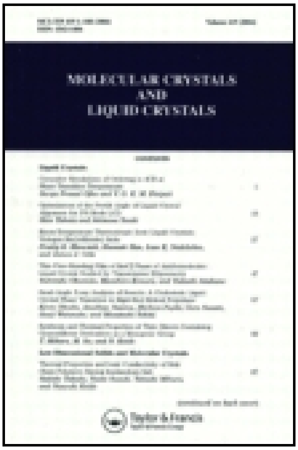

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An Unusual Solid State Reaction Leading to the Photochromic N-(3,5 Dichlorosalicylidenem)-4-Aminopyridine

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AN UNUSUAL SOLID STATE REACTION LEADING TO THE PHOTOCHROMIC N-(3,5 DICHLOROSALICYLIDENE)-4-AMINOPYRIDINE

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Abstract The photochromic and thermochromic properties of N-salicylidene-2-aminopyridines, N-salicylidene-3-aminopyridines and N-salicylidene-4-aminopyridines were investigated in the crystalline state and the results are compared with each other and with findings on N-salicylideneanilines. The first and the 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 molecular structure in the solid state and is accompanied by intramolecular proton transfer. In a certain compound of the third group, namely the N-(3,5 dichlorosalicylidene)-4-aminopyridine there are indications of both photochromic and thermochromic properties contrary to N-salicylideneanilines which are either photochromic or thermochromic but not both. This compound results from an unusual solid state reaction which is discussed.

I. INTRODUCTION

Solid N-salicylideneanilines are classified as photochromic or thermochromic, i.e. they show a reversible colour change under the influence of ultraviolet irradiation or as a result of a variation in temperature.[1] The photochromic compounds develop an absorption band around 480nm upon irradiation with UV-light, while the thermochromic exhibit an absorption band at room temperature in the same region which diminishes with decreasing temperature. The processes are mutually exclusive.[1] Since, however, the same compound may occur in dimorphs of which one is photochromic and the other thermochromic, it seems that the crystal structure determines their chromobehaviour, rather than the molecule as such. From the crystal structure determination of the thermochromic N-(5-chlorosalicylidene)aniline[2] and the photochromic 2-chloro-N-salicylideneaniline[3] the hypothesis has been advanced that an "open" crystal structure, associated with non-planar molecules and allowing for molecular movement, is necessary for the photochromic crystals, whereas in thermochromic crystals the molecules are planar and closely packed. Thus, the following model is proposed[1,4]: in the crystal, in planar molecules exhibiting thermochromism there is a temperature sensitive equillibrium (Fig.1),

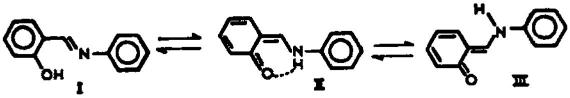

FIGURE 1. The thermochromic and photochromic mechanism of N-salicylideneanilines.

between a yellow "enol" form, the "OH-form" (I) stable at low temperature, where the hydrogen is covalently bonded to the oxygen and a red "keto" form, the "NH-form" (II) stable at high temperatures, with the hydrogen covalently bonded to the nitrogen. The intramolecular proton transfer would thus occur in the thermochromic systems both in the ground and the excited electronic state, whereas in photochromic systems this transfer occurs only in the excited electronic state.[4] This is, according to the proposed model, a result of the fact that too high an energy would be required for proton transfer in the ground state in view of the non-planarity of the photochromic molecules and thus a *trans*-keto form (III) may be produced.[1]

However, no clear direct evidence on the nature of the thermo-induced or photo-induced coloured species in the crystalline state has been obtained so far.[2,3] Some evidence for a keto-like structure has been derived from IR spectroscopic studies.[5,6] The first direct evidence for the nature of the coloured species in the solid state comes from our observations on the changes in the ^{14}N NQR spectra of thermochromic N-(5 -chlorosalicylidene)aniline induced by temperature variations and the the changes in the photochromic 2-chloro-N-(salicylidene)aniline induced by UV light[7](Fig.2).

