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PHOTOCHROMISM AND THERMOCHROMISM OF *N*-SALICYLIDENEANILINES AND *N*-SALICYLIDENEAMINO-PYRIDINES*

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Summary

The photochromic and thermochromic properties of salicylidene-2-aminopyridine, salicylidene-3-aminopyridine, salicylidene-4-aminopyridine and their derivatives were investigated in the crystalline state, in the glassy state and in solution in various environments. In the crystalline state, the first and second groups of compounds exhibit exclusively thermochromic properties while the third group contains compounds which are either photochromic or thermochromic. The appearance of the photochromic and thermochromic phenomena depends on the crystal structure and the molecular orientation of the compounds and is accompanied by intramolecular proton transfer, as is exemplified for salicylideneanilines by the changes in the proton–nitrogen ^{14}N nuclear quadrupole double-resonance spectra. In fluid solution, where the orientation of the molecules is random, all the compounds exhibit photochromic phenomena. However, the process is so fast that it can be monitored only by flash photolysis in rigid matrixes or at liquid nitrogen temperature. The results and mechanisms of photochromism and thermochromism in the three classes of compounds are compared with each other and with findings on salicylideneanilines. The study was completed with structure determinations of a representative number of compounds from each group by X-ray crystallography methods, and complete neglect of differential overlap (CNDO/2) calculations were carried out to rationalize the resulting geometries of each system.

1. Introductory review

The phenomena of photochromism and thermochromism in the Schiff-base series were observed a long time ago by Senier and Shepheard [1]. However, extensive investigations on this subject were carried out later by Cohen and Schmidt [2, 3] who suggested that the appearance of these phenomena depends on the crystal structure of the compounds. Thus, photochromism is associated with non-planar molecules allowing molecular movement, whereas in thermo-

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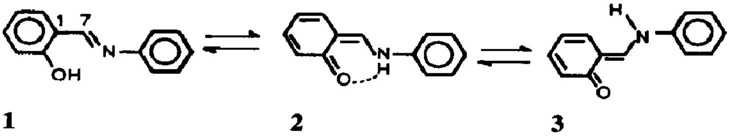
chromic crystals the molecules are planar and closely packed. Structural studies, although limited, support this idea [4, 5].

The presence of the *ortho* OH group is considered to be an essential condition for both effects since the proposed [2, 6] model for the mechanism includes the tautomeric equilibrium



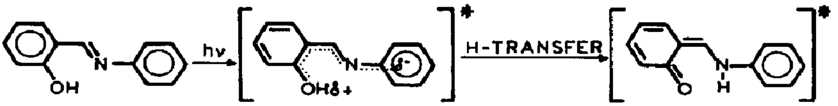
1 2 3 (1)

in which the last step accounts only for photochromic systems [6, 7].

In spite of continued efforts, no clear direct evidence on the nature of the thermoinduced or the photoinduced coloured species in the solid state has been obtained so far [4, 5]. Some evidence for a keto-like structure has been derived from IR spectroscopy studies [8, 9].

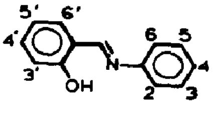
Although the solid state studies are important with respect to applications, significant evidence for the molecular nature of photochromism has been derived from solution studies. Thus, Wettermark and coworkers [10, 11] have observed a transient species with a spectrum similar to that of the photoproduct in solid solution, while Rosenfeld *et al.* [12], on the basis of two transients observed, have suggested, in addition to proton transfer, a simultaneous rotation around the C_1–C_7 and C_7–N bonds. However, in some systems **2** is considered to be already present in the dark in equilibrium with **1** [13], although this has been questioned by Richey and Becker [14].

More recently Barbara *et al.* [15], employing time- and wavelength-resolved picosecond and nanosecond emission spectroscopy, have shown that an excited tautomeric proton transfer occurs within 5 ps above 4 K:



They have also observed bimodal fluorescence kinetics which appear to represent excited state vibrational relaxation occurring on a 10 ps time scale. However, as these researchers have observed, such "hot" fluorescence for such a large molecule is quite unusual and interesting for further examination.

In conclusion, the nature of the coloured species in the solid state and the photochromic mechanism in solution are still subjects for research. In this paper I report the results of our studies on photochromism and thermochromism in the solid state, in rigid glasses and in a solution of *N*-salicylidene-2-aminopyridines **4**, *N*-salicylidene-3-aminopyridines **5** and *N*-salicylidene-4-aminopyridines **6** and I make comparisons between them and with *N*-salicylideneanilines **1** (Fig. 1). The heterocyclic Schiff bases have lower symmetry than **1** does and possess an additional permanent dipole which affects the magnitude and the direction of the total molecular moment as well as the lateral dipole without increased molecular breadth [16].



