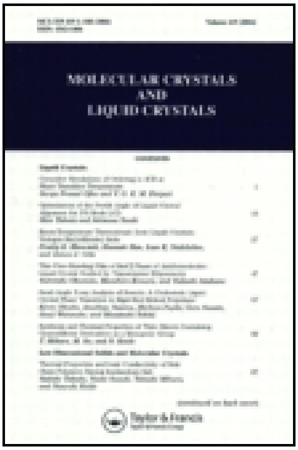

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Solid State Photochromism and Thermochromism of N-Salicylidene-Benzylamines and N-Salicylidene-2-Thenylamines

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SOLID STATE PHOTOCHROMISM AND THERMOCHROMISM OF N-SALICYLIDENE-BENZYLAMINES AND N-SALICYLIDENE-2-THENYLAMINES

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Abstract: The photochromic and thermochromic properties in various classes of the Schiff bases of salicylaldehydes with benzylamine and thenylamine were investigated in the crystalline state at various temperatures. The reaction involved is an intramolecular hydrogen transfer where the enol-keto tautomeric species are in equilibrium. In all of 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 into the planar configuration. It is suggested that what determines thermochromic or photochromic behaviour is not planarity or non planarity, respectively, of the molecules, but rather the electron density of the lone pair of the imino nitrogen atom.

INTRODUCTION

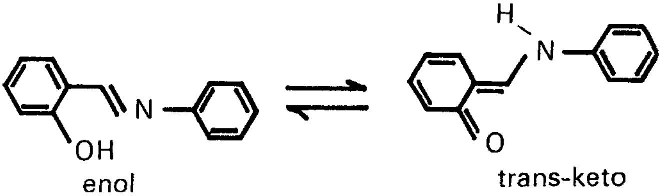
Photochromism is defined as the reversible photocoloration of a single chemical species between two states having distinguishably different absorption spectra, brought about in at least one direction by the action of electromagnetic radiation. Photochromism, compared to other photochemical reactions, 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 tautomerism 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, 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 existing data compilations it appears 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 photochromic 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 photochromic or thermochromic but not both. The interpretation is as 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[3]. N.m.r. studies in naphthalideneanilines were suggestive also of quinoid forms[4]. The fluorescence spectra of thermochromic crystals of N-salicylideneanilines, which mirror the thermochromic absorption band, leads to the same conclusion[5].

(1)

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 thus stabilizing the photoproduct[7].

The present contribution presents a comparative study between N-salicylidene-benzylamines and N-salicylidene-2--thenylamines 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.

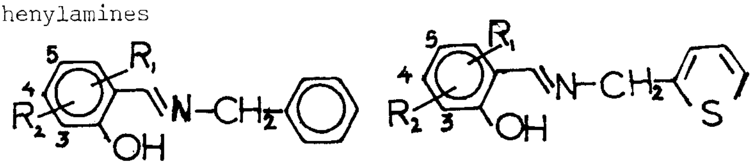
RESULTS

N-Salicylidene-benzylamines and N-Salicylidene-2-thenylamines

N-salicylidene-benzylamines and N-salicylidene-2-thenylamines differ from the previous series of the Schiff bases in that the amino group is insulated from the phenyl or the thenyl ring by a -CH_2- group. The examination of such molecules 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[8].

Crystalline state: Table 1 shows the results of screening polycrystalline powders for photochromic and thermochromic properies.

Table 1. N-Salicylidene-benzylamines and N-Salicylidene--thenylamines



No.	R_1 , R_2	Property	No.	R_1 , R_2	Property
1	H , H	p	6	H , H	p
2	H , 5-Br	p	7	H , 5-Br	p
3	3-Br , 5-Br	t	8	3-Br , 5-Br	t
4	3-Cl , 5-Cl	t	9	3-Cl , 5-Cl	t
5	H , 4-OCH_3	p+t	10	H , 4-OCH_3	p+t

p=photochromic, t=thermochromic

An examination of the above Table shows that most of the compounds are photochromic and two compounds, 5 and 10, present both photochromic and thermochromic properties. Figure 1 shows representative results in thin polycrystalline films

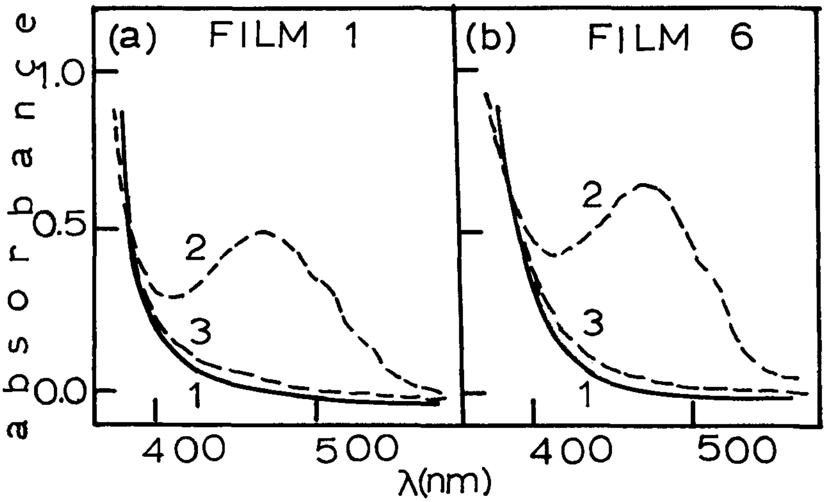


Figure 1. Absorption spectra of (a) N-salicylidene-benzylamine. 1, before uv-irradiation, 2, after uv-irradiation at room temperature, **3, return to the** dark. (b) of N-salicylidene-2-thenylamine. 1, at room temperature, 2, after uv-irradiation at room temperature and 3 return to the dark at room temperature. The number of the FILM corresponds to the numbering of compounds in Table 1.