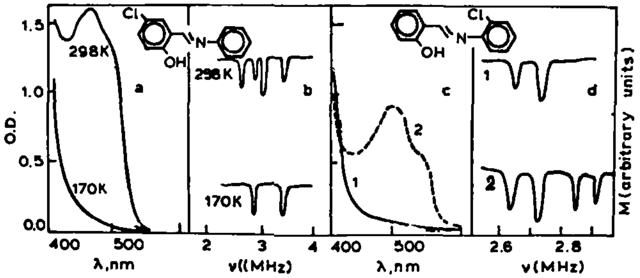

FIGURE 2. (a) The effect of temperature on the absorption spectrum of N-(5-chlorosalicylidene)aniline;(b)the pure ^{14}N NQR spectra at 170 and 298 K; (c) the effect of UV light on the absorption spectrum of 2-chloro-N-(salicylidene)aniline;(d) the pure ^{14}N NQR spectra before (1) and after (2) irradiation with UV light.

Thus the pure ^{14}N NQR (Spin 1) spectra of the solid N-(5 -chlorosalicylidene)aniline of low temperatures shows two spectra lines and at high temperatures four spectral lines corresponding to one and 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. The calculated ^{14}N quadrupole coupling constants are of the correct order of magnitude for the =N- and >N-H groups demonstrating the presence of a keto-enol equilibrium (I $\rightleftharpoons$ II). The results obtained with the photochromic 2-chloro-N-(salicylidene)aniline are also a superposition of the spectra before and after irradiation, demonstrating again the presence of the keto and enol forms (I $\rightleftharpoons$ III).

We extended our studies on thermochromism and photochromism of heterocyclic anils namely N-salicylidene-2-aminopyridines IV, N-salicylidene-3-aminopyridines V, and N-salicylidene-4-aminopyridines VI and make comparisons between these and N-salicylideneanilines I (Fig. 3).

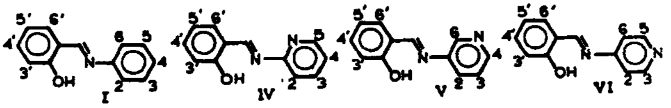

FIGURE 3. N-salicylideneanilines, N-salicylidene-aminopyridines and atom numbering system.

The heterocyclic anils have lower symmetry and possess an additional permanent dipole which affects the magnitude of the direction of the total molecular moment as well as the lateral dipole without increased molecular breadth[8].

II. N-SALICYLIDENE-2-AMINOPYRIDINES

All derivatives of N-salicylidene-2-aminopyridine (IV) (about 25 compounds) are strongly thermochromic, i.e. photochromic compounds as in the case of N-salicylideneanilines(I) are not observed. This generality can be explained by examining the molecular structure of the above compounds. Thus, the following representative members of this class, salicylidene-2-aminopyridine, N-(5-bromosalicylidene)-2-aminopyridine, 5-chloro-N-(5-methoxysalicylidene)-2-aminopyridine and 3-methyl-N-(3-methoxysalicylidene)-2-aminopyridine investigated by X-ray diffraction methods[9], show that the molecules are essentially planar; the flat molecules are arranged in stacks along the shortest crystal axis with mean interplanar distance of 3.5Å.

Based on their identical behaviour it may not be unjustified to suppose that all the salicylidene-2-aminopyridine compounds investigated will have similar packing arrangements.

We suggest that the planarity is achieved because of the position of the hetero-nitrogen atom of the pyridine ring (Fig. 4).

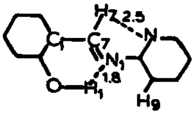

FIGURE 4. Intramolecular distances (Å) for N-salicylidene-2-aminopyridine.

In the case of salicylideneanilines there is steric hindrance due to the short distance between the H-atom <u>ortho</u> to the imino group and the exocyclic hydrogen H(7) when the molecule is planar.[3] This repulsion is relieved in the case of salicylidene-2-aminopyridines because the hetero-nitrogen atom is always at the <u>cis</u> position with respect to the H(7) hydrogen atom. The distance of about 2.5 Å between these atoms corresponds to normal van der Waals contact. In this planar molecular structure 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 N-atom and hence the strength of the hydrogen bond between the OH group and the imino N aton is higher. In addition, all the examined structures show a strong intramolecular hydrogen bond with a mean H(1)---N(1) distance of 1.95 Å and the appropriate geometry, so that the hydrogen atom points toward the lone pair of the N(1) atom.

Therefore, the proton transfer (quinoid cis form) shown in Fig. 5 is favoured in the planar as against a non-planar conformation and thermochromism can be interpreted with this shift in the tautomeric equilibrium as in the case of thermochromic anils for which a similar interpretation was given.[1]

FIGURE 5. The mechanism of thermochromism.

