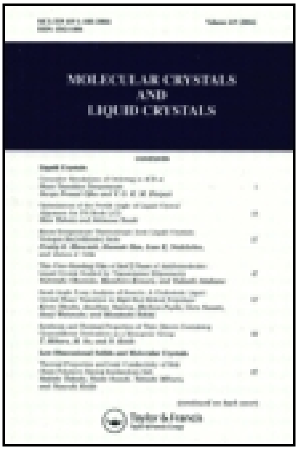

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PHotochromism and Thermochromism of Solid Salicylidene-Dehydroabietylamines and Salicylidene-6-Amino Methyl-Dehydroabietates

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PHOTOCHROMISM AND THERMOCHROMISM OF SOLID SALICYLIDENE-DEHYDROABIETYLAMINES AND SALICYLIDENE-6-AMINO METHYLDEHYDROABIETATES

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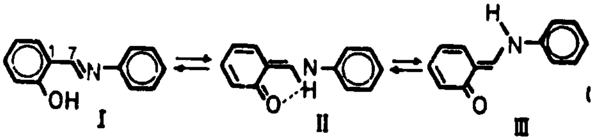
Abstract: Photochromic and thermochromic phenomena have been observed in a number of crystalline salicylidene-dehydroabietylamines and salicylidene-6- aminomethyldehydroabietates. Among the compounds studied in the solid state, some were found to exhibit both photochromic and thermochromic phenomena as compared to crystalline salicylideneanilines which are either photochromic or thermochromic but not both.

INTRODUCTION

Salicylideneanilines (I) in the crystalline state exhibit photochromism or thermochromism i.e. they show a reversible colour change, mostly from yellow to red, as a result of ultraviolet irradiation or under variation of temperature[1,2].

It was suggested[3,4] that the appearance of these phenomena depend upon the structure of the compounds, since no correlation exists between them and the chemical nature of the ring substituents. Thus, in the crystalline state, an "open" crystal structure associated with non-planar molecules and allowing molecular movement is necessary in order to allow photochromism, whereas in thermochromic crystals the molecules are planar and closely packed. Structural studies[5,6] support this idea.

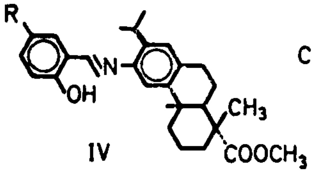
The ortho-OH group is considered to be an essential condition for both phenomena. The following model is proposed[2,7] to explain the mechanism in the solid state. For planar molecules exhibiting thermochromism there is a temperature sensitive equilibrium,(Eq. 1), between two tautomeric forms, a yellow "enol" form, the "OH-form" (I) stable at low temperature, where the chelating hydrogen is covalently bonded to the oxygen and a red quinoid "keto" form, the "NH- form" (II), 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[8,9].



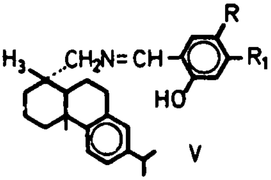
(1)

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 an E-keto form (III) may be produced.

In previous work[10] with salicylidene-2-aminopyridines it was found that the appearance of the thermochromic phenomenon in the solid state depends upon the crystal structure and the molecular orientation of the compounds. However the nature of the coloured species in the solid state and the photochromic mechanism are still subjects for research. The purpose of the present paper is to report the results of our studies on thermochromism and photochromism in a number of crystalline salicylidene-6-aminomethyldehydroabietate (IV) and salicylidenedehydroabietylamines (V) Schiff bases and to compare them with their benzene analogs (I).



IV



V

The studied compounds of group IV are: 1;(R = H), 2;(R = CH_3) and 3;(R = Cl) and of group V: 4;(R = CH_3, R_1 = H), 5;(R = H, R_1 = $N(CH_3)_2$, 6;{R = H, R_1 = H (no ortho-OH group)}, and 7;{R = CH_3, R_1 = H ($NHCH_2$ instead of N = CH)}.

These Schiff bases, when compared to salicylideneanilines, have lower symmetry and present increased breadth (addition of two more rings than aniline in the corresponding part of the molecule) and therefore substantial structural differences are expected which could affect both the photochromic and thermochromic properties, if present.

EXPERIMENTAL

The salicylidene-6-aminomethyldehydroabietate (IV) and salicylidenedehydroabietylamine (V) Schiff bases were prepared according to published processes[11]. All the compounds were purified by repeated recrystallization from ethanol, Infra-red spectra of the compounds 1-3 showed strong absorption around 1720 and 1620 cm^{-1} characteristic of the CO and > C =N- groups and compounds 4-7 around 1620 cm^{-1} characteristic of the >C =N- group.

Crystalline thin films were prepared from the melt between two quartz optical plates under pressure. The films were examined under polarized microscope and showed pleochromism.

The experiments in rigid glasses were conducted with solutions in EPA (ether:isopentane: alcohol, 1:5:5) at liquid nitrogen temperature and in polymerized methyl methacrylate (PMMA) at room temperature and at liquid nitrogen temperature. In these rigid media, the fading of the photo--colour was not appreciable during the measurements and therefore all the spectra were obtained satisfactorily. No correction was made to the spectra for concentration of the solution upon cooling as this was found to be less than 10% in EPA and of the order of 5% in PMMA.

Absorption spectra were recorded on a Cary-17 spectrophotometer. A quartz Dewar vessel with quartz windows was used for the measurements of optical spectra in thin films and rigid glasses at low temperatures.

Steady-state irradiations were carried out with a 200W high pressure Hg lamp and appropriate filters.

RESULTS

POLYCRYSTALLINE POWDERS

By screening the compounds of group IV in the form of polycrystalline powders for photochromic and thermochromic properties, it was found that compound 1 presents, although weakly, both photochromic and thermochromic phenomena. Thus the compound changes reversibly from yellow, at room temperature, to white, at liquid nitrogen temperature. This white colour turns to red under UV-irradiation at liquid nitrogen temperature. The yellow crystals at room temperature do not change colour under UV-irradiation, indicating that the photochromic phenomenon operates at low temperatures. The compound shows weak fluorescence at room temperature and stronger at liquid nitrogen temperature.

Compound 2 is photochromic at room temperature down to liquid nitrogen temperature. The colour changes on UV-irradiation from light yellow to red-orange. The process is reversible, thus the compound returns to its original colour thermally or under visible light. The compound is non-fluorescent and presents no change in colour with temperature. Compound 3 behaves in general like compound 1.

Among compounds of group V, compound 4 behaves like compound 1 and compound 5 is only thermochromic and fluorescent, 6 and 7 are inactive and are not fluorescent.

THIN POLYCRYSTALLINE FILMS

The results for polycrystalline powders are exemplified by experiments on thin polycrystalline films. Fig. 1(a) shows both the photochromic and the thermochromic phenomena at -40^{o}c for compound 1. Irradiation at room temperature brings no changes in the spectrum. However, an examination for photochromism over a range of temperature shows that there is a "working range" between -70^{o}C and -100^{o}C in which the phenomenon appears stronger. Figs. 1(b), (c) and (d) show the photochromic phenomenon of compounds 2 and 3, and the photochromic/thermochromic properties of compound 4 respectively.

Finally, it was noted that powders of compounds 6 and 7 are inactive. Their thin films, under UV-irradiation or temperature variation, also remain unchanged.

