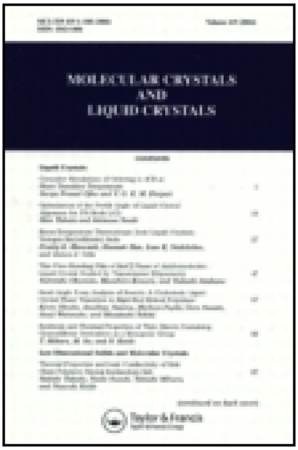

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Structural Directing Effects in Solid State Organic Photochemistry

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STRUCTURAL DIRECTING EFFECTS IN SOLID STATE ORGANIC PHOTOCHEMISTRY

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Abstract: Structural directing effects seem to be operating in solid state photochemistry. Thus the findings in the N-salicylidene-aminopyridine series show that such effects may be accomplished through heteronuclear substitution while in N-salicylidene-2-thenylamines we can produce desired properties by proper substitution in the salicylaldehyde moiety of the molecule.

INTRODUCTION

The work in progress in our group[1-3] is intended to examine the major feature of the crystalline state, namely the three-dimensional regularity and its effect on solid state photochemistry.

Although lattice imperfections may play an important role in solid state photochemical reactions, it has been possible in a number of cases to correlate the reactivity with the packing of the reactant molecules in the crystal lattice. Thus, a systematic chemical and crystallographic study[4] showed that halo-substituted anthracenes, like cinnamic acids[5], fall into at least three packing types according to whether the product of irradiation is a head-to-tail dimer, a head-to-head dimer or the compound is light-stable[6].

In another example, p-nitrophenol crystallizes in two modifications, one of which, the α-form, is light-sensitive while the β-form is light-stable. The explanation of this photochemical behavior in the solid state was accomplished by analyzing the structures of the two modifications by X-ray crystallographic methods[7].

A further aspect of solid state reactivity concerns the role of reactant conformation, a role which should be most clearly discernible in monomolecular reactions[8]. However, the factors of molecular packing and conformation are not independent of one another. Thus 4-chloro-N-salicylideneaniline and 4-bromo-N-salicylideneaniline can be readily incorporated into one another's stable structures by changing markedly their molecular geometry and consequently their thermochromic or photochromic property[9]. In another case 2,4-dichlorobenzylideneaniline, a non-planar structure is transformed into a planar one by transposing the 2-chloro substituent to position 4 of the aniline ring. It seems that there is a specific role for the chloro group in the crystal engineering of 4Å short axis crystal structures of planar choro-aromatics[10].

In the following discussion on the photochromism and thermochromism of solid Schiff bases, these two factors (molecular packing and conformation) probably are the dominant ones and structural-directing effects will be applied to them in order to achieve desired properties. However certain new results, as we will see later, raise new questions concerning the role of structure especially in connection with the phenomena of photochromism and thermochromism in this class of compounds.

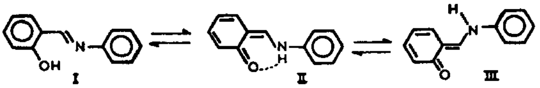
SCHIFF BASES

Solid Schiff bases undergo photochromism or thermochromism by hydrogen transfer and present common features in their structures and reaction mechanisms. This hydrogen transfer is intramolecular, occurs via a six-membered ring transition state and produces quinoid structures. The thermally stable forms are the ortho-OH substituted aromatic structures. One or more processes occur that bring some stability to the photocolòred species formed by the endothermic photolysis step.

The thermochromic compounds display close packed planar structures with 3.5Å interplanar distances while the photochromic ones have open non-planar structures with distances between ring planes of about 4.5Å. Both thermochromic and photochromic compounds show, in their hydrogen transfer reaction, a high degree of reversibility. The photo or thermochromic processes are mutually exclusive, that is, a compound is photochromic or thermochromic but not both.

For thin polycrystalline films prepared between quartz plates, the photochromic phenomenon is shown in Figure 1a for salicylidene-2-chloroaniline. Figure 1b shows the thermochromic phenomenon for 5-chlorosalicylideneaniline. This illustrates the reversible spectral color changes that result from photoirradiation or temperature variation.[11,12]

The interpretation of the color formation is as follows[13]: there is a temperature sensitive equilibrim in the crystal between two tautomers of the molecule, one with the chelating hydrogen covalently bonded to the oxygen, the "OH-form" (I), and the "NH-form" (II) with the hydrogen bonded to the nitrogen (equation 1).



