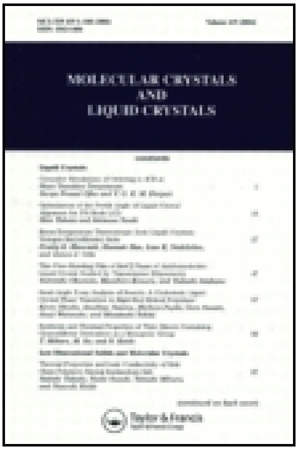

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Solid State Photochromism of Anils

Eugene Hadjoudis [a]

[a] Institute of Physical Chemistry, N. C. S. R. “Demokritos”, 153 10, Aghia Paraskevi Attikis, Greece

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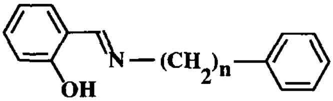
SOLID STATE PHOTOCHROMISM OF ANILS

EUGENE HADJOUDIS
Institute of Physical Chemistry, N.C.S.R. "Demokritos"
153 10 Aghia Paraskevi Attikis, Greece.

Abstract: The anils of ortho-hydroxybenzaldehyde comprise a chemical system which exhibits the properties of solid state photochromism and thermochromism. These properties are exclusive in this system and therefore there is a problem which may be described as the relation between photochromism and thermochromism on the one hand and crystal structure on the other. Thus in this work the topochemical factors responsible for these properties are explored and "structural engineering" approach are applied in order to prepare solid anils which are photochromic and/or thermochromic at will. Literature data on crystal structure and photo-behaviour of anils are presented and discussed under the same light in order to have a more complete understanding of the problem.

INTRODUCTION

The anils of ortho-hydroxybenzaldehyde (1), i.e. condensation products of salicylaldehydes with amines, are usually crystalline materials with color ranging from light yellow to red orange presenting polymorphism and undergoing reversible solid state photocoloration. The phenomenon is not general and polymorphic modifications of a certain photochromic anil are not necessarily all photochromic, a fact revealing the topochemical effect on photochromism. In general, the non photochromic compounds are thermochromic[1].

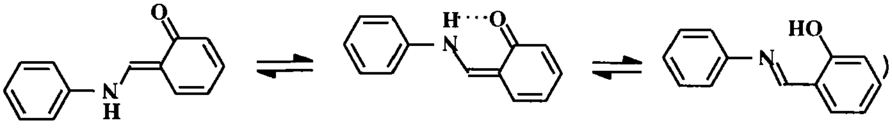


$n=0-2$ (1)

However, scientists in the beginning of the century who first observed the reversible solid state photocoloration of these compounds, because of ill defined experiments, did not made a firm statement at that time especially with regard to variations of temperature.

Cohen and co-workers[2-4] classified the crystals of anils (η=0) into two types, on the basis of their molecular structure and spectroscopic properties. According to this classification of crystalline N-salicylideneanilines type α posess a non-planar molecular structure and the effect of uv-light upon them results in reversible coloration: thus their name photochromic. In type β the molecular structure is planar, the effect of uv-light results in fluorescence without any coloration, while the effect of heat brings reversible coloration and hence their name thermochromic.

In addition to the above "spectroscopic" approach, on the basis of structural studies, the authors concluded that there is a general distinction between the structures of crystals of types α and β: in the thermochromic crystals the molecules are planar and pack face-to-face with short intermolecular contacts, of the order of 3.3 A, normal to the molecular planes; in the photochromic crystals, the salicylaldimino part of the molecule is planar, but the aniline-ring lies 40 to 50° out of this plane, and the resulting structure is relatively open with no close face-to-face contacts between molecules. Furthermore, in order to interpret the phenomena of photochromism and thermochromism, they proposed an intramolecular H-transfer mechanism as follows: there is a temperature-sensitive equilibrium in the crystal between the two tautomers (2) of the molecule, the one with the chelating hydrogen covalently bonded to the oxygen, the "OH-form", and the "NH-form" with the hydrogen bonded to the nitrogen. The <u>cis</u>-keto NH-form absorbs at longer wavelengths; the population of this form increases with increasing temperature and thus causes a deepening of color.



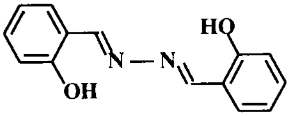
enol OH-form   <u>cis</u>-keto NH-form   <u>trans</u>-keto NH-form

The intramolecular H-transfer can occur in either the ground or the excited electronic state. High energy is required for H-transfer in the ground electronic state of molecules in photochromic crystals owing to their twisted conformation and, as a result, no absorption attributable to the NH-form is observed. H-transfer can occur, however, in the excited electronic state, and the crystal structure is sufficiently open to permit a subsequent geometric isomerization leading to the colored trans-keto NH-form which is stabilized as a result of the rupture of the intramolecular hydrogen bond. Thus, according to this interpretation, in the crystalline N-salicylideneanilines, photochromism and thermochromism are mulually exclusive properties[2].

