to be photochromic unlike (i) in glassy solvent ( $T=77 \text{ K}$ ) in spite of the ESIPT and of the ring A twist opportunity. However, according to our preliminary data of quantum-chemical calculations, the rotation around the C=N bond by itself ( $0^\circ < \phi < 180^\circ$ ) cannot lead to the appearance of the typical long-wavelength bands.

On the other hand, there are some findings [21,22] indicative of the existence of a metastable twisted NH zwitterion structure formed by a rotation around both the C=C and the C=N bonds ( $\theta=70^\circ$ ;  $\phi=180^\circ$ ) which may be responsible for coloration.

Preliminary supposition may therefore be made about the role of the steric interactions in the (*E*)-isomer of NH structure with respect to the C=N bond between the N-Ph group and ring A, resulting in twist of the latter in the concerted diabatic process of photocoloration.

The mechanism of colored structure formation is explored now and will be discussed in detail in the next communication.

On the basis of the above-described results, using the well-known kinetic data concerning the photoinduced processes in (i) [6,20–22], a simplified scheme may be suggested (Fig. 4). The primary photoinduced process, a fast ESIPT in the  $S_1$  state, leads to the formation of the planar NH structure ( $i^*$ ) which is responsible for the ASS fluorescence displayed in rigid media only. Afterwards, two processes competing with the ASS fluorescence and between themselves can occur, adiabatic ring A twist leading only in the liquid solvent to the 'TICT' state ( $i^*$ ,  $\theta=90^\circ$ ) in the (*Z*) structure of the NH form with respect to the C=N bond. This structure makes a considerable contribution to the ASS fluorescence quenching. The process is reversible completely via the ground state and inhibited by the rigid media ('viscosity barrier') in the  $S_1$  state. In both liquid and rigid media, in spite of a 'viscosity barrier' in the latter, the concerted diabatic process including (*Z*)–(*E*) isomerization about the C=N bond and ring A  $70^\circ$  rotation around the C=C bond may be the origin of the feebly fluorescent colored form ( $i_{col}$ ). It is assumed to have a non-planar structure as the result of a steric interaction between the *N*-aryl and keto A rings solely in the (*E*)-isomer with respect to the C=N bond. The photochromic reaction may be an additional efficient channel of ASS fluorescence quenching. In liquid solvents the ground-state reverse process of

Table 6  
The distribution of the charge on the fragments of the NH structure of (i) depending on A-ring twist

$\theta$ (°)	O atom	A ring	C=N group	B ring	$\mu_g$ (D) <sup>a</sup>
0	–0.458	+0.133	–0.180	+0.504	3.78
60	–0.500	+0.017	–0.018	+0.501	5.21
80	–0.527	+0.077	+0.090	+0.514	6.78
90	–0.545	+0.140	+0.162	+0.523	7.85

<sup>a</sup> Electric dipole moment in the ground state.

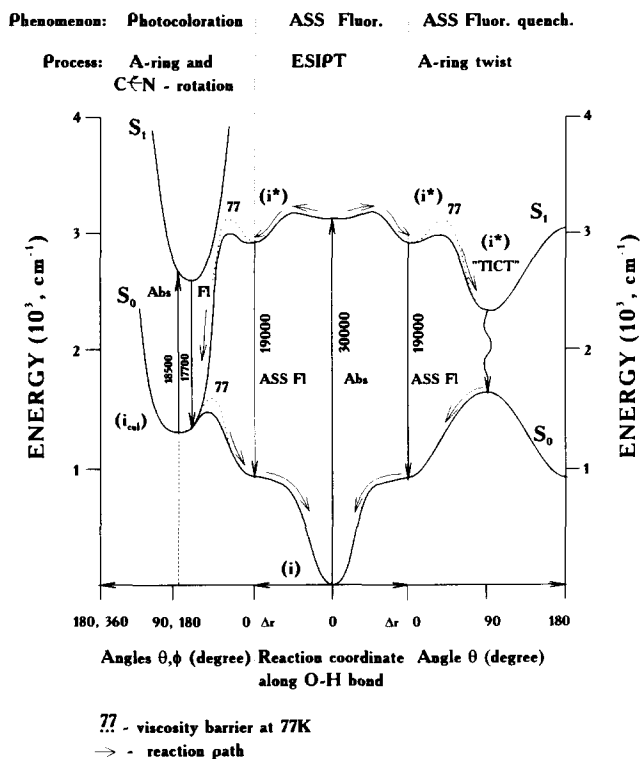


Fig. 4. Schematic representation of the photoinduced processes in the salicylideneaniline molecule.

bleaching ( $t = 10^{-7}$  s) occurs. In rigid media the bleaching is drastically delayed ( $t = 10$  s in poly(methyl methacrylate), at  $T = 290$  K, and depends on temperature and viscosity) [4] and was found to be virtually absent in the glassy solvent at liquid-nitrogen temperature owing to the "viscosity barrier" in the ground state.

The scheme is proposed to be qualitatively valid for crystals also.

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