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PHOTOCHROMISM AND THERMOCHROMISM OF SCHIFF BASES IN THE SOLID STATE AND IN RIGID GLASSES

E. HADJOUDIS*, M. VITTORAKIS and I. MOUSTAKALI-MAVRIDIS

Department of Chemistry, N.R.C. "Democritos",
Aghia Paraskevi, Attiki, Greece.

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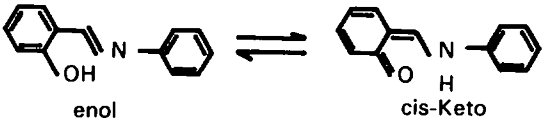
Abstract.- The photochromic and thermochromic properties in various classes of the Sciff bases of salicylaldehydes with anilines, aminopyridines or benzylamines were investigated in the crystalline state and in rigid glasses at various temperatures. The reaction involved is an intramolecular hydrogen transfer where the enol-keto tautomeric species are in equilibrium. In all the series studied, the salicylaldimino group that takes part in the reaction has the same geometry in the crystalline state: a strong intramolecular hydrogen bond that "locks" it in the planar configuration. It is suggested that what determines thermochromic or photochromic behaviour is not planarity or non planarity of the molecules respectively, but rather the electron density of the lone pair of the imino nitrogen atom.

INTRODUCTION

Photochromism, a purely optical phenomenon, is defined as the reversible photocoloration of a single chemical species between two states having distinguishably different absorption spectra, brought about in at least one direction by the action of electromagnetic radiation. Photochromism, compared to other photochemical reactions, poses the same problems with two exceptions: the system generally represents a photoequilibrium, and the photoproduct does not appear as a separate phase.

Schiff bases undergo photochromism in the solid state by hydrogen transfer and present common features in their structures and reaction mechanisms. The observation, that the same photoprocesses are taking place in the crystalline state, in rigid glasses and in solution (by flash photolysis techniques), led to the interpretation of photochromism, in the Schiff base series, as being an intrinsic property of the molecules[1]. Thus the hydrogen transfer is intramolecular, occurs via a six-membered ring transition state and produces enol-keto tautomeric species with the keto forms having bathochromically shifted spectra. However, from the existing compilations it comes out that a photochemically driven tautomeric reaction does not always take place in the crystalline state, since the rules governing the photoequilibrium are not determined by purely chemical factors but reside in the properties of the crystal structure as well. Thus the non-photochromic compounds are thermochromic and develop on heating a spectrum closely resembling the spectrum of the colored photocromic solid.

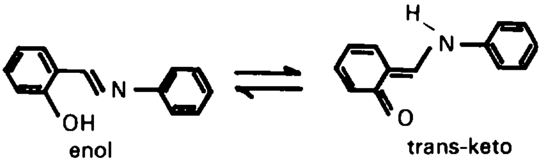
Photochromism and thermochromism were found to be mutually exclusive properties in the series of crystalline N-salicylideneanilines[2]. Thus a certain compound is either phorochromic or thermochromic but not both and the interpretation is a follows: thermochromism is attributed to a shift of the tautomeric equilibrium 1 because of the general resemblance of this system to the well established tautomerism of phenylazonaphthols in which the presence, in the crystalline state, of both tautomers was indicated by i.r. methods[3]. N.m.r. studies in napthalideneanilines were suggestive also of quinoid forms[4]. Finally, towards the same conclusion lead the



(1)

fluorescence spectra of the thermochromic crystals of N-salicylideneanilines which mirror the thermochromic absorption band being thus appreciably Stokes-shifted with respect to the absorption band of the enol species[5].

In the photochromic compounds, the colorless ground-state enol form, upon illumination with uv light, changes to the keto form through the hydrogen bridge with a concomitant rotation around the central C=N double bond. The photoproduct is described as a trans-keto configuration[6] (eq.2).



(2)

More recently, at least two quinoid intermediate states have been identified in the course of the above reaction. This is a direct consequence of the fact that the reaction is not restricted to the proton migration, but it involves framework changes as well, which disrupt the hydrogen bond between the oxygen and the nitrogen atoms stabilizing thus the photoproduct[7]. However the principal features of photochromism and thermochromism in the Schiff base series and the interpretation of these properties in terms of crystal structure is still a matter of investigation.

The present contribution presents a comparative study among various groups of the Schiff base series in the crystalline state and the glassy state in order to shed more light in the operating mechanism(s) and especially on the relationship between structure or configuration and photochromic and thermochromic properties.

EXPERIMENTAL

Preparation of compounds

The compounds were synthesized by direct condensation of the appropriate salicylaldehyde with the appropriate amine, aminopyridine or benzylamine in ethanol, followed by repeated recrystallization from the same solvent. Mass spectra, i.r., melting points and elemental analysis were utilized to establish the purity of the compounds.

Methods

The compounds were screened, in powder polycrystalline form, for photochromic and thermochromic properties. For more quantitative experiments thin polycrystalline films were used. These films were prepared from the melt between two optical quartz plates under pressure and their quality was examined under a polarizing microscope. To measure their optical spectra at various temperatures a quartz Dewar vessel with quartz windows was used. Relative fluorescence intensities were measured in the above thin films, positioned at a 45° angle towards the incident radiation with an Aminco or Farrand MK II spectrofluorimeter.

The rigid-state experiments were conducted in polymerized methyl methacrylate (PMMA) and in EPA (ether: isopentane: ethanol, 1:5:5). In these rigid media, the fading of the photocolor was not appreciable during the measurement of the spectrum; therefore, all the spectra were obtained satisfactorily. No correction was made to the spectra for contraction of the solution on cooling, as this was found to be less than 10% in EPA and of the order of 5% in PMMA. Other solvents used for low temperature measurements and for formation of rigid glasses included methylcyclohexane, isopentane: methylcyclohexane 1:1, 3:1 and ethanol.

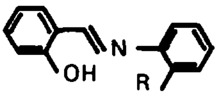
The absorption spectra were recorded with a Cary-17 or Varian Techtron 635 spetrophotometer. Steady state photochemical experiments employed a 200 W high pressure Hg lamp with Corning glass filters.

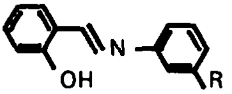
RESULTS

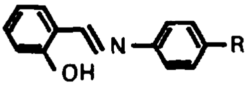
N-Salicylideneanilines

Crystalline state : The results by screening polycrystalline powders for photochromic and thermochromic properties are shown in Tables 1-4 according to substitution as being aniline monosubstituted, salicylaldehyde monosubstituted, di-substituted and di-and tri-substituted derivatives of N-salicylideneanilines.

