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Solid State Photochromy†

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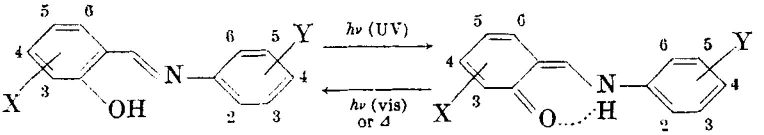
Abstract—The photochromic properties of some benzylideneaniline derivatives, namely of the *o*-carboxy-(I), *o*-methyl-(II), *o*-nitro-(III) and *o*-aminobenzylideneaniline (IV) have been investigated and the results have been compared with those of the photochromic system of salicylideneaniline and its derivatives. The solid compound (I) did not show any observable change in its color by illumination while compound (II) is liquid at room temperature and was not tested as a glass. Compound (III) undergoes a photochemical rearrangement in the crystalline state leading to a stable photoproduct. Compound (IV) undergoes reversible color change when irradiated in the crystalline state with U.V. light. In the case of rigid glasses the color-formation is reversed upon softening. Kinetic data are reported for the fading of the photo-colored solid compound (IV). It is suggested that photochromy involves an *intra*-molecular proton shift from a suitable *ortho*-group to the nitrogen of the >C=N-group leading to quinoid type molecules.

Salicylideneaniline and its derivative belong to a photochromic system which has been extensively investigated. As noted more than 30 years ago,⁽¹⁾ crystals of salicylideneaniline undergo reversible color changes induced by UV light. Thus their color turns from yellow to red and this color formation can be reversed by illumination with blue light or thermally in the dark. The phenomenon was readily explained in terms of the light-induced equilibrium.



(1)

More detailed information on this system is due to the recent investigation by Hirshberg, Cohen and Schmidt⁽²⁻⁵⁾ who classified

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the crystals of these compounds into two types on the basis of their spectroscopic properties (see Table 1).

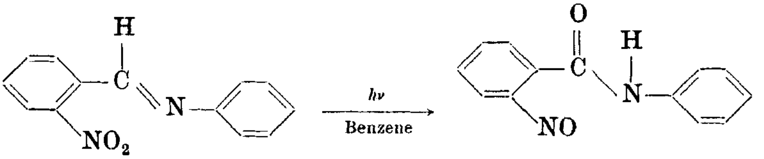
It is to be stressed that this classification refers to the various compounds in given crystal structures. Thus, both compounds given as examples in Table 1 are dimorphic, with the metastable and stable forms of different types;⁽⁶⁾ the classification given in the table refers to the modifications which are the stable ones at room temperature and above.

TABLE 1 Classification of Crystalline N-Salicylideneanilines

	Type α	Type β
Effect of UV light	reversible coloration; no fluorescence	no coloration; fluorescence
Effect of heat	no coloration	reversible coloration
Name	photochromic	thermochromic
Example	X=H; Y=2–Cl	X=H; Y=4–Cl

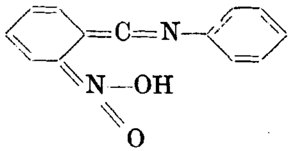
In addition to the above " spectroscopic " approach, structural studies have been carried out on a number of these materials. Two full three-dimensional analyses have been performed;⁽⁷,⁸⁾ another structure has been solved by analysis of two zones;⁽⁹,¹⁰⁾ a further structure has been analyzed in projection only;⁽¹¹,¹²⁾ and, finally, in many cases the space group and cell dimensions of other N-salicylideneanilines⁽⁴⁾ allow reliable conjecture regarding the molecular and crystal structures involved. From this information it has been 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 3.3Å) 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 of the molecules. The above authors⁽²⁻⁵⁾ considered the *ortho*-OH group as an essential condition for coloration and they interpreted the phenomenon of thermochromism as follows: there is a temperature-sensitive equilibrium in the crystal between the two tautomers 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 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 can occur in either the ground- or excited-electronic state. In contrast, a high energy is required for hydrogen transfer in the ground-electronic state of molecules in photochromic crystals; as a result no absorption attributable to the NH-form is observed. Hydrogen transfer can occur, however, in the excited-electronic state, and the crystal structure is sufficiently open to permit a subsequent geometric isomerization which leads to the colored photo-product. It has been further noted that all salicylideneanilines are photochromic in rigid solutions and they interpreted photochromism as an intrinsic property of the individual anil molecule rather than a result of molecular interaction in the crystal.(12) With the help of flash techniques, the reaction has also been observed in liquid solutions.(13) More recent works(14–16) on the mechanism of photochromic anils attempt a detailed study of the electronic absorption and emission spectra in order to re-evaluate the identity of the photocolored product. A comparison between the results of these works and those of Cohen and Schmidt appears in Ref. (16), and shows that the mechanism of photochormism is not yet answered. The general statement that the *ortho*-OH group is an essential condition for photochromism has been critisized by some authors. Thus Becker and Richey(15) reported that several nitrosalicylaldehyde derivatives do not show this phenomenon. In an attempt to clarify the role of the *ortho*-OH group, we have extended the study to include compounds with *ortho*-groups other than hydroxy. Thus we have studied the *ortho*-carboxy, *o*-methyl, *o*-nitro and *o*-amino derivatives of benzylideneaniline including flash photolysis techniques together with spectroscopic observations. The data(17) from the flash work show that a new absorption band in the region 410–470 nm appears on flash photolysis of the above compounds in different solvents indicating the possibility of a common transient species. This band seems to be similar to the so-called photochromic band observed on flash photolysis(13,18) of *ortho*-hydroxy-benzylideneaniline or on photolysis(3,12) in rigid glasses or in the crystalline state. This band was attributed(3,12) to the formation of a quinoid isomer, reaction (1). It thus seems probable that the transients observed above, which give rise to a similar band in the same wavelength region, are also of quinoid character.