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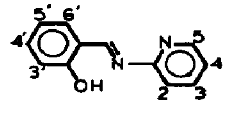

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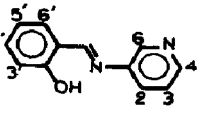

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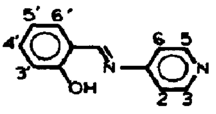

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Fig. 1.

To study the influence of molecular structure and the packing arrangement of the reactant species on the type and course of the reactions in the solid, a fuller examination of the crystal structure of heterocyclic anils was undertaken.

2. Proton transfer thermochromism and photochromism in the solid state: results and discussion

2.1. N-Salicylideneanilines

With the failure of X-ray analysis in mind, to distinguish the coloured thermoproducts of anils we decided to use as a complementary method the nuclear quadrupole resonance (NQR) technique, in order to distinguish not only the coloured thermoproduct but also the photoproduct. Thus the first direct evidence for the nature of the thermoinduced and photoinduced coloured species in the solid state came from our observations on the changes in the ^{14}N NQR spectra of thermochromic *N*-(5'-chlorosalicylideneaniline) induced by temperature variations and on the changes in the photochromic *N*-salicylidene-2-chloroaniline induced by UV light [17]. Figure 2(a) shows the effect of temperature on the absorption spectrum of *N*-(5'-chlorosalicylideneaniline). The pure ^{14}N NQR spectra of the same solid compound at 170, 210 and 298 K are shown in Fig. 2(b). At low temperatures we observed two spectral lines in the NQR spectrum of

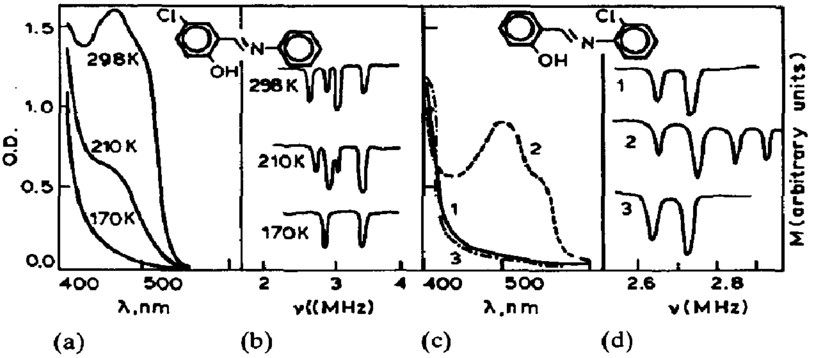
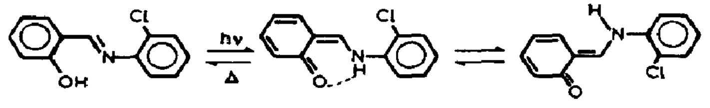


Fig. 2. (a) The effect of temperature on the absorption spectrum of *N*-(5'-chlorosalicylideneaniline); (b) the pure ^{14}N NQR spectra at 170, 210 and 298 K; (c) the effect of UV light on the absorption spectrum of *N*-salicylidene-2-chloroaniline; (d) the pure ^{14}N NQR spectra before (curve 1) and after (curve 2) irradiation with UV light and after being left overnight in the dark (curve 3).

^{14}N (spin, 1) and therefore one chemically non-equivalent ^{14}N site per unit cell. At high temperatures we observed four spectral lines and consequently two chemically non-equivalent ^{14}N sites per unit cell. The results obtained at high temperatures are evidently a superposition of the low and high temperature spectra, thus demonstrating the presence of a keto–enol equilibrium in solid *N*-(5′-chlorosalicylideneaniline). The calculated ^{14}N quadrupole coupling constants are of the correct order of magnitude for the =N– and >N–H groups of solid imidazols, as shown by Edmonds [18]. Figure 2(c) shows the effect of irradiation on the absorption spectrum of *N*-salicylidene-2-chloroaniline and Fig. 2(d) shows the pure ^{14}N NQR spectra of the same solid compound before and after irradiation. The results obtained in this case are also a superposition of the spectra before and after irradiation, demonstrating again the presence of the keto and enol forms. However, the order of the quadrupole coupling constants is reversed. This may be due to the different structure of the photoproduct *trans*-"keto" which results from the geometric isomerization of the non-planar *N*-salicylidene-2-chloroaniline shown in eqn. (2) against the planar [4] thermoproduct *cis*-"keto" shown in eqn. (3).