Table 1. Aniline monosubstituted N-salicylideneanilines[a]







No.	R	Property	No	R	Property	No	R	Property
1	Cl	Photochromic[8]	8	Cl	Thermochromic	15	Cl	Thermochromic
2	Br	Photochromic	9	Br	Thermochromic	16	Br	Photochromic
3	I	Photochromic	10	I	Thermochromic	17	I	Thermochromic
4	F	Thermochromic	11	F	Thermochromic	18	F	Thermochromic
5	CH_3	Photochromic	12	CH_3	Photochromic[9]	19	CH_3	Thermochromic
6	OCH_3	Photochromic	13	OCH_3	Thermochromic	20	OCH_3	Thermochromic
7	NH_2	Photochromic	14	OH	Thermochromic	21	COOEt	Thermochromic

a. The parent compound (R = H) is photochromic.

Table 2. Salicylaldehyde monosubstituted N-salicylideneanilines

No	R	Property
22	5-Cl	thermochromic[8]
23	4-CH_3	thermochromic
24	4-OH	thermochromic

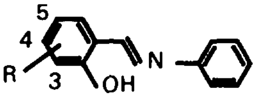
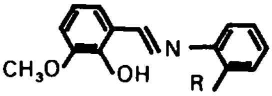
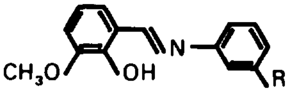
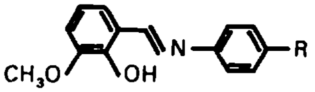


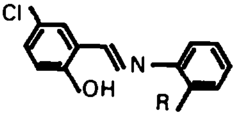
Table 3. Di-substituted N-salicylideneanilines

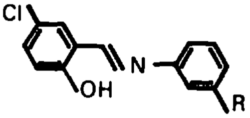


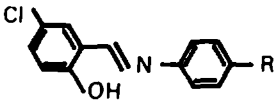




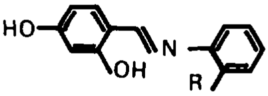
No.	R	Property	No.	R	Property	No.	R	Property
25	Cl	thermochromic	29	Cl	thermochromic	32	Cl	thermochromic
26	Br	thermochromic	30	Br	thermochromic	33	Br	thermochromic
27	CH_3	thermochromic	31	OCH_3	thermochromic	34	CH_3	thermochromic
28	OCH_3	thermochromic				35	OCH_3	thermochromic

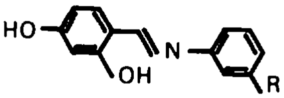


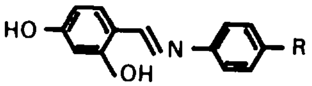




No.	R	Property	No.	R	Property	No.	R	Property
36	Cl	thermochromic	39	Cl	thermochromic	42	Cl	thermochromic
37	Br	thermochromic	40	Br	thermochromic	43	Br	photochromic
38	OCH_3	thermochromic	41	CH_3	thermochromic	44	CH_3	thermochromic

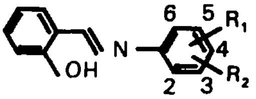


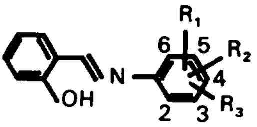




No.	R	Property	No.	R	Property	No.	R	Property
45	Br	thermochromic	46	Br	thermochromic	47	Br	thermochromic

Table 4. Aniline di-and three-substituted N-salicylideneanilines





No.	R_1 , R_2	Property	No.	R_1 , R_2 , R_3	Property
48	2-CH_3, 4-CH_3	thermochromic	52	2-CH_3, 4-CH_3, 5-CH_3	thermochromic
49	2-CH_3, 5-CH_3	thermochromic	53	2-CH_3, 4-CH_3, 6-CH_3	thermochromic
50	3-CH_3, 5-CH_3	thermochromic			
51	3-CH_3, 4-CH_3	thermochromic[10]			

At first examination, the above results show that:

i. photochromism is less common than thermochromism

ii. ortho-substitution in aniline monosubstituted N-salicylideneanilines favours the appearance of photochromism

It should be pointed out as was also noted by early workers[11], that the same compound can crystallize in two polymorphic forms one of which may be photochromic and the other thermochromic, as was noted with compounds 5, 21 and 23.

As mentioned in the Experimental section, for more quantitative measurements thin polycrystalline films were used and their spectra were recorded after uv-irradiation or at various temperatures. Figure 1 shows the photochromic and thermochromic properties of compounds 1 and 22. These compounds were extensively investigated at the Weizmann Institude of Science[8] and their X-ray structure, as we will see in the Discussion section, was the basis of the interpretation of photochromism and thermochromism in terms of crystal structure.

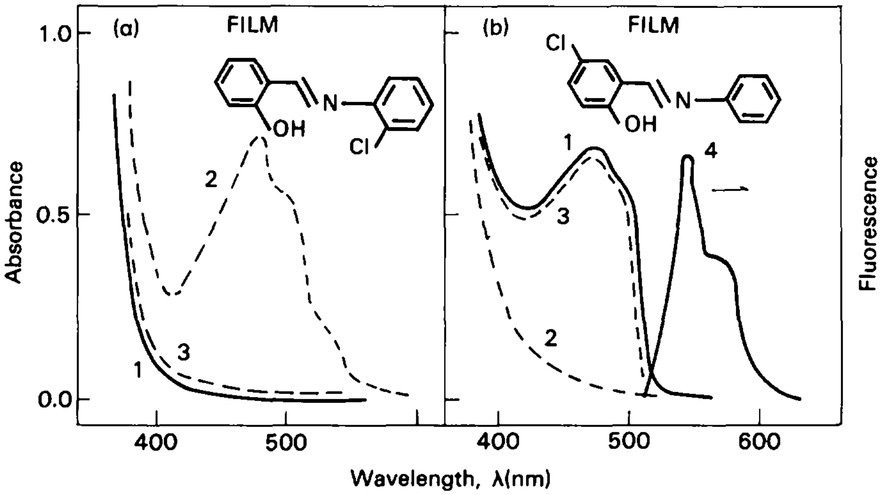


Figure 1. Absorption spectra of (a) 2-chloro-N-salicylideneaniline before (1), after (2); illumination and back in the dark (3). (b) Absorption spectra of N-5-chlorosalicylideneaniline at room temperature (1), liquid nitrogen temperature (2) and back at room temperature (3). Fluorescence (4) at room temperature, exciting light 365 nm.

Rigid Glasses: All N-salicylideneanilines which are photochromic or thermochromic in the solid state, are reversibly photochromic in rigid glasses; in the case of EPA, the effect is reversed when the rigid solution softens and in PMMA when the sample is illuminated with visible light or warmed up. Thus Figure 2 shows the results in PMMA of two compounds, 15 and 16, which in the crystalline state are thermochromic and photochromic respectively. Both of them are photochromic in the rigid state. It should be pointed out that the phenomenon of photochromism in the rigid state is stronger at liquid nitrogen temperature. Sometimes however at low temperatures negative thermochromism (appearance of color on cooling) is observed instead of photochromism as we will see later.