(1)

The "NH-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 of thermochromic crystals occurs in the ground electronic state. In contrast, high energy is required

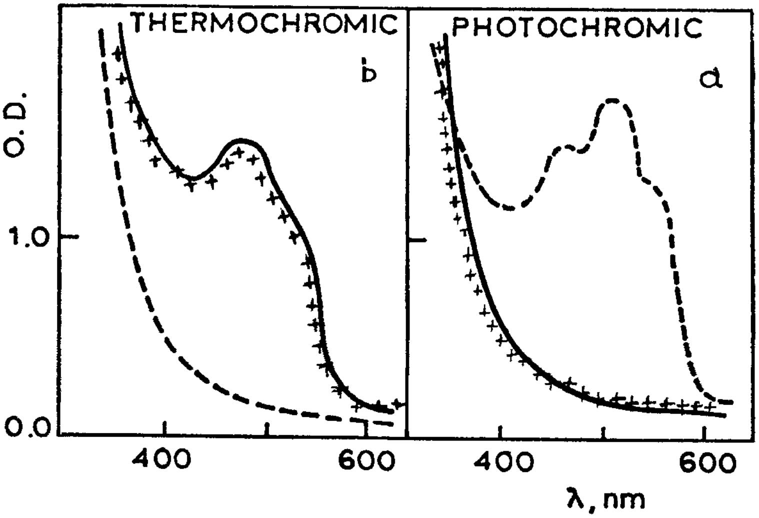
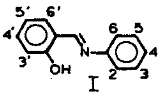


FIGURE 1. (a). Photochromism of salicylidene-2-chloroaniline, before (-), after (---) illumination and back in the dark (++), and (b) thermochromism of 5-chlorosalicylideneaniline at RT (-), liquid nitrogen temperature (---) and back at RT (++).

for hydrogen transfer in the ground electronic state of molecules in photochromic crystals because of the non-planarity. As a result, no absorption attributable to the NH-form is observed. However, hydrogen transfer can occur in the excited state. The crystal structure is sufficiently open due to the non-planarity of the molecules so as to permit subsequent geometric isomerization which leads to the colored photoproduct, III. However, the nature of the colored species in the solid state is still a matter of controversy.

The purpose of the present paper is twofold :

1. To describe the structural directing effects we can produce in the N-salicylideneaniline (I) series by introducing, an heteroatom, e.g. nitrogen, in the ortho (IV), meta (V) and para-position (VI) of the aniline ring, and the subsequent changes in their photochromic or thermochromic properties which have been associated with their crystal structures[14].



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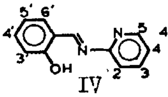

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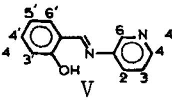

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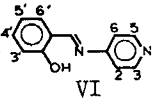
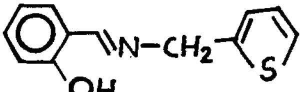


VI

2. To describe the changes we can bring in the N-salicylidene-2- thenylamine (VII) series by proper substitution in the salicylaldehyde ring, and the subsequent changes in



VII

photochromic behaviour.

RESULTS AND DISCUSSION

In order to face the first problem we introduced into a number of photochromic and thermochromic N-salicylideneanilines a nitrogen heteroatom in the ortho-position of the aniline ring. Analogs with the heteroatom placed in the meta and para-position were also made. Thus, we produced N-salicylidene-2-aminopyridines (IV), N-salicylidene-3-aminopyridines (V) and N-salicylidene-4-aminopyridines (VI).