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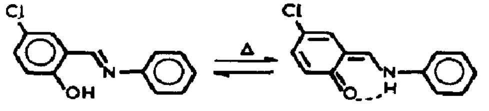


(3)

2.2. *N-Salicylideneaminopyridines*

As was mentioned in Section 1, the *N*-salicylideneaminopyridines were chosen to study more systematically the influence of molecular structure and packing arrangement on the photochromic and thermochromic phenomena. By screening polycrystalline powders for photochromic and thermochromic properties we found all *N*-salicylidene-2-aminopyridines (16 compounds) to be thermochromic and strongly fluorescent and *N*-salicylidene-3-aminopyridines (11 compounds) to be weakly thermochromic. Among the *N*-salicylidene-4-aminopyridines (six compounds) most derivatives were photochromic. Photochromism or thermochromism is not observed (a) in the absence of the *ortho* OH group from the salicylaldehyde moiety, (b) when the OH group is in a position other than *ortho*, (c) when the hydrogen of the *ortho* OH group is methylated or (d) when the *ortho* OH group is in the pyridine ring. Finally, in cases where the amino group is insulated from the pyridine ring by –CH_2– groups, the crystals of the corresponding compounds are photochromic.

Among the *N*-salicylidene-4-aminopyridines the parent compound is photochromic and, in contrast with *N*-salicylideneanilines, strongly fluorescent, while *N*-(3′,5′-dichlorosalicylidene)-4-aminopyridine (also strongly fluorescent) shows both photochromic and thermochromic properties after pretreatment with heat. If we represent this compound by *a* and a certain crystalline modification of it by $\{\alpha\}$ (superscripts indicate the temperature and subscripts indicate the colour: Y ≡ yellow; R ≡ red, O ≡ orange), then the observed processes may be represented as follows:

$$\begin{tikzcd}
\{\alpha\}_Y^{RT} \arrow[r, "\Delta"'] & \{\alpha\}_R^{HT} \arrow[r, "\Delta"'] & \{\alpha\}_O^{RT} \arrow[r, shift left, "h\nu_1"] \arrow[d, shift right, "\triangleleft"'] \arrow[dr, "\triangleleft"] & \{\alpha\}_R^{RT} \arrow[l, shift left, "h\nu_2"] \arrow[d, "\Delta"] \\
 & & \{\alpha\}_Y^{LN} \arrow[u, shift right] \arrow[r, phantom, "=?="] & \{\alpha\}_Y^{LN}
\end{tikzcd}$$

It seems that $\{\alpha\}_Y^{RT}$ changes on heating to a new crystalline modification $\{\alpha\}_O^{RT}$ which is both photochromic and thermochromic. In this scheme we have not verified whether the modifications $\{\alpha\}_R^{HT}$ and $\{\alpha\}_R^{RT}$ are the same. This is also the case for the two yellow forms $\{\alpha\}_Y^{LN}$.

For more quantitative measurements spectra of thin polycrystalline films were recorded at various temperatures or after UV irradiation. Figure 3 shows the spectra of *N*-salicylidene-2-aminopyridine (Fig. 3(a)), *N*-salicylidene-3-aminopyridine (Fig. 3(b)) and *N*-salicylidene-4-aminopyridine (Fig. 3(c)). The phenomenon of "negative" thermochromism (colour development on cooling) (*e.g.* Fig. 3(b)) in solid Schiff bases was observed for the first time. The phenomenon has been observed so far only in rigid glasses. This observation together with the previously mentioned behaviour of *N*-(2′,3′-dichlorosalicylidene)-4-aminopyridine shows the significance of the various crystalline modifications which these compounds may adopt under various conditions (*e.g.* heating, melting etc.).

The variation with temperature in the optical density of the maximum of the thermochromic band near 500 nm where there is almost no overlap of bands of the two species leads to an energy difference of about 2 kcal mol^{-1} for a number of the thermochromic compounds examined so far. All the thermochromic crystals are strongly luminescent with a short cut-off at about 480 - 500 nm.