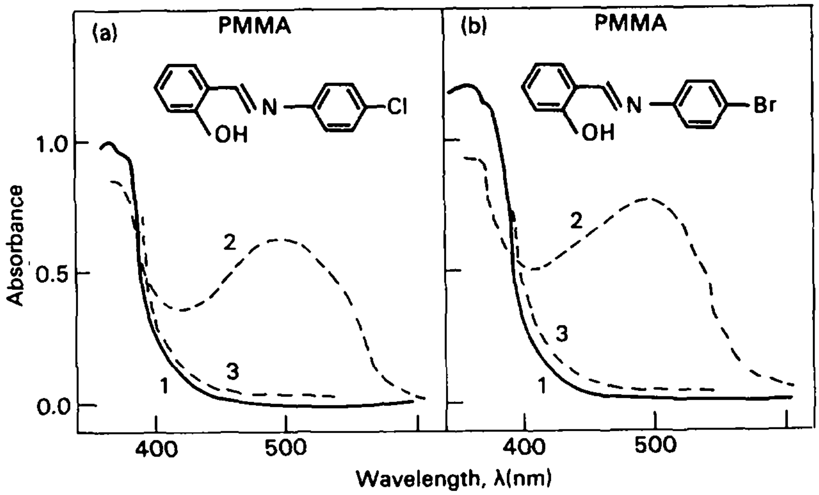


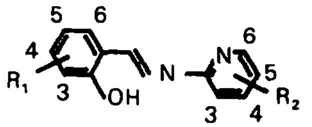
Figure 2. Absorption spectra of (a) 4-chloro-N-salicylideneaniline and (b) 4-bromo-N-salicylideneaniline in PMMA. 1, before irradiation, 2 after irradiation with 365 nm light and 3 back in the dark at room temperature.

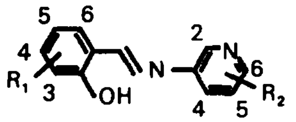
N-Salicylideneaminopyridines

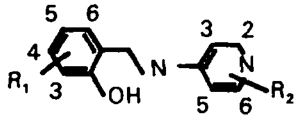
The heterocyclic Schiff bases have lower symmetry and possess an additional permanent dipole which affects the magnitude and direction of the total dipole moment as well as the lateral dipole without increase of molecular breadth[12].

Crystalline state: Table 5 shows the results by screening polycrystalline powders for photochromic and thermochromic properties.

Table 5. N-salicylideneaminopyridines







No.	R_1,R_2	Property	No	R_1,R_2	Property	No	R_1,R_2	Property
54	H,H	therm/mic	65	H,H	therm/mic[a]	76	H,H	Phot/mic
55	H,5-Cl	therm/mic	66	H,6-OCH_3	therm/mic	77	5-Br,H	Therm/mic
56	H,6-CH_3	therm/mic	67	H,2-Cl	therm/mic	78	5-OCH_3,H	Phot/mic
57	H,3,5-Cl	therm/mic	68	5-OCH_3,H	therm/mic	79	3,5-Cl,H	Phot/mic
58	5-Br,H	therm/mic	69	5-OH,H	therm/mic	80	3,5-Br,H	Phot/mic
59	5-OCH_3,H	therm/mic	70	5-Cl,H	therm/mic			
60	3-OCH_3,H	therm/mic	71	5-Br,H	therm/mic			
61	3-OCH_3,3-CH_3	therm/mic	72	5-OCH_3,6-OCH_3	therm/mic			
62	5-OCH_3,5-Cl	therm/mic	73	5-OCH_3,5-Br	therm/mic			
63	3-OCH_3,4-OCH_3	therm/mic	74	5-Cl,6-OCH_3	therm/mic			
64	3-OCH_3,4-OCH_3	therm/mic	75	5-Cl,5-Br	therm/mic			

a. The thermochromic phenomenon of all the N-salicylidene-3-aminopyridines is weak.

An inspection of the above results shows that all the N-salicylidene-2-aminopyridines are strongly thermochromic while N-salicylidene-3-aminopyridines present weak thermochromism. Among N-salicylidene-4-aminopyridines we find again photochromic and thermochromic compounds. It should be pointed out also that N-salicylidene-2-aminopyridines are strongly fluorescent and N-salicylidene-3-aminopyridines weakly fluorescent.

Figure 3 shows the results of thin polycrystalline films of the three parent compounds, 54, 65 and 76. The fluorescence spectra, in the first two cases, are displayed for comparison.

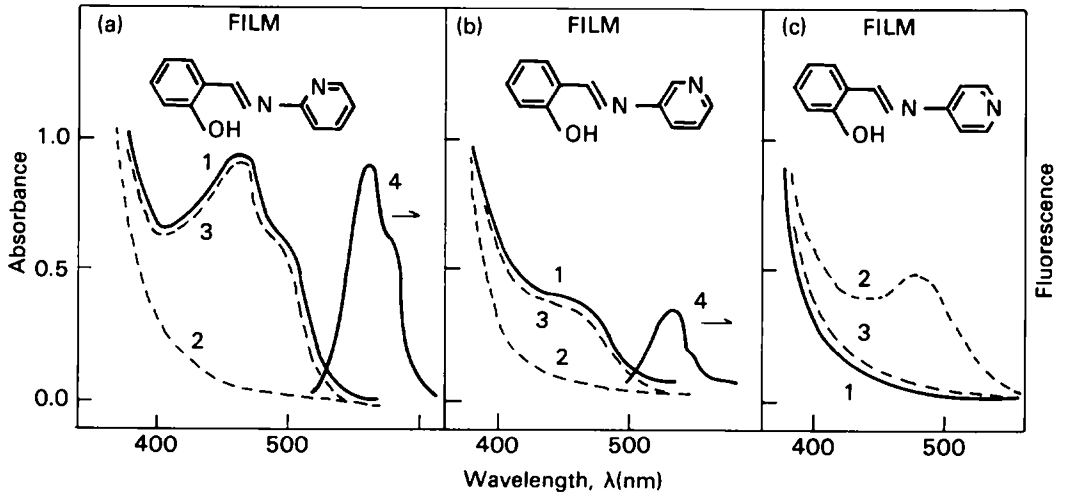


Figure 3. Absorption spectra of (a) N-salicylidene-2-aminopyridine and (b) of N-salicylidene-3-aminopyridine. 1 at room temperature, 2 at liquid nitrogen temperature and 3 back at room temperature. 4 Fluorescence at room temperature, exciting light, 365 nm. (c) Absorption spectra of N-salicylidene-4-aminopyridine, before (1) and after (2) irradiation with 365 nm light. 3 back in the dark.