To test the importance of the heterocyclic nitrogen atom in the ortho-position with respect to the C=N bridge and to explore whether certain geometries can be alloted on the basis of their response towards heat or light, we have prepared a number of salicylidene-3-aminopyridines and salicylidene-4-aminopyridines.

III. N-SALICYLIDENE-3-AMINOPYRIDINES

By screening polycrystalline powders for photochromic and thermochromic properties we found salicylidene-3-aminopyridines (11 compounds) to be weakly thermochromic. The crystal structure analyses for two of them, the parent compound and N-(5 -methoxysalicylidene)-3-aminopyridine was done.[10]

In contrast to N-salicylidene-2-aminopyridine, the first compound shows a small deviation from planarity: the pyridine ring is rotated by 14.8° with respect to the rest of the molecule. The second molecule shows a statistical disorder of the pyridine ring: in 25% of the molecules the N(2) atoms is cis with respect to the H(C7) atoms and

75% trans (Fig. 6). 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(C7). As a result of this repulsive interaction, an in-plane deformation: N(1)-C(8)- C(12) = 124.7° along with the above mentioned rotation of the pyridine ring occurs to give a separtion of 2.0 Å between H(C7) and H(C12).

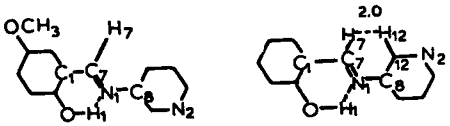

FIGURE 6. N-(5-methoxysalicylidene)-3-aminopyridine and N-salicylidene-2-aminopyridine.

The observed deviation from planarity in this class of compounds may be responsible for the weak thermochromism.

IV. N-SALICYLIDENE-4-AMINOPYRIDINES.

Among the N-salicylidene-4-aminopyridines we found photochromic or thermochromic compounds. However, these compounds are not stable and are difficult to crystallize. A certain compound of this group, the N-(3 ,5 -dichlorosalicylidene)-4-aminopyridine VII (Fig. 7) is the result of an unusual solid state reaction: The co-crystallization from a mixture of ethanol and chlorobenzene of 3,5-dichlorosalicylaldehyde and 4-aminopyridine with water gives good qua-

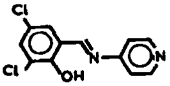

FIGURE 7. N-(3,5 -dichlorosalicylidene)-4-aminopyridine

lity yellow crystals. By examining these crystals for photochromic and thermochromic properties in the solid state, we found the compound to be insensitive to light and changing permanently colour on heating from yellow to orange. This orrange modification presents photochromic behaviour but there are some indications of thermochromic behaviour as well. The latter is contrary to the N-salicylideneanilines which are photochromic or thermochromic but not both. Thus if we represent this compound by α and a certain crystalline modification of it by $\{\alpha\}$ (superscripts indicate the temperature and subscripts the colour: Y≡yellow; R≡red, O≡orange), then the observed processes may be represented as in Fig.8.

FIGURE 8. Solid state transformations of N-(3,5-dichlorosalicylidene)-4-aminopyridine.

Since this observation presents the first serious critisism against the up-to-now well established exclusive mechanism (planar molecules-thermochromism, non-planar molecules-photochromism), we decided to look more carefully this solid state reaction.

In a previous communication[11] we thought that the insensitive to light modification $\{\alpha\}^{RT}_{Y}$ changes on heating to a new crystalline modification $\{\alpha\}^{RT}_{O}$ which presents both photochromic and thermochromic properties. However, the X-ray study[12] showed that the yellow crystals are formed from a co-crystallization of the hydrolysis products of the N-(3 ,5 -dichlorosalicylidene)-4-aminopyridine, namely the phenolic anion (VIII) and the pyridinium cation (IX) with a water molecule (Fig. 9).

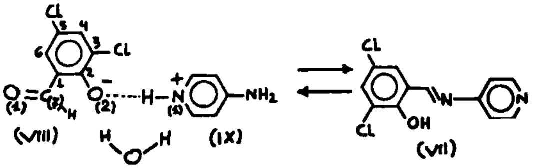

FIGURE 9. The hydrolysis products of the N-(3,5-dichlorosalicylidene)-4-aminopyridine.

The asymmetric unit contains two crystallographycally independent groups of molecules of the hydrated salt, hereafter referred to as molecules A and B, related by a pseudo center of symmetry. Fig. 10 shows a view of the unit cell in projection along to b axis.