In the case of the N-salicylidene-2-aminopyridines all the examined molecules turned out to be thermochromic, i.e. photochromism was not observed[15] as in the case of N-salicylideneanilines. We explained this phenomenon by suggesting that the planarity is achieved because of the position of the hetero-nitrogen atom of the pyridine ring which is always at the cis-position with respect to the H(7) hydrogen atom as shown in Fig. 2. The suggestion originated from the X-ray crystal structure determination of four representative members of this class inluding the parent compound[1]. Thus salicylidene-2-aminopyridine (IV), 5-bromo-salicylidene-2-aminopyridine (VIII), 5-methoxy-salicylidene-

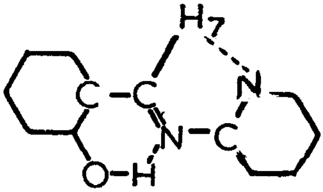
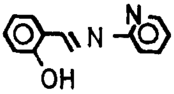


FIGURE 2. Salicylidene-2-aminopyridines. The hetero-nitrogen atom at cis-position with respect to the hydrogen 7.

-2-amino-4-chloro-pyridine (IX) and 3-methoxysalicylidene-2-amino-6-methyl pyridine (X) are essentially planar. In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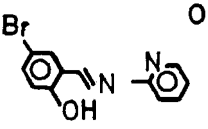
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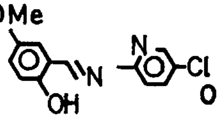
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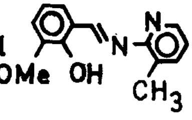

X

the planar molecular structure the lone pair of the imino nitrogen atom does not overlap the electrons of the pyridine ring and consequently the basicity of the bridge nitrogen atom and hence the strength of the hydrogen bond between the H atom of the OH group and the imino N atom should be high. Therefore, the proton transfer shown in eq. 2 is favoured in the planar as against a non-planar conformation.


(2)

The molecular structures of the four salicylidene-2-aminopyridines 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 toward the lone pair of N(1) atom as it is shown in Fig. 3 for the case of salicylidene-2-aminopyridine.

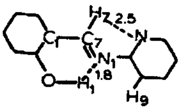


FIGURE 3. Geometry and relevant distances (Å) for salicylidene-2-aminopyridine.

The molecular packing of the four compounds for which the crystal structure was solved, is characteristic of flat molecules arranged in stacks along the shortest crystal axis with mean interplanar distance of 3.54 Å. The structures are shown in Fig. 4.

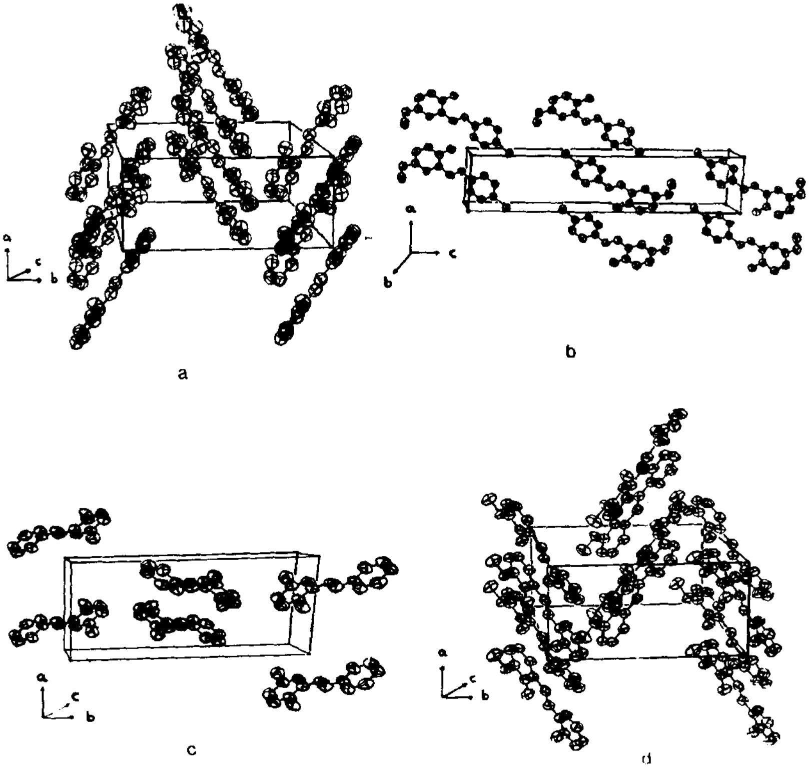


FIGURE 4. Packing arrangement of salicylidene-2-aminopyridine (a), 5-methoxysalicylidene-2-amino-4-chloropyridine (b), 5-bromosalicylidene-2-aminopyridine (c) and 3-methoxysalicylidene-2-amino-6-methyl-pyridine (d)

Based on their identical behaviour, thermochromic in each case, it may not be unjustified to suppose that all the salicylidene-2-aminopyridine compounds investigated will have similar packing arrangement.