The variation of maximum of the optical density with temperature near 480 nm where there is no overlap of bands of the two species leads to an energy difference of about 2 Kcal/mol for a number of the thermochromic compounds examined so far.

Rigid Glasses: When the factor of crystallinity is lost, as in rigid glasses where the orientation of the molecules is random, all the N-salicylideneaminopyridines, whether photochromic or thermochromic in the solid state, appear to be photochromic as in the case of N-salicylideneanili-

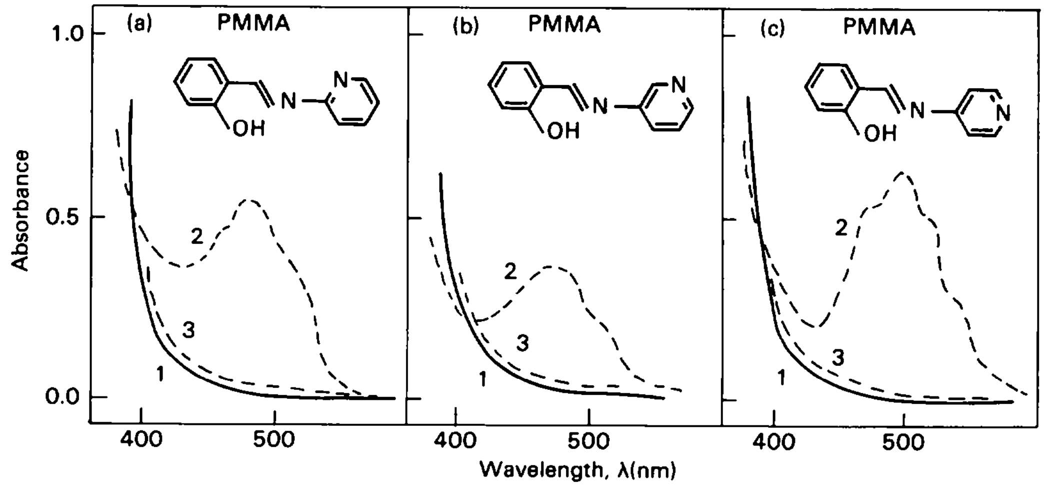


Figure 4. Absorption spectra of N-salicylidene-2-amonopyridines (a), N-salicylidene-3-aminopy-

ridine (b) and N-salicylidene-4-aminopyridine (c) in PMMA. At liquid nitrogen temperature, (1) before uv-irradiation, (2) after uv-irradiation and 3 when the PMMA is left in the dark and back at room temperature.

nes. Figure 4 shows the results in PMMA at liquid nitrogen temperature, of the three parent compounds, 54, 65 and 76. Experiments conducted with solutions of EPA at liquid nitrogen temperature gave similar results. It should be pointed out, however, that photocoloration at room temperature in PMMA, was hardly observed.

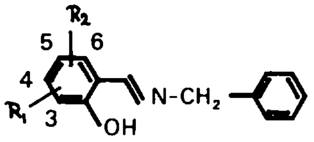
N-Salicylidene-benzylamines

N-salicylidene-benzylamines differ from the previous series of the Schiff bases in that the amino group is insulated from the phenyl ring by a-CH$_2$-group. The examination of such molecules, as in the case of N-salicylidene-2-thenylamines[13], aims at finding molecules displaying both photochromic and thermochromic properties as opposed to the mutually exclusive photochromic or thermochromic behaviour of the crystalline Schiff bases studied so far[14].

Crystalline state: Table 6 shows the results of screening polycrystalline powders for photochromic and thermochromic properties.

Table 6. N-Salicylidene-benzylamines

No.	R$_1$,	R$_2$	Property
81	H,	H	Photochromic
82	H,	5-Br	Photochromic
83	H,	5-OCH$_3$	Photochromic
84	H,	3-OCH$_3$	Photochromic
85	3-Br,	5-Br	thermochromic
86	3-Cl,	5-Cl	thermochromic
87	H,	4-OCH$_3$	photo/thermochromic



An examination of the above Table shows that most of the compounds are photochromic and one compound, 87, presents both photochromic and thermochromic properties. Figure 5 shows representative results in thin polycrystalline films.

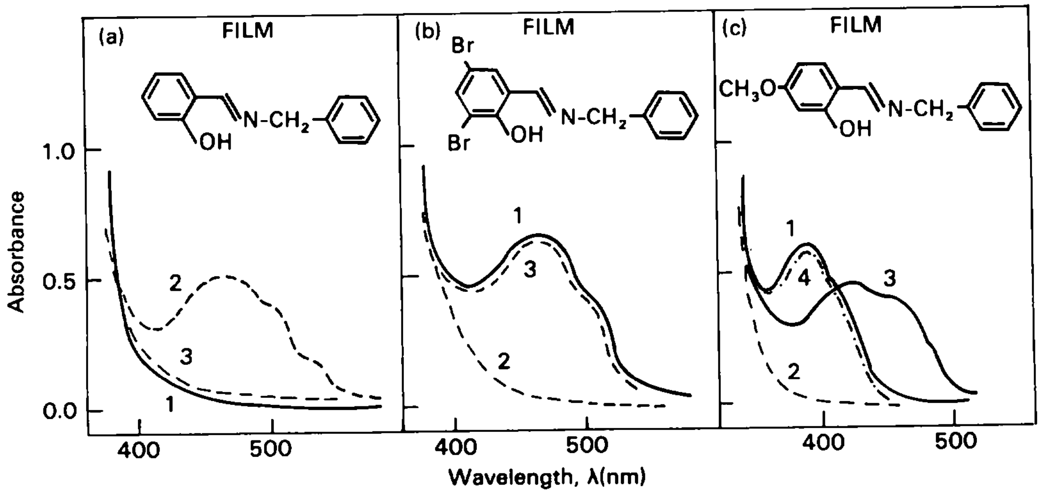


Figure 5. Absorption spectra of (a) N-salicylidene-benzylamine. 1, before uv-irradiation,

2, after uv-irradiation at room temperature and 3 back in the dark. (b) of N-3,5-dibromo-salicylidene-2-benzylamine. 1, at room temperature, 2 at liquid nitrogen temperature and 3 back at room temperature. (c) of N-4-methoxy-salicylidene-benzylamine. 1, at room temperature, 2 at liquid nitrogen temperature, 3 after uv-irradiation with 365 nm light at liquid nitrogen temperature and 4 after staying in the dark overnight at room temperature.

In Figure 5(c) we observe the double phenomenon. The color dissapears on cooling and a new colored band develops on irradiation with uv-light at liquid nitrogen temperature. The phenomenon is observed at room temperature also but much weaker. Fluorescence is not observed in this compound as opposed to all other purely thermochromic compounds examined so far.