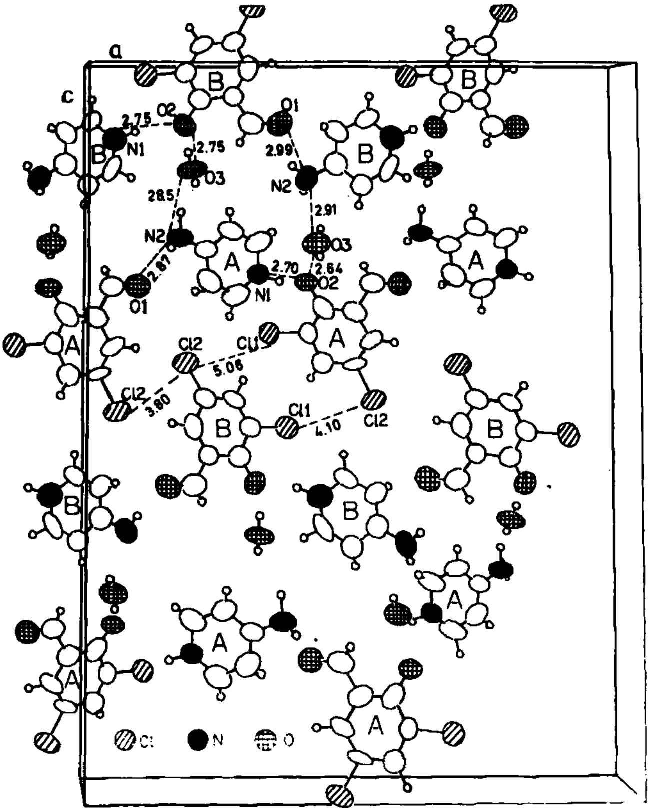

FIGURE 10. A view of the unit cell along the b axis.

The phenolate ions are held by hydrogen bonds to the pyridinium cations: the phenolate O(2) atom to the the H(N1) atom of the pyridinium cation and the carbonyl O(1) atom to the NH_2 group of another pyridinium cation, so that they form chains almost parallel to the α axis. More hydrogen bonds via the water molecules link two neighboring chains together and form a sort of double chains. The latter are stacked antiparallel along the c axis interacting weakly by van der Waals forces. In the very extensive net of H-bonds involving all six molecules of the asymmetric unit not only the H-bond between the charged atoms N(1) and O(2) is very strong, but also the H-bonds of the latter to the water molecule and that of the **carbonyl** O(1) atoms to the NH_2 group. The water molecule and the NH_2 group act both as hydrogen donors and acceptors forming longer H-bonds.

Fig. 11 depicts a view of the unit cell which shows that molecules A and B are almost coplanar (4.8° and 1.6° between the aldehyde and pyridine molecular planes respectively).

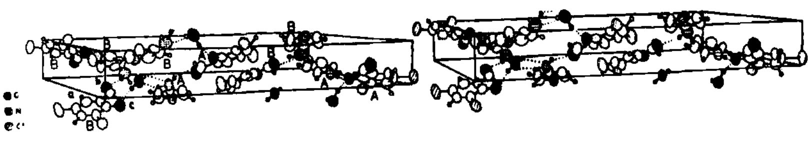

FIGURE 11. Stereoscopic view of the molecular packing. Hydrogen-bonds are indicated by dotted lines.

The salicylaldehyde and 4-aminopyridine molecules are in an appropriate relative geometry to react and form the corresponding Schiff base. The N(2)... O(1) distances are 2.87 Å and 2.99 Å for molecules A and B respectively (Fig. 10) and the dihedral angles between the ring planes of the salicylaldehyde and 4-aminopyridine molecules are small, 14° and 19° for A and B respectively (Fig. 11). However, the resulting Schiff base will not have the OH group close to the bridge N atom and consequently no internal H-bond will be formed. Therefore, concomitant to the removal of a water molecule a rotation of the aldehyde moiety around the C(1)-C(7) bond should take place in order to result a Schiff base of the known geometry.[9,10]

The resulting Schiff base is easily hydrolysed back to the hydrated salt. Thus the orange polycrystalline powder (mp=174°C) in a water atmosphere turns yellow showing identical i.r. spectrum with that of the original yellow solid salt (mp=84°C). Experiments in a Cahn R.G. electrobalance equipped with a Glass Vacuum Bottle Accessory showed a water uptake corresponding to 2 molecules of water per molecule of the Schiff base.

Comparison of the present structure to that of the resulting Schiff base will show the intermolecular interactions and therefore the reason that the compound is so easily hydrolysed and probably the sequence of events during the solid state reaction.

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