For compounds *ortho*-carboxy, *ortho*-methyl, and *ortho*-amino, the quinoid isomer can be produced by a mechanism similar to that suggested for salicylideneaniline, i.e., a hydrogen transfer from the *ortho*-group to the nitrogen atom of the C = N group. The *ortho*-nitro compound does not, however, have a hydrogen atom in the *ortho*-position. It is suggested that this compound initially forms an intermediate H-atom adduct, $-NO_2H$, similar(19) to the suggested photochemical rearrangement of *ortho*-nitro-benzaldehyde to *o*-nitrosobenzoic acid, since an analogous photo-induced isomeric change was found(20) on irradiation of *ortho*-nitrobenzylideneaniline in benzene solution, resulting in the formation of *ortho*-nitrosobenzanilide.



(2)

We found that this compound undergoes the photochemical rearrangement (2) in the crystalline state.(21) During this rearrangement a similar band is observed (by reflectance spectroscopy) with that of its transient in heptane solutions ($\lambda_{max} \sim 460$ nm) and is assigned to the quinoid form



the precursor of *ortho*-nitrobenzanilide.

The solid *ortho*-carboxy compound did not show any observable change in its color by illumination. The *ortho*-methyl compound is liquid at room temperature and it was not tested as a glass.

The *ortho*-amino compound was prepared from the condensation of the *ortho*-amino-benzaldehyde with aniline. N.m.r., i.r., and chromatography were utilized to establish the purity of the compound. Figure 1 shows the two absorption bands in the NH stretching region (3500–3300 cm^{-1}), arising from the symmetric and asymmetric vibrations of the hydrogen atoms, characteristic for a primary amine.(22)

We found that *ortho*-NH_2-benzylideneaniline undergoes reversible color changes in the crystalline state and also in rigid glass form induced by UV light ($\lambda = 365$ nm). Thus its color turns from yellow to red and the light-induced absorption band extends from 450 nm to about 600 nm with a maximum near 515 nm. This color formation can be reversed by light absorbed in the latter band or thermally in the dark. Curves showing typical variation associated with the formation and eradication of the color are given in Fig. 2. In the case of rigid glasses (EPA) the color-formation is reversed upon softening. This is shown in Fig. 3. The rate of fading of a crystalline film of this compound was determined at various temperatures and it was found to follow a first-order process. Atypical rate runs are shown in Fig. 4, and the corresponding Arrhenius plot in Fig. 5. The rate constants and activation energy are given in Table 2. The rate of fading increases with increasing temperature.

TABLE 2 First-order constants and activation energy for fading of photo-colored *ortho*-amino-benzylidene-aniline

t °C	10^4 K (min^{-1})	$\Delta H\ddagger$ (kcal. mol^{-1})
27	24.6	36
40	62.7	
55	156.0	

The color change in the crystals of this compound is not accompanied by any observable changes in the X-ray diffraction pattern. It should be mentioned that the color change in photochromic crystals of salicylideneanilines is not accompanied by any observable changes in the infra-red spectrum and the X-ray diffraction pattern.(4)