Rigid glasses: The behavior of this group of Schiff bases in rigid glasses is more complex than the previous, but interesting. Considering the photochromic compounds 81-84 we observe the following: the parent compound (81) and the two 5-substituted derivatives (82,83) are photochromic in rigid glasses. Figure 6(a) shows the characteristic behaviour of the parent compound in rigid EPA. We observe that the absorption spectrum of the photoproduct is extended to 550 nm with a maximum between 450 and 460 nm. In addition, it is structured, an indication of a broken internal hydrogen bond as the trans-keto form of the photoproduct requires. The spectrum returns to the initial one when the rigid glass softens.

Contrary to the above behaviour, compound 84 presents "negative" thermochromism. Thus on cooling EPA to form the rigid glass, a strong absorption band is developed with a maximum around 420 nm. If the rigid glass is irradiated with 365 nm light, green fluorescence is observed with minor changes in the absorption spectrum. Again, when the rigid glass softens (room temperature), the spectrum returns to the initial one. Figure 6(b) shows these spectral changes.

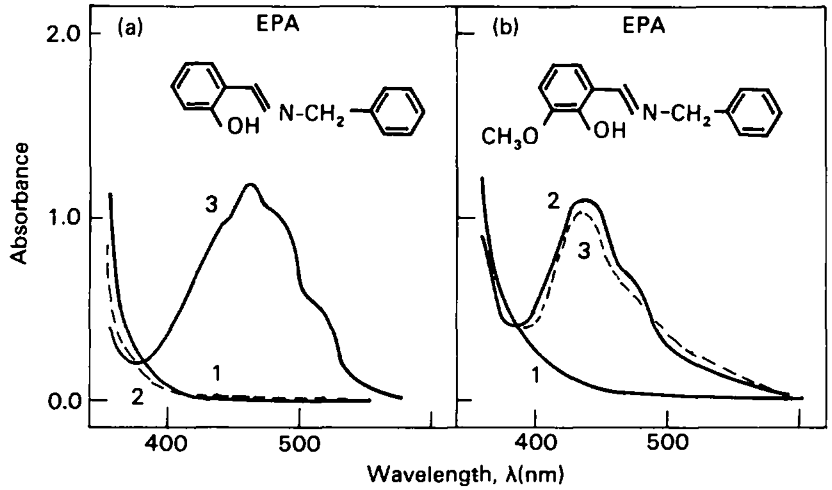


Figure 6. (a) Absorption spectra of N-salicylidene-benzylamine in EPA 10^{-4} M. 1 at room temperature, 2 at liquid nitrogen temperature, 3 after irradiation for 10 min with 365 nm light. (b) of N-3-methoxy-salycylidene-benzylamine in EPA 10^{-4} M. 1 at room temperature, 2 at liquid nitrogen temperature and 3 after 10 min irradiation with 365 nm light. Both spectra return in the initial (1) when the rigid glass softens (room temperature).

The thermochromic compounds 85 and 86 present strong "negative" thermochromism in EPA. Upon irradiation with 365 nm light green fluorescence is developed but no changes in the absorption spectrum are observed. These results are shown in Figure 7(a) for the case of compound 86. The phenomenon of "negative" thermochromism appears also in rigid glasses of methylcyclohexane (MCH) and isopentane: methylcyclohexane (iP:MCH). It should be pointed out also that there is not a concentration effect either in EPA or in MCH. Another important fact is that the "negative" band develops in a continuous way with the decrease of temperature and not after the formation of the rigid glass. Thus on cooling (Figure 7(b)) a 2×10^{-4} M solution of 86 in EPA from 17°C down to -40°C, the maximum in the optical density (at about 340 nm) increases by 11% while at 430 nm it decreases by 40%.

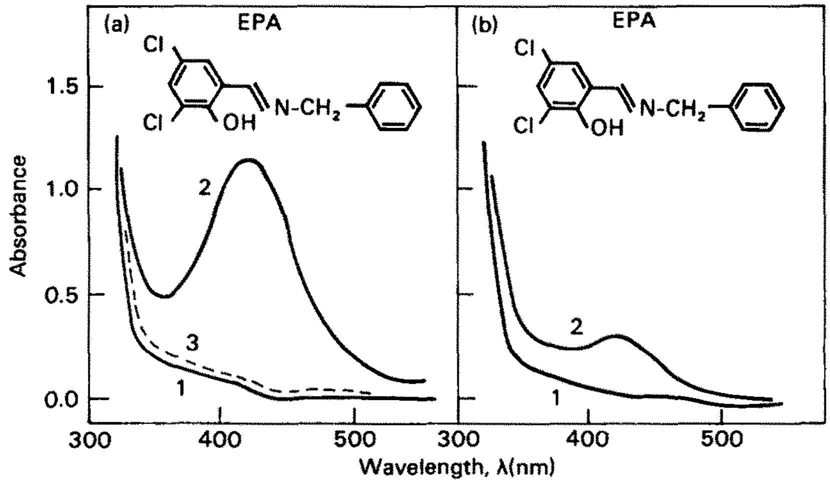
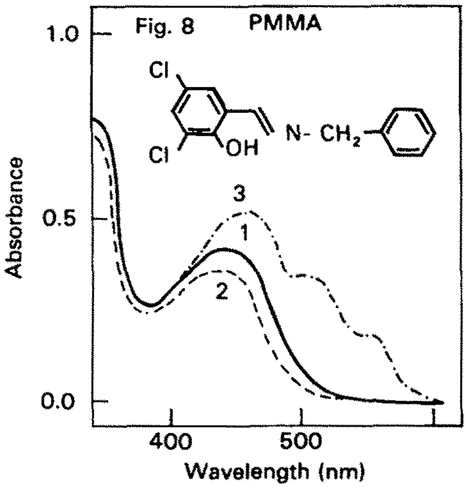


Figure 7. (a) Absorption spectra of N-3,5-dichloro-salicylidene-benzylamine in EPA. (1) at room temperature, (2) at liquid nitrogen temperature and (3) back at room temperature. (b) Absorption spectra of N-3,5-dichloro-salicylidene-benzylamine. (1) at 17°C and (2) at -40°C.

In the mixed solvent iP: MCH (3:1) "negative" thermochromic bands have been recorded at temperatures -80°C and -120°C in which this solvent is still fluid. In one of these experiments the solution at -120°C was retained for more than two hours without any change, an indication that the phenomenon is probably not connected with the formation of aggregates. In PMMA (1% W/W) however, a strong band at 420 nm is already present at room temperature, as is shown in Figure 8.