We, therefore, suggest that the planarity is achieved because of the hetero-nitrogen of the pyridine ring at the ortho - position. In the case of salicylideneanilines there is steric hindrance due to the short distance of about 2 Å between the ortho - hydrogen H_9 and exocyclic hydrogen H_7 when the molecule is planar[16]. This repulsion is relieved in the case of salicylidene-2-aminopyridines because the nitrogen heteroatom is always at the cis-position with respect to the H_7 hydrogen atom. The distance of about 2.5Å between these atoms corresponds to normal van der Waals contact. These findings indicate that the driving force for the observed planarity of the salicylidene-2-aminopyridine is twofold : the intramolecular hydrogen bond which "locks" the salicylaldimino group in the planar position, and the presence of the nitrogen atom of the pyridine moiety which allows the pyrimidino ring to be co-planar with the salicylaldimino group. Therefore, the thermochromic behaviour in the crystalline state of this class of compounds can be interpreted as due to a shift in the tautomeric equilibrium shown in equation 2.

To test the importance of the nitrogen heterocyclic atom in the ortho-position with respect to the C =N bridge we have prepared, as we have said, a number of salicylidene-meta-aminopyridines and salicylidene-para-aminopyridines.

By screening the salicylidene-meta-aminopyridines for photochromic and thermochromic properties we found all of them to be weakly thermochromic.

The crystal structure analyses for the parent compound and for 5-methoxysalicylidene - 3 - aminopyridine shows the following features[2] : the structure of 5-methoxysalicylidene - 3 -aminopyridine is disordered (Fig. 5a), the molecules having two orientations of the pyridine ring in a statistical sense. Thus N_2 occupies two positions corresponding to a rotation by 180° of the ring around N_1-C_8.

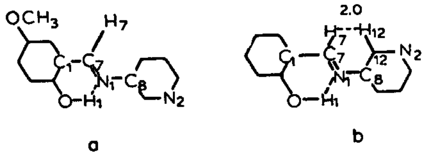


FIGURE 5. Conformations of 5-methoxysalicylidene-3-aminopyridine (a) and salicylidene-3-aminopyridine (b).

In salicylidene - 3 - aminopyridine (b), the heteronitrogen atom is cis with respect to H_7, as opposed to the heteronitrogen atom of 5-methoxysalicylidene - 3 -aminopyridine which is mainly (75%) trans.

Apparently, there is no appreciable energy difference between the two orientations due to the symmetry of interaction of both H atoms ortho to the imino group with H_7. This is in contrast to salicylidene-ortho-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 N_1-C_8 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 for $H_7 \ldots H_{12}$. The observed deviation from planarity in this class of compounds and the weak thermochromic behaviour indicate that the strength of the latter might be a monotonic function of the dihedral angle defined by the rotation of the pyridine ring with respect to the planar salicylideneimine part of the molecule.

The screening of salicylidene-para-aminopyridines for photochromic and thermochromic phenomena showed the existance of photochromic and thermochromic compounds 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. Thus, of the two compounds which have been examined in detail one, 3,5-dichlorosalicylidene - 4 -aminopyridine, is found to be photochromic but is readily hydrolyzed in the solid state and the hydrolysis products cocrystallize[3] with one water molecule. Figure 6 shows that the two precursor compounds, 3,5-dichlorosalicylaldehyde and 4-aminopyridine, form a solid salt with water participation. The hydrogen of the hydroxy group has been moved to the nitrogen of the pyridine ring. The aldehyde group on the other hand points to the amino group of another pyridine molecule ready to form the Schiff base, while a molecule of water co-crystallised in the system. There are two different salicylaldehyde-pyridine pairs in the unit cell. The angles between the ring planes are 14° and 19° respectively. On heating this yellow salt, water comes off and the 3,5-dichlorosalicylidene-4- aminopyridine is formed. This is an orange solid compound and is, as was mentioned before, photochromic. The reaction is reversible. Thus, the orange compound takes two moles of water to give again the yellow salt in the presence of water.