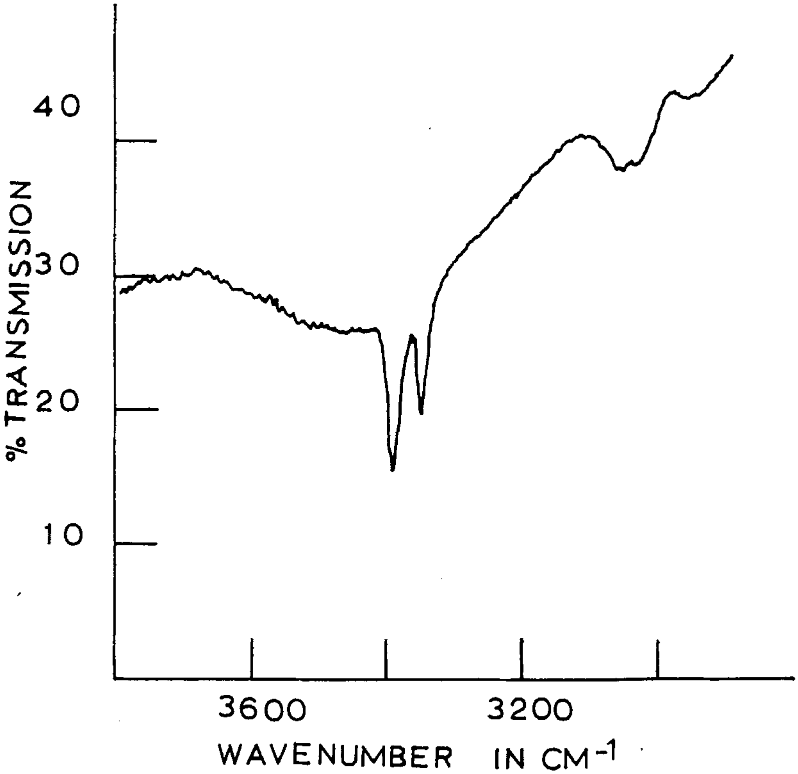


Figure 1. I.r. solid spectrum of *ortho*-amino-benzylideneaniline.

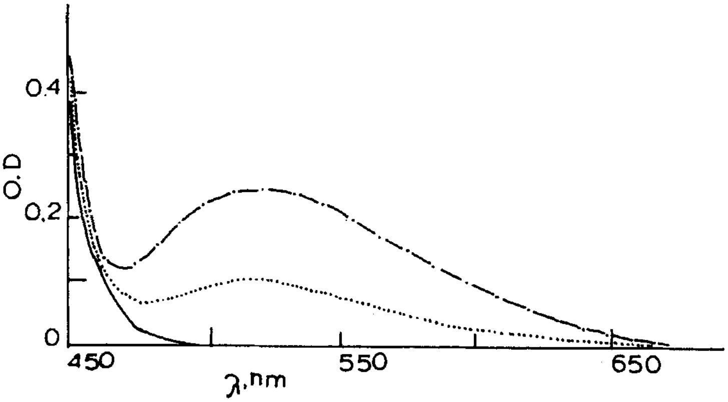


Figure 2. Color formation and eradication in crystalline (film) *ortho*-NH_2-benzylideneaniline. ——, initial spectrum; —·—·—, after 80 min. irradiation with 365 nm light; ...., after subsequent irradiation with 540 nm light (30 min). All at room temperature.

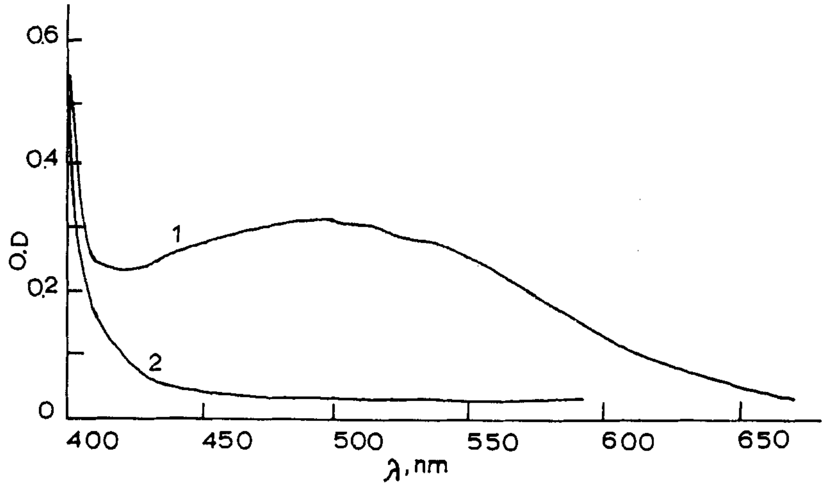


Figure 3. Color formation in rigid glass (EPA) of *ortho*-NH_2-benzylideneaniline. (1) after 20 min. irradiation with 365 nm light; (2) the above on softening.