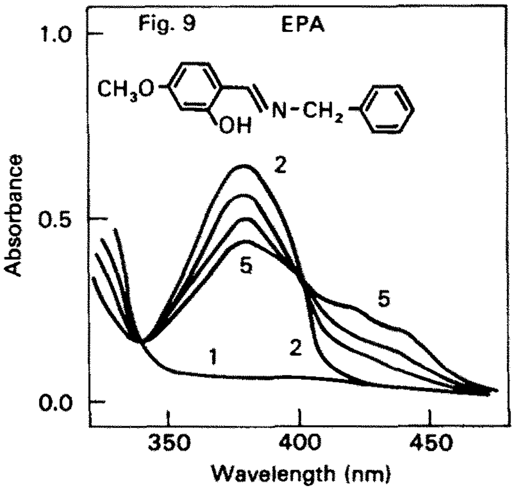


Figure 8. Absorption spectra of N-3,5-dichloro-salicylidene-benzylamine. (1) at room tempera-

ture, 2 at liquid nitrogen temperature and 3 after 20 min irradiation with 365 nm light. The spectrum returns to 1 when left in the dark at room temperarure.
Fig. 9 Absorption spectra of N-4-methoxy-salicylidene-benzylamine in EPA. (1) at room temperature, 2 at liquid nitrogen temperature and 3,4,5 after 5,10, and 20 min irradiation with 365 nm light. The spectrum returns to 1 when the solution softens in the dark.

On cooling down to liquid nitrogen temperature there is a small drop of this band and subsequent irradiation with uv-light results in the appearance of a structured band extended to 550 nm.

The photo/thermochromic compound 87 has different behaviour in rigid glasses. Thus in EPA (10^{-4} M) it shows "negative" thermochromism and photochromism as well as fluorescence. Figure 9 shows the "negative" thermochromism and photochromism of this compound. On cooling the solution of EPA down to liquid nitrogen temperature, a new strong absorption band is formed with a maximum around 380 nm and the solution turns light yellow. Subsequent irradiation with 365 nm light, leads to a strong blue fluorescence which decreases with the time of irradiation while the solution turns yellow and a new absorption band develops with a maximum at about 430 nm and two isosbestic points at 335 nm at 400 nm. Upon irradiation at 436 nm,. in the absorption maximum of the photoproduct, green fluorescence appears.

This double behaviour in rigid glasses is observed for the first time in the Schiff base series and it is solvent independent. Thus the results are similar in ethanol, isopentane: methylcyclohexane and MCH.

Experiments with solvents which are fluid at low temperatures showed the formation of the "negative" band before rigidity is attained and also the appearance of the photochromic band on irradiation with 365 nm light. Another important point is the fact that the blue fluorescence mirrors the absorption spectrum at liquid nitrogen temperature (max. 380 nm) an indication that it is produced from the species responsible for the "negative" thermochromism.

In PMMA the behaviour of compound 87 is more or less similar to that of 86 with the observation that fluorescence does not appear neither at room temperature nor at liquid nitrogen temperature.

DISCUSSION

Rigid glasses

N-Salicyledeneanilines and N-Salicylideneaminopyridines: All the members of these two groups which are photochromic or thermochromic in the crystalline state, are photochromic in rigid glasses at spectroscopic dilution a fact which ruled out explanations based on intermolecular effects. The application of flash techniques has permitted the analysis of similar but transient phenomena in solution[15].

As a general conclusion we may state that when the factor of crystallinity is lost, as in rigid glasses, and therefore the orientation of the molecules is random, all the molecules of these two classes appear to be photochromic.

N-Salicylidene-benzylamines: The results of this group of compounds are complex and can be summarised as follows: The photochromic compounds in the crystalline state are also photochromic in rigid glasses while the thermochromic ones show strong "negative" thermochromism. The compound which is both photochromic and thermochromic in the crystalline state in the glassy state shows "negative" thermochromism and photochromism. This behaviour is observed for first time in the Schiff base series.

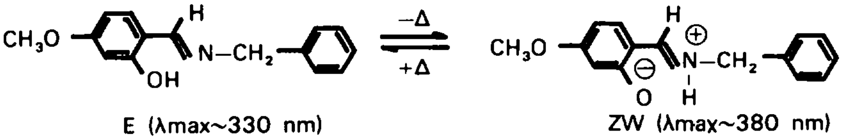
Weak "negative" thermochromism has been observed in polycondensed aromatic molecules[16] and stronger in anils of hydroxynaphthaldehyde[17].

In the first case, it was suggested[16] that a more planar configuration of the polycondensed molecule at low temperature resulting in higher resonance, might be responsible for the weak phenomenon. In the anils it was suggested[5] that incorporation into an aggregate at low temperatures is probably associated with a change of the molecule from a non-planar to a planar configuration. In the latter, the nitrogen lone pair would not have the appropriate direction to overlap with the aromatic ring, thus rendering the nitrogen atom a stronger proton acceptor and stabilizing the keto tautomer. However in the present case concentraction effect experiments are against aggregation and or dimerization although not conslusively.

In the case of N-salicylidene-benzylamines the equilibrium E(enol form) $\rightleftarrows$ QC(*cis*-keto form) is exothermic[18]. Therefore, at lower temperatures the equilibrium favors the formation of the *cis*-keto form which absorbs at longer wavelengths with maximum at about 430 nm. According to this approach we can write the following tentative mechanism for N-3,5-dibromosalicylidene-benzylamine and N-3,5-dichlorosalicylidene-benzylamine (85 and 86).

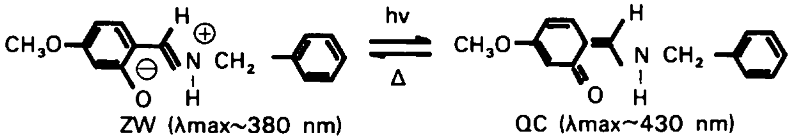
E $\xrightarrow{-\Delta}$ QC "negative" band
QC $\xrightarrow{h\nu}$ QC*
QC* $\longrightarrow$ QC $+h\nu_F$ "green" fluorescence
QC $\xrightarrow{+\Delta}$ E

In the case of N-4-methoxysalicylidene-benzylamine (compound 87) which shows photochromism and thermochromism in the solid state a different tentative mechanism is proposed which should be tested with additional, properly *para*-substituted compounds, since proper *para*-substitution is important for the formation of the needed zwitterionic forms. Thus the "negative" band with a maximum at 380 nm is attributed to a zwitterion (ZW)



(3)

The photochromic process, according to the observed isosbestic points (Figure 9), appears to be a monomolecular reaction. The photoproduct with maximum at about 430nm is attributed to the *cis*-keto form as opposed to the *trans*-keto for the other compounds. Therefore the photoproduct of compound 87 is different from that of the other photochromic compounds (e.g. compare Figures 6(a) and 9).