TOPOCHEMICAL EFFECT

Since the photochromic species is associated with the keto-trans form, the required cis→trans conversion is highly improbable in the plane-to-plane packing type of the thermochromic crystalline compounds but possible in the open structure of the photochromic crystals.

The work of Arcovito and co-workers[5], who determined the crystal and molecular structure of salicylaldehyde azine (3), is in accordance with the above.



(3)

The molecules are centrosymmetric and nearly planar; the small deviations from planarity are indicative of intramolecular overcrowding between the two ortho-substituents in the benzene ring. The distribution of bond distances within the benzene ring is consistent with the significance of the contribution to the structure from a resonance cis-quinonoid form. A strong internal hydrogen bond of 2.645 A binds the phenolic hydroxy-group to the nearest nitrogen atom in the azine chain.

The molecules are packed in plane-to-plane stacks within the crystal, with a perpendicular spacing between adjacent molecules of about 3.4 A, which in part accounts for its thermochromic properties.

The colored cis-quinonoid form is stabilized by the parallel packing of the molecules through dipole-dipole interactions[2,6].

Burr and Hobson[7] added later, using only two-dimensional data, the crystal and molecular structure of 2-bromo-N-salicylideneaniline. The main interest of this structure lies in the comparative intramolecular and intermolecular O---N distances. After computation of the interatomic spacings in the two cases, it was found that the intramolecular distance (2.62+0.08 A) was less than the shortest intermolecular O---N distance (4.99+0.8 A), thus supporting the thesis that the movement of the hydroxylic hydrogen atom during the photochromic change is intramolecular rather than intermolecular. Also, the structure of photochromic N-salicylideneaniline although without accurate molecular parameters showed confidently the angles between the main molecular planes (e.g. 49^0 between the two phenyl rings) and thus proved that N-salicylideneaniline was correctly assigned to the family of anils whose benzene rings are not coplanar in the solid state, on the basis of their behaviour under ultraviolet irradiation[8].

However, structural and optical studies of the thermochromism of N-tetrachlorosalicylideneaniline and n-tetrachlorosalicylidene-1-pyrenylamine indicated an intermolecular charge-transfer interaction in the latter crystal[9] in which the interplanar distances between the mean planes of the entire molecule are short, i.e. 3.37 and 3.39 A. Thus in the first crystalline compound, a thermochromic-type behaviour has been observed as a shift of the absorption edge, while that of the second crystalline compound is much less pronounced. In both compounds, however, fairly short O-H....N hydrogen bonds have been found, which may be mainly due to a steric effect of chlorine substituents. The difference in the proton transfer between these two compounds should presumably be caused by the above mentioned intermolecular charge-transfer interaction.

In the case of the second compound, it is observed that the hydrogen-bond structure is nearly intermediate between the NH and OH forms.

It thus follows that by applying structural-directing effects, producing planar or non-planar structures, one may achieve desired properties[10,11].

STRUCTURAL ENGINEERING EFFECTS

In our laboratory we introduced[10,11] a nitrogen heteroatom in the ortho-position of the aniline ring into a number of photochromic and thermochromic N-salicylideneanilines and all the examine molecules turned out to be thermochromic, i.e. photochromism was not observed like 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. 1. The suggestion originated from the X-ray crystal structure determination of four representative members of this class including the parent compound[12]. Thus salicylidene-2-aminopyridine, 5-bromo-salicylidene-2-aminopyridine, 5-methoxy-salicylidene-2-amino-4-chloro-pyridine and 3-methoxy-salicylidene-2-amino-6-methyl-pyridine are essentially planar. In 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. Moreover, 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 A, and the appropriate geometry for the H atom to point toward the lone pair of N(1) atom.

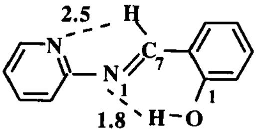


Fig. 1. Distances (A) for salicylidene-2-aminopyridine

Based on their identical behaviour, in each case thermochromic, we proposed that all the salicylidene-2-aminopyridine compounds will have similar packing arrangement. We, therefore, suggested that the planarity is achieved because the hetero-nitrogen of the pyridine ring is at the ortho-position. In the case of salicylideneanilines there is steric hindrance due to the short distance of about 2 A between the ortho-hydrogen H_9 and exocyclic hydrogen H_7 when the molecule is planar[10]. 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 2.5 A 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 as shown in the first part of equation 2.