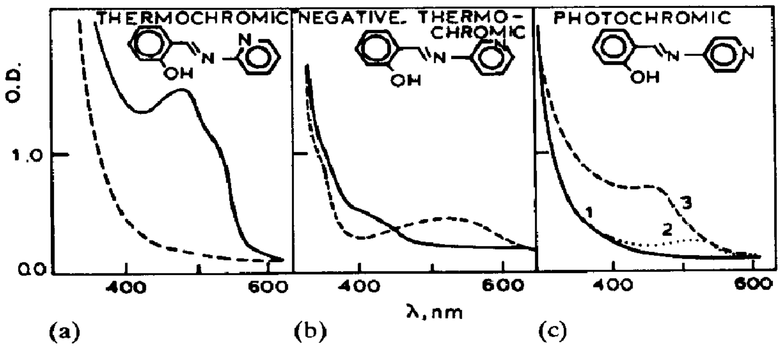


Fig. 3. (a), (b) The absorption spectra of crystalline films of the indicated compounds at room (full lines) and liquid nitrogen (broken lines) temperature; (c) absorption spectra at room temperature (curve 1), at liquid nitrogen temperature (curve 2) and after UV irradiation at liquid nitrogen temperature (curve 3). The UV light has no effect on the spectra in (a) and (b).

When the factor of crystallinity is lost, as in rigid glasses and fluid solutions where the orientation of the molecules is random, all the *N*-salicylideneaminopyridines, whether thermochromic or photochromic in the crystalline state, appear to be photochromic (Fig. 4) as for *N*-salicylideneanilines. In solution the photoprocess is so fast that it can be monitored only by flash photolysis. In Fig. 4 the transient absorption spectra of *N*-salicylidene-2-aminopyridine and *N*-salicylidene-3-aminopyridine in ethanol are shown for comparison. It should be mentioned that we observed one transient ($E_{\text{decay}} \approx 2$ kcal mol^{-1}) in these two cases compared with two transients ($E_{\text{decay}} \approx 2$ kcal mol^{-1} and $E_{\text{decay}} \approx 6$ kcal mol^{-1}) in *N*-salicylideneanilines.

We now turn again to the problem of thermocoloured and photocoloured species in the crystalline state where the molecules possess a certain crystal and molecular structure. For *N*-salicylidene-2-aminopyridines all the molecules examined were strongly thermochromic. This generality can be explained by examining the crystal and molecular structure of this class of compounds. Thus *N*-salicylidene-2-aminopyridine, *N*-(5′-bromosalicylidene)-2-aminopyridine, *N*-(5′-methoxysalicylidene)-2-amino-4-chloropyridine and *N*-(3′-methoxysalicylidene)-2-amino-3-methoxypyridine, investigated by X-ray diffraction, show that the molecules are essentially planar [19]. The lone pair of the imino nitrogen atom does not overlap with the electrons of the pyridine ring and consequently the basicity of the bridge hydrogen 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 non-planar conformation. The molecular structures of all *N*-salicylidene-2-aminopyridines investigated so far show a strong intramolecular hydrogen bond with a mean $H_1 \cdots N_1$ distance of 1.8 Å and the appropriate geometry for the hydrogen atom to point towards the lone pair of N_1, as shown in Fig. 5 for *N*-salicylidene-2-aminopyridine.

The molecular packing of the four compounds mentioned is characteristic of that of flat molecules arranged in stacks along the shortest crystal axis with a mean interplanar distance of 3.5 Å . On the basis of their identical behaviours it

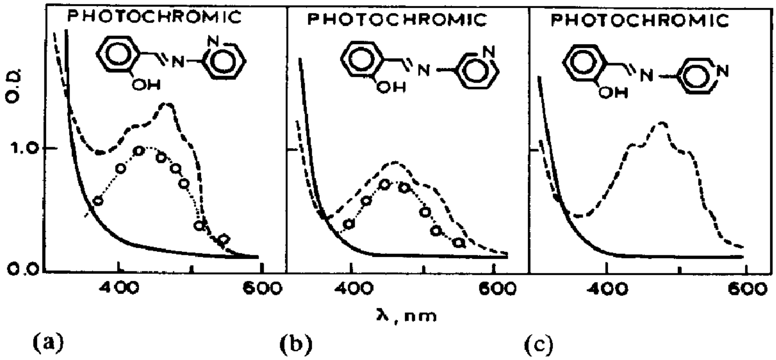


Fig. 4. Absorption spectra of the indicated compounds (rigid) in ether–isopentane–ethanol at liquid nitrogen temperature (full lines) and after UV irradiation at the same temperature (broken lines). The dotted lines in (a) and (b) are the transient absorption spectra in ethanol solution.