(4)

The "blue" fluorescence with maximum at about 460 nm is due to the ZW while the "green" fluorescence with maximum at about 500 nm, is due to the photoproduct QC. Thus the overall behaviour of this compound can be summatized as follows:

E $\xrightarrow{-\Delta}$ ZW "negative" band
ZW $\xrightarrow{h\nu}$ ZW*
ZW* $\xrightarrow{h\nu}$ QC photochromic band
ZW* $\xrightarrow{h\nu}$ ZW$+h\nu_{F(B)}$ "blue" fluorescence
QC $\xrightarrow{h\nu}$ QC*
QC* $\xrightarrow{h\nu}$ QC $+h\nu_{F(G)}$ "green" fluorescence
QC $\xrightarrow{+\Delta}$ E
ZW $\xrightarrow{+\Delta}$ E

Crystalline state

N-Salicylideneanilines: Structural studies on many of these compounds, namely the full three-dimensional crystal and molecular structure analysis of 1,22, partial analysis based on two zones, of 15 and finally determination of space groups and unit cell dimensions[8] for the rest allowed some generalizations regarding the molecular structures of the compounds. Thus, in thermochromic crystals the molecules are planar and the molecular planes pack with short intermolecular distances of the order of 3.5A^{o} normal to the molecular planes; in the photochromic crystals the salicylaldimino-part of the molecule is planar, but the aniline ring is rotated 40 to 50^{o} out of this plane, and the resulting structure is relatively open with no close contacts of the molecules. The interpretation of thermochromism is as follows[19]: there is a temperature-sensitive equilibrium in the crystal between the two tautomers of the molecule the one with the chelating hydrogen covalently bonded to the oxygen, the enol form, and the cis-keto form with the hydrogen bonded to the nitrogen (see eq. 1). The cis-keto form absorbs at longer wavelengths: raising the temperature increases the population of this form and thus causes a deepening of color. The intramolecular hydrogen-transfer can occur in either the ground or exctited-electronic state. In contrast, a higher energy is required for hydrogen transfer in the ground-electronic state of molecules in photochromic crystals; as a result no absorption attributable to the cis-keto form is observed. Hydrogen transfer can occur, however, in the excited-electronic state, and the crystal structure is sufficiently open to permit a subsequent geometric isomerization which leads to the colored trans-keto photoproduct (see eq. 2).

The non-planarity of the photochromic crystals is supported by the fact that photochromism in the solid state is more frequent among ortho-aniline substituted derivatives (see Table 1). The repulsion between the ortho-substituent and the aldimino group of the bridge render those derivatives as the most probable to constitute non-planar molecules.

N-Salicylidene-2-aminopyridines: All the examined molecules of this class were found to be strongly thermochromic. This generality can be explained by examining the crystal and molecular structure of four of these compounds (Figures 10-13).

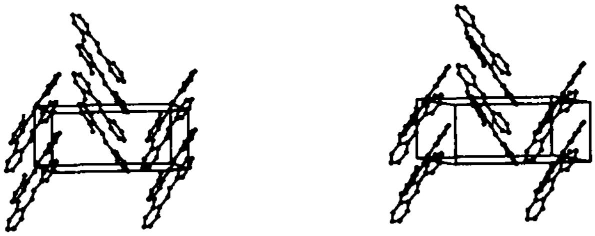


Figure 10. Stereoscopic view of N-salicylidene-2-aminopyridine (54)

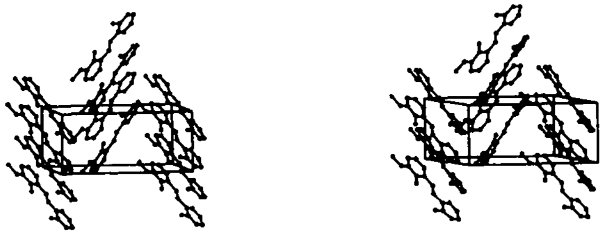


Figure 11. Stereoscopic view of 3-methyl-N-(3-methoxysalicylidene)-2-aminopyridine (61)

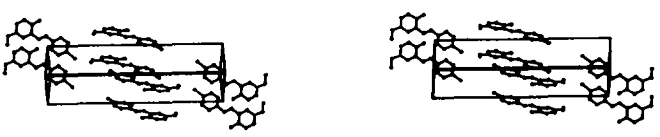


Figure 12. Stereoscopic view of 5-cloro-N-(5-methoxysalicylidene)-2-aminopyridine (62)

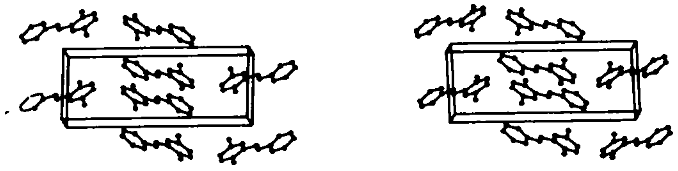


Figure 13. Stereoscopic view of N-(5-bromosalicylidene)-2-aminopyridine (58)

Compounds 54, 58, 62 and 63 are planar. The planarity is achieved because of the nitrogen of the pyridine ring[20]. In the case of N-salicylideneanilines there is steric hindrance due to the short distance between the *ortho*-hydrogen H(9) and the exocyclic hydrogen H(7) when the molecule is planar. This repulsion is relieved in the case of N-salicylidene-2-aminopyridines because the pyridine nitrogen atom is always at the *cis*-position with respect to the H(7) atom. The distance of about 2.5 Å between these atoms corresponds to a normal van der Waals contact (Figure 14)

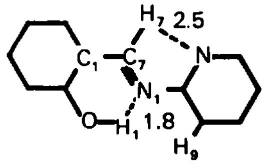


Figure 14. Distances (Å) for N-salicylidene-2-aminopyridine

The molecular packing of the compounds is characteristic of that of planar molecules arranged in stacks along the shortest crystal axis with a mean interplanar distance of 3.5 Å. Based on their identical behaviour it may be justified to suppose that all N-salicylidene-2-aminopyridines will have similar structures.

The lone pair of the imino nitrogen atom does not overlap with the electrons of the pyridine ring in the planar molecules. Consequently, the basicity of the bridge nitrogen atom, and hence the strength of the hydrogen bond between the hydrogen atom of the OH group and the imino nitrogen atom, should be higher. Therefore, the proton transfer is favoured in a planar rather than a nonplanar conformation. The molecular structures of all N-salicylidene-2-aminopyridines investigated so far show a strong intramolecular hydrogen bond with a mean H(1)...N(1) distance of 1.8 Å and the appropriate geometry for the H atom to point towards the lone pair of N(1) as shown in Figure 14 for the case of compound 54. Thermochromism, therefore, in the crystalline state of N-salicylidene-2-aminopyridines can be interpreted as being due to a shift in the tautomeric equilibrium 5 as in the case of the thermochromic N-salicylideneanilines for which a similar *cis*-keto form was assigned as the thermo-product.

