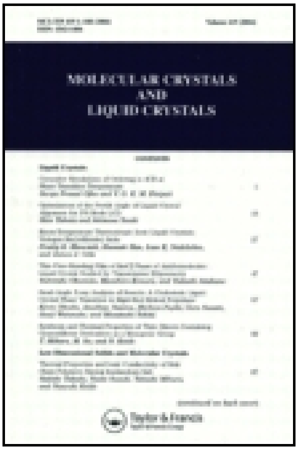

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Solid State Anil Photochromism

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SOLID STATE ANIL PHOTOCHROMISM+

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Abstract We report in this paper on the work in photochromism and thermochromism of anils in our laboratory and put this work in context with the past. Thus, results with anils containing a hetero-atom in the aniline ring, anils with the thenylamine moiety instead of aniline and anils with the CH_2 grouping between the nitrogen in the bridge and the aniline or the thenylamine group are compared with those of N-salicylideneanilines.

INTRODUCTION

The basic research on solid photochromic materials is growing since, in addition to the scientific interest, there is considerable commercial interest. Anils constitute a large class of photochromic compounds in which the crystal structure has been correlated with photochromism.

ANILS OF SALICYLALDEHYDES

The reversible solid state photocoloration of anils of salicylaldehydes (1) was first observed by Senier and co-workers[1], who noted that of the ring-substituted anils only a few were photochromic and that polymorphic modifications of the same anil were not necessarily all photochromic. These two observations revealed the topochemical effect on photochromism, but a firm statement at that time was not made because of ill defined

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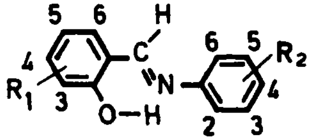
+ The present paper is dedicated to MENDEL D.COHEN who contributed a lot in the field of anil photochromism.



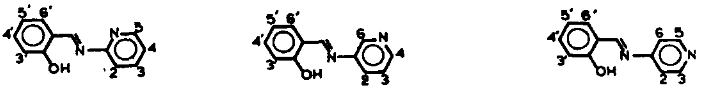
(1)

experiments, especially with properly ring-substituted derivatives and variations of temperature.

Cohen and co-workers[2-4] undertook a more systematic study of crystalline anils of salicylaldehydes and confirmed that many anils are dimorphic and that the two forms occasionally differ in color, yellow and orange-red. They also noted, in the photochromic anils, the existence of two temperature limits, the variation of size of the temperature interval (the "working range") and the importance of the <u>ortho</u>-OH group[2,3]. It was further found that "structural mimicry" was operating, an effect that constitutes a particularly striking example of topochemical control. For example, the stable crystal form of N-salicylidene-4-chloroaniline is thermochromic, whereas the stable form of the corresponding bromo-derivative is photochromic, thus showing the absence of an apparent correlation of chemical properties with the electronic characteristics of the substituents[4].

HETEROCYCLIC ANILS

We have extended the structural studies[5] in three analogous series of heterocyclic anils (2). In the case of salicylidene-2-aminopyridines, all the crystalline



(2)

salicylidene-2-aminopyridines salicylidene-3-aminopyridines salicylidene-4-aminopyridines

compounds examined were found to be thermochromic. This generality was explained on the basis of their crystal and molecular structure. Thus the molecular packing of four compounds for which the crystal structures were solved[8], is characteristic of that of planar molecules arranged in stacks along the shortest crystal axis with a mean interplanar distance of 3.5 A. The planarity is achieved because of the hetero-nitrogen of the pyridine ring. In the case of N-salicylideneanilines, there is steric hindrance due to the short distance of ~2 A 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 hetero-nitrogen atom is always at the *cis* position with respect to the H_7 hydrogen atom (Figure 1). The distance of about 2.5 A between these atoms corresponds to normal van der Waals contact[8].

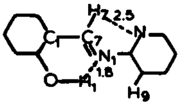
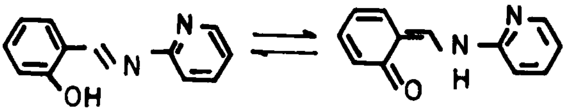


FIGURE 1. Distances (A) for N-salicylidene-2-aminopyridine.