To test the importance of the nitrogen heterocyclic atom in the ortho-position with respect to the C=N bridge we prepared[10] a number of salicylidene-meta-aminopyridines and salicylidene-para-aminopyridines. The screening of salicylidene-para-aminopyridines for photochromic and thermochromic phenomena showed the existance of photochromic and thermochromic compounds. Therefore, non-planar and planar structures are expected as in the case of N-salicylideneanilines. Thus photochromism and thermochromism in the crystalline state were found to be mutually exclusive properties in the series of aniline and aminopyridine derivatives.

Towards Photochromism

When the amino (or aminopyridino) group is insulated from the aromatic ring, the crystals of the corresponding salicylidene derivatives are expected to be both photochromic and thermochromic. Thus we found crystalline 5-bromo-2-hydroxyphenylethylamine to exhibit both phenomena (Figure 2). The molecule is not planar. The dihedral angle between the two phenyl rings is 17.8°. This conformation is attributed to the introduction of the two methylene groups which separate the rings. The H bond holds the bromosalicylidene part in the planar geometry, thus allowing the formation of the intramolecular hydrogen bond.

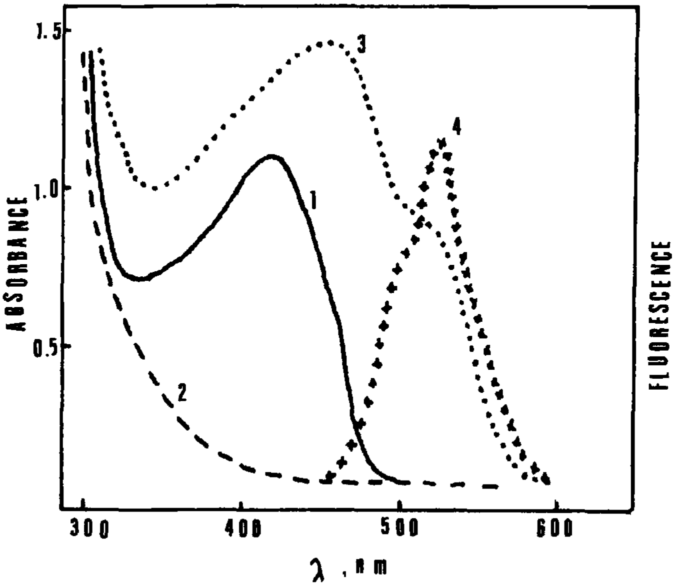


Fig. 2. Absorption and fluorescence spectra of 5-bromo-2-hydroxyphenylethylamine in thin polycrystalline film: 1) at room temperature 2) at liquid nitrogen temperature 3) after irradiation with 365 nm light at liquid nitrogen temperature and 4) the fluorescence spectrum at room temperature.

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. This structure does not preclude the hypothesis of cis→trans isomerization for photochromic behaviour; it is, however, dissimilar to the structures of the thermochromic N-salicylideneanilines and N-salicylideneaminopyridines determined so far[15]. However, the phenomenon is not general, that is the introduction of group -CH_2-which separate the rings does not always lead to both thermochromic and photochromic phenomena as it was found from the examination of a number of such solid compounds.

Thus, among these compounds, in which the amino group is insulated from the ring by the -CH_2-grouping, photochromic examples have been observed and also another clear case of a compound displaying both phenomena. However, when the grouping -CH_2CH_2- is introduced, the phenomenon is more general.

Provided that photochromism is induced by *cis*-*trans* isomerization then these molecules must be non-planar so as to preclude close intermolecular packing. This is the case indeed as it is seen from their molecular packing. This packing arrangement is different from that of the thermochromic anils (e.g. 5-chloro-N-salicylideneaniline and N-salicylidene-2-aminopyridines[1]) in which planar molecules lie plane-to-plane. This then suggests that close plane-to-plane packing, and hence molecular interactions, is not a primary requisite of thermochromism. It has been suggested that a principal difference between thermochromic and photochromic molecules lies in the valence state of the nitrogen lone-pair; that the nitrogen lone-pair density, in the benzeno*d species is not diminished in the planar thermochromic molecule but is so in the photochromic non-planar molecule in which it interacts with the aniline ring. However in the non planar N-5-bromo-2-hydroxyphenylethylamine the aliphatic system -CH_2-CH_2-blocks interaction of the nitrogen lone-pair thus leaving it undiminished in density and fully available for O-H...N hydrogen bonding in favour of the proposed enol⇄keto tautomerism in the thermochromic series. Thus the compound exhibits both phenomena.

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