(5)

N-Salicylidene-3-aminopyridines: It is suggested that the same mechanism explains the behaviour of this class of compounds. All compounds examined exhibit weak thermochromism (Table 5). The fact that the phenomenon is weak is attributed to a small deviation from planarity based on the crystal and molecular structures of two of its members (compounds 65 and 68)[21] As in N-salicylidene-anilines there is a repulsive interaction between the ortho hydrogen of the aminopyridine moiety and the exocyclic hydrogen H7. As a result of this interaction, a rotation of the pyridine ring around the N_1-C_8 bond by 14.8° and an in plane deformation $|N_1-C_8-C_{12}=124.7^{\circ}|$ occur to give a separation of

2.0 Å for H7...H(12) (Figure 15). However, this small deviation from planarity does not prevent the close parallel packing of the molecules along the shortest axis with an interplanar distance of 3.44 Å as in the case of N-salicylidene-2-aminopyridines. The molecular packing diagrams of the compounds 65 and 68 are shown in Figures 16 and 17.

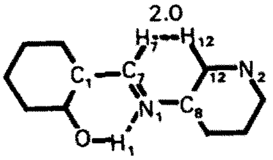


Figure 15. Some characteristic distances (Å) for N-salicylidene-3-aminopyridine

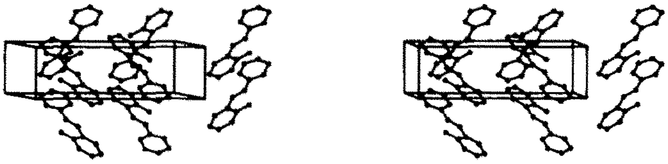


Figure 16. Stereoscopic view of N-salicylidene-3-aminopyridine

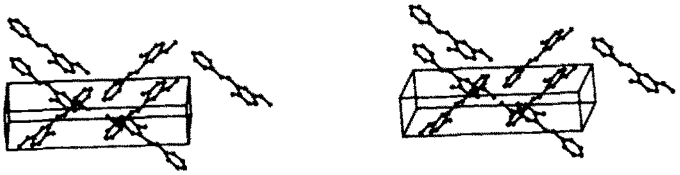


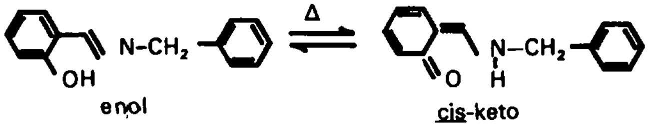
Figure 17. Stereoscopic view of N-(5-methoxy-salicylidene)-3-aminopyridine

N-Salicylidene-4-aminopyridines: Among these compounds (Table 5) we found photochromic and thermochromic ones and therefore non-planar and planar structures are expected. However these compounds present difficulty in crystallization and the solvent used may play an important role[21]. Structural studies are under way for this group of compounds.

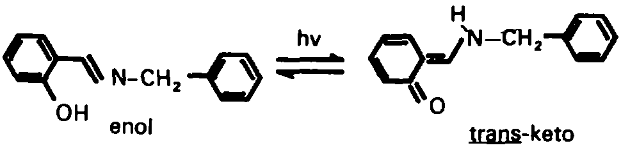
N-Salicylidene-benzylamines: Among these compounds (Table 6) we found not only photochromic and thermochromic ones but also a clear case of a compound, N-4-methoxysalicylidene-benzylamine (87), which presents both photochromic and thermochromic properties in contrast to N-salisylidene-anilines and N-salicylidene-aminopyridines in which either photochromic or thermochromic properties have been observed. The two processes, in these two last groups, have been interpreted in terms of an enol-keto tautomerism. In the thermochromic crystals the molecules are intramolecularly hydrogen-bonded and essentially planar, thereby allowing close plane-to-plane van der Waals contacts; in the photochromic crystals the molecules are also intramolecularly hydrogen-bonded but non-planar, thus precluding close intermolecular contacts. In this case it has been postulated that stabilization of the keto species is provided by cis-trans isomerization around the exocyclic C (1) - C (7) bond which was supported by spectroscopic studies[7]. (eq's 1 and 2).

In this work, the compounds 85 and 86 behave like thermochromic N-salicylideneanilines and N-salicylideneaminopyridines.

The compounds 81, 82, 83 and 84 behave, more or less, like photochromic N-salicylideneanilines and N-salicylideneaminopyridines. Therefore we can write the corresponding equilibria 6 and 7.



(6)



(7)

The occurance of the geometrical change from the cis-keto to the trans-keto isomer in the photochromic process is supported by the fact that the electronic absorption spectrum of the photochromic colored species is different from that of the cis-keto amine formed simply by the hydrogen transfer in the ground state (see Figures 5(c)).

Concerning the behaviour of compound 87 in the crystalline state (both photochromic and thermochromic) wich is in contradiction to the crystalline N-salicylideneanilines and N-salicylideneaminopyridines, we note that this compound behaves similarly with the recently studied N-4-methoxysalicylidene-2-thenylamine which also shows both phenomena in the crystalline state[13]. The latter molecule is not planar due to the methylene group inserted in the bridge[23]. The salicylaldimino moiety, however, of the molecule is planar, thus allowing the formation of the intramolecular hydrogen bond. Due to the non planarity of the molecule the characteristic packing of flat molecules with a 3.5 Å distance between planes is not observed (Figure 18). This structure does not precludes the hypothesis of cis - trans isomerization for the photochromic behaviour. However, it is dissimilar to the structures of the thermochromic N-salicylideneanilines and N-salicylideneaminopyridines determined so far (Figure 18).

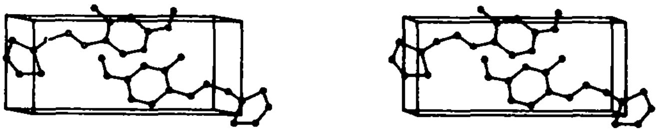


Figure 18. Stereoscopic view of N-4-methoxy-salicylidene-2-thenylamine[23].

This class of compounds shows that planarity or non planarity of the molecule is not the determining factor for thermochromic or photochromic behaviour respectively. The aliphatic methylene group forbids the molecules to be planar. Therefore, contrary to what it is obsereved in compounds 85, 86 and 87, no thermochromic behaviour should be expected. On the other hand, the nature of the substituents of the salicylaldimino part of the N-salicylidenebenzylamines leads to the hypothesis that the electron density of the lone pair of the imino nitrogen is what determines their chromobehaviour. If this electron density is high, the compound is thermochromic, if low, it is photochromic. The role of planarity or non planarity of the molecules is important only in so far as it affects the nitrogen electron density. More substituted N-salicylidenebenzilamines are needed to prove this hypothesis.

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