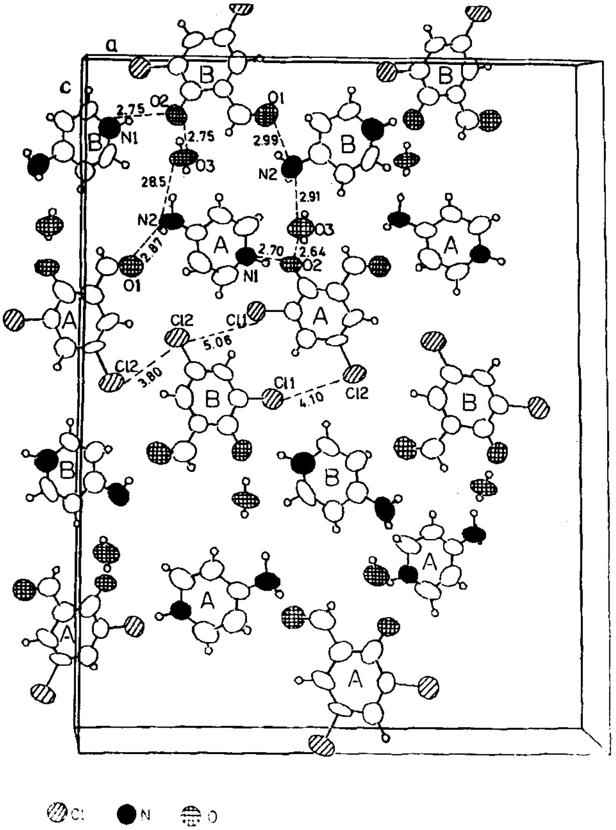


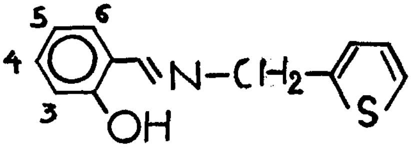
FIGURE 6. A view of the unit cell along the b axis.

Structural studies of the orange compound are already under way and it is believed they will elucidate the above behaviour.

SALICYLIDENE-2-THENYLAMINES

In order to adress the second purpose we prepared a number of

N-salicylidene-2-thenylamines (VII). This class of compounds



(VII)

presents very interesting photochromic and thermochromic phenomena and a complete study will appear elsewhere. Here we will report some preliminary results in the solid state in connection with the problem set. Thus, the parent compound (VII) of this class is, in the crystalline state, photochromic. Substitution in the benzene ring of this compound bring interesting results which appear in Table I. The presence of the methylene group in the bridge disconnects the resonance between the two aromatic rings and introduces a

TABLE I. Photochromic and Thermochromic Properties of Some Crystalline N-salicylidene-2-thenylamines.

Compound	Property
R_1 = H R_2 = H	Photochromic
R_1 □ H R_2 = 5-Br	Photochromic
R_1 = H R_2 = 3-MeO	Photochromic
R_1 = 3-Br R_2 = 5-Br	Thermochromic
R_1 = 3-Cl R_2 = 5-Cl	Thermochromic
R_1 = H R_2 = 4-MeO	Photo/thermochromic

tetrahedral carbon which forces the molecule into a non planar geometry. Thus it was expected that all the above compounds would be photochromic. Instead, we observe not only photochromic compounds but thermochromic as well. And finally, for the first time observed in the Schiff base series, the clear case of a compound with both photochromic and thermochromic properties. The above results show the need for a re-investigation of the whole area and especially the thesis that planar molecules are connected with thermochromism and non-planar with photochromism.

The structure of compound (VII) is under investigation and it is believed will elucidate the connection between crystal structure and photochromic and/or thermochromic properties.

The above findings show that structural-directing effects may be accomplished through proper substitution. The examination of more structures in combination with desired properties of photochromism and or thermochromism will add in this relatively new field of crystal engineering.

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