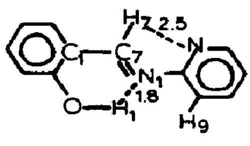
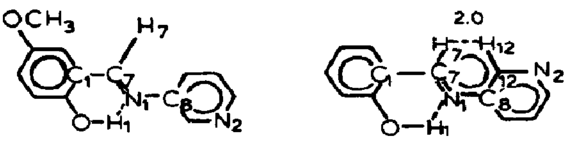


Fig. 5.



(a) (b)

Fig. 6.

may not be unjustified to suppose that all the *N*-salicylidene-2-aminopyridines investigated have similar packing arrangements. We suggest that the planarity is achieved because of the hetero nitrogen atom of the pyridine ring. For *N*-salicylideneanilines there is steric hindrance due to the short distance (about 2 Å) between the *ortho* hydrogen H_9 and the exocyclic hydrogen H_7 when the molecule is planar [5]. This repulsion is relieved for *N*-salicylidene-2-aminopyridines because the hetero nitrogen atom is always in a position that is *cis* with respect to the H_7 atom. The distance of about 2.5 Å between the atoms corresponds to normal van der Waals' contact. These findings are in agreement with complete neglect of differential overlap (CNDO/2) calculations [19].

Thermochromism in the crystalline state of *N*-salicylidene-2-aminopyridines can be interpreted as due to a shift in the tautomeric equilibrium

(4)

as for the thermochromic *N*-salicylideneanilines for which a similar interpretation has been given [2]. The NQR results on the *N*-(5′-chlorosalicylideneaniline) provide confirmation of equilibrium (1) and consequently of equilibrium (4).

Finally, we are possibly dealing with a case of the newly defined concept of "crystal engineering" [20, 21] according to which we can design molecules to guide their choice of crystal structure and obtain desired chemical and physical properties. Thus, insertion of a nitrogen atom in position 2 of the aniline ring of any anil molecule, which is normally non-planar (photochromic crystal), yields a planar molecule (thermochromic crystal) (*e.g.* compare *N*-salicylideneaniline (non-planar; photochromic) with *N*-salicylidene-2-aminopyridine (planar; thermochromic)). On the assumption that the phenomenon of thermochromism and/or photochromism is a monotonic function of the molecular geometry, *i.e.* of the angle variable which defines the orientation of one ring with respect to the other, we are exploring whether certain geometries can be allotted on the basis of their response towards heat or light.

As we have shown, *N*-salicylidene-3-aminopyridine and *N*-(5′-methoxysalicylidene)-3-aminopyridine exhibit only weak thermochromism in the crystalline state. Their structure analyses were undertaken to shed more light on the relation between the geometry in the crystalline state and the chromic behaviour.

The crystal structure of *N*-(5′-methoxysalicylidene)-3-aminopyridine (Fig. 6(a)) is disordered; the molecules have two orientations for the pyridine ring, in statistical proportions. Thus N_2 occupies two positions corresponding to a rotation by 180° of the ring around the N_1–C_8 bond. In *N*-salicylidene-3-aminopyridine (Fig. 6(b)) the hetero N_2 atom is *cis* with respect to H_7, whereas N_2 in *N*-(5′-methoxysalicylidene)-3-aminopyridine is mainly (75%) *trans* with respect to H_7.

Apparently, there is no appreciable energy difference between the two orientations owing to the symmetry of interaction of both hydrogen atoms *ortho* to the imino group with H_7. This is in contrast with *N*-salicylidene-2-aminopyridines where the observed unique conformation does not involve such an interaction. As a result of this repulsive interaction, a rotation of the pyridine plane around the N_1–C_8 bond by 14.8° and an in-plane deformation (N_1–C_8–C_{12} = 124.7°) occur to give a separation of 2.0 Å between H_7 and H_{12}. The charge distribution on *N*-salicylidene-3-aminopyridine calculated by the CNDO/2 method shows, as in the case of *N*-salicylidene-2-aminopyridine, strong intramolecular hydrogen bonding from the hydroxylic H_1 to the imino N_1 atoms [22]. The observed deviation from planarity in this class of compounds may be responsible for the weak thermochromism.

The results obtained with *N*-salicylidene-4-aminopyridines, and especially the facts that we observe fluorescence in photochromic crystals and that one crystalline modification of a certain compound presents both photochromic and thermochromic properties, show that the simple picture of planar and non-planar molecules cannot account for all the cases observed, and more data are needed for the elucidation of these problems. The structure from the X-ray analysis of *N*-(3′,5′-dichlorosalicylidene)-4-aminopyridine which is under way and other structures of this group will be of great value to the exploration of the role of crystal and molecular structure on the course of both photochromic and thermochromic processes.

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