The same notation holds also for the next Figure,2.

In Figure 2 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 is weaker. Fluorescence is not observed in this compound, as opposed to all other purely thermochromic compounds examined so far.

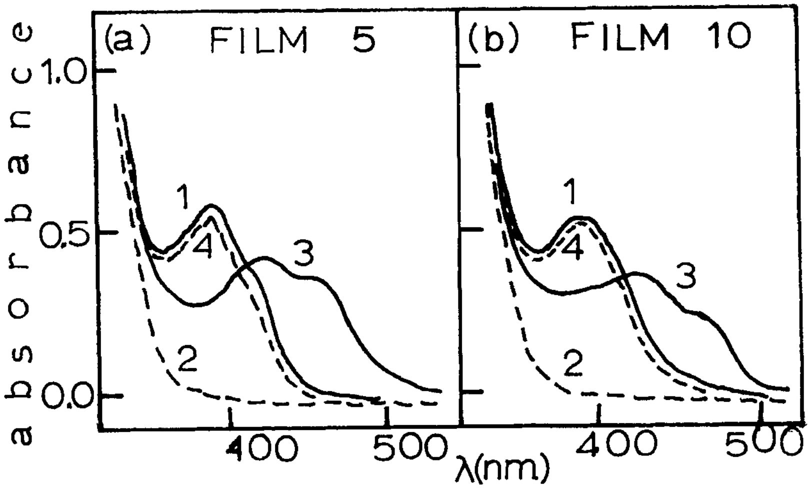
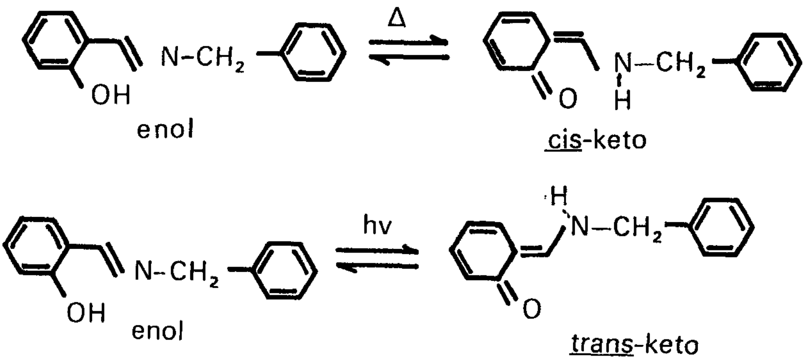


Figure 2. Absorption spectra of (a) N-4-methoxy-salicylidene-benzylamine. 1, at room temperature, 2, at liquid nitrogen temperature, 3, after uv-irradiation with 365 nm light at liquid nitrogen temperature and 4, return to the dark overnight at room temperature. (b) of N-4-methoxy-salicylidene-2-thenylamine. 1, at room temperature, 2, at liquid nitrogen temperature, 3, after uv-irradiation with 365 nm light at liquid nitrogen temperature and 4, return to the dark overnight at room temperature[9].

DISCUSSION

Among these compounds (Table 1) we found not only photochromic and thermochromic ones but also two clear cases of compounds, N-4-methoxysalicylidene-benzylamine(5) and N-4-methoxy-salicylidene-2-thenylamine (10), which present both photochromic and thermochromic properties in contrast to N--salicylidene-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 <u>cis-trans</u> isomerization around the exocyclic C (1) - C (7) bond. This was supported by spectroscopic studies[7].(eq's 1 and 2).

In this work, the compounds 3 and 4 behave like thermochromic N-salicylideneanilines and N-salicylideneaminopyridines.



The compounds 1 and 2 behave, more or less, like photochromic N-salicylideneanilines and N-salicylideneaminopyridines. Therefore we can write the corresponding equilibria 3 and 4, as shown above.

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 Figure 2 (c)).

Concerning the behaviour of compounds 5 and 10 in the crystalline state (both photochromic and thermochromic) which is in contradiction to the crystalline N- salicylideneanilines and N-salicylideneaminopyridines, we note that the latter molecule is not planar due to the methylene group inserted in the bridge[10]. **However, the salicylaldimino moiety of the molecule is planar thus allowing the for**mation 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 3). This structure does not preclude 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[11].

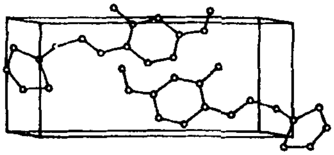


Figure 3.
View of N-4-methoxy-salicylidene-2-thenylamine[2,3].

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 is observed in compounds 3, 4 and 5, 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 chromo-behaviour. If this electron density is high, the compound is thermochromic, if low, it is photo-chromic. 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-salicylidenebenzylamines are needed to prove this hypothesis.

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