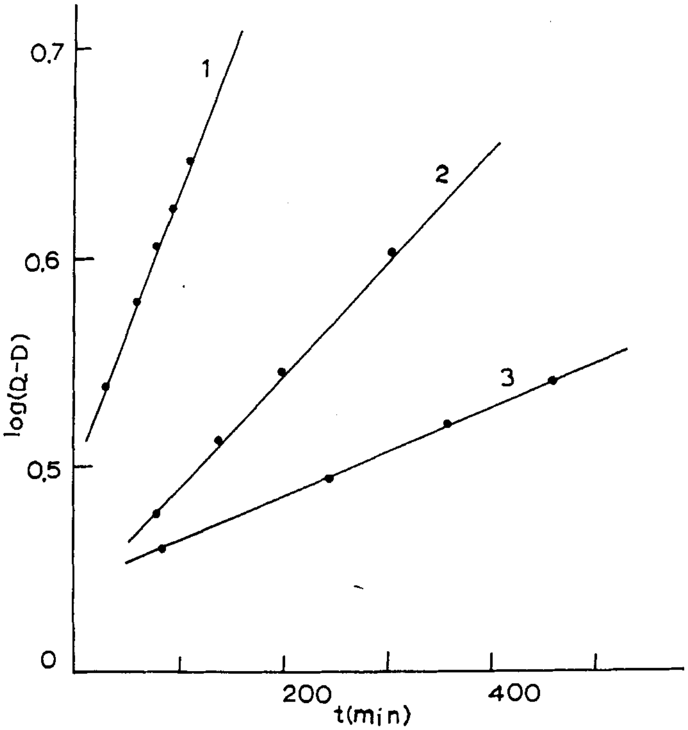


Figure 4. First-order plots for fading of photo-colored *ortho*-NH_2-benzylideneaniline at: 1, 55°; 2, 40°; 3, 27°.

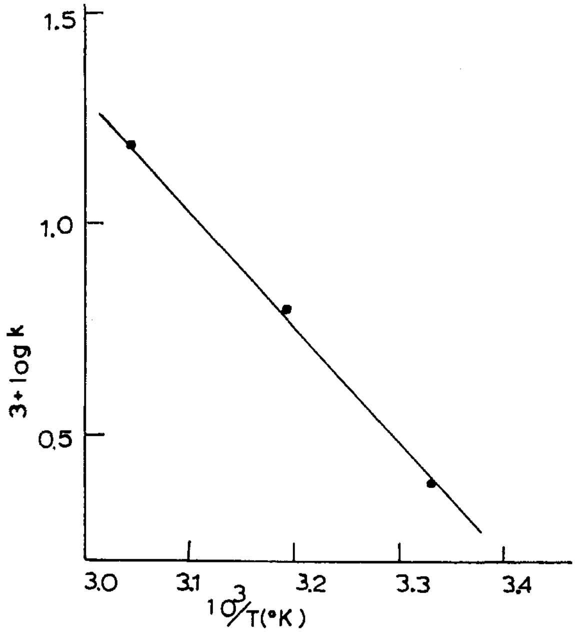
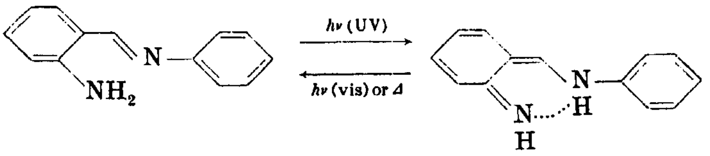


Figure 5. Arrhenius plot for fading rates of photo-colored *ortho*-NH_2-benzylideneaniline.

A comparison between the spectral changes of *ortho*-NH_2-benzylideneaniline and those of salicylideneaniline and its derivatives show that they are similar. Therefore, one might suggest that the mechanism (1) is also valid in the present case, thus



(3)

This then suggests that we could extend the general statement of Cohen and Schmidt that the *ortho*-OH group is an essential condition for photochromism in this class of crystalline compounds to any other *ortho*-group which is capable to transfer a proton to the nitrogen of the C = N group leading to quinoid type molecules. The fact that the phenomenon takes place in rigid glasses and disappears when the rigidity is destroyed suggests that the previously⁽¹²⁾ made statement that photosensitivity is a property of an isolated molecule in a rigid matrix holds also here.

Work continues with fluorescence, i.r., and n.q.r. measurements in an effort to verify the tautomerism (3) in the solid state, and thus have direct formation concerning the nature of the photo-formed red color.

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