The thermochromic phenomenon was interpreted as due to a shift in the tautomeric equilibrium (3) as in the case of



(3)

N-salicylideneanilines in which such a tautomerization is in agreement with infrared studies[7].

N-Salicylidene-3-aminopyridines are weakly thermochromic[8] in the solid state. The crystal structure analysis for the parent compound and for 5-methoxysalicylidene-3-aminopyridine shows[9] a rotation of the pyridine plane by 14.8°. This deviation from planarity may be related to the weak thermochromic behavior[10].

Among N-salicylidene-4-aminopyridines, photochromic and thermochromic compounds have been found and therefore non-planar structures are expected[9].

All the members of the heterocyclic anils (4) examined by us have been found to be photochromic in rigid glasses at spectroscopic dilution and the application of flash techniques has permitted the analysis of similar but transient phenomena in solution[10]. Thus the transient absorption spectrum of N-salicylidene-2-aminopyridine shows a spectrum similar to that of the photoproduct in rigid glasses. The kinetic and spectral considerations of this compound indicated a quinoid photoproduct having an activation energy of 2.6 kcal/mole for the dark back reaction. Thus again, as in N-salicylideneanilines, when the factor of crystallinity is lost, as in rigid glasses and solutions, and the orientation of the molecules is random, all the molecules of these three classes appear to be photochromic.

EFFECT OF CRYSTAL STRUCTURE

The problem of the effect of crystal structure on the photochromic properties of Schiff bases continues to be of interest.

In a continuation of previous efforts[5,10] to correlate the crystal structure with photochromism and/or thermochromism of the crystalline Schiff bases, we prepared a number of compounds among which we hoped to find molecules clearly displaying both photochromic and thermochromic properties, as opposed to the exclusive photochromic or thermochromic behavior studied so far. The compounds prepared were derivatives of N-salicylidene-2-thenylamine and N-salicylidene-2-benzylamine[11], since it appeared that such behavior might result from salicylidene derivatives in which the amine is aliphatic or the amino group is insulated from the ring.

Among the compounds prepared, in which the amino group is insulated from the ring by the $-CH_2$-grouping, photochromic and thermochromic examples have been observed and also a clear case (in each group) of a compound displaying both phenomena. These molecules are not planar due to the methylene group inserted in the bridge[12]. The salicylaldimino moiety of the molecule is planar, however, 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 A distance between planes was not observed (Figure 2).

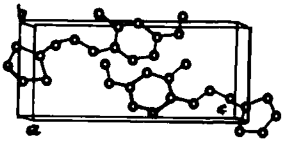


FIGURE 2. A view of N-(4-OCH_3-salicylidene)-2-thenylamine.

CONCLUDING REMARKS

In the Schiff base series the hydrogen atom of the *ortho*-OH group, which forms a hydrogen bond with the nitrogen of the C=N bridge *via* a six-membered ring,can be considered as having two wells in the pontential energy surface, corresponding to two possible states, one in which the hydrogen is bonded to the oxygen and one to the nitrogen. The latter, is different in the thermochromic crystals than that of the photochromic ones since in the latter case an isomerization about the C=N bond is required in order to stabilise the photoproduct. In connection with this, a remark made by the late G.M.J. Schmidt is relevant: if the hypothesis of geometrical isomerization correctly accounts for solid-state photochromy, the rates of coloration and fading should be sensitive to molecular environment, i.e. to the presence of impurities. Experiments to test this possibility are under way. The colored tautomers, corresponding to the second well, are so unstable that they have never been isolated either in the thermochromic compounds or in the photochromic ones and it has not been established what fraction of the OH-form molecules is converted to the NH-form molecules.

The position of the proton, as in early x-ray diffraction studies, has not been located crystallographically and infra red spectroscopy is still the more persuasive technique.

This class of compounds shows that the planarity or non-planarity of the molecule is not the only determining factor for thermochromic or photochromic behavior, respectively, and more structures are needed in order to clarify the extent of the structure effect on these properties.

Thus concerning the prevailing mechanism(s) of photochromism and thermochromism of Schiff bases, a number of investigators confirm the basic proposals of Cohen and Schmidt in that they identify the cis-keto form as the species produced in the thermochromic process (as well as the second species formed in hydrogen-bonding solvents) and the trans-keto form as the species produced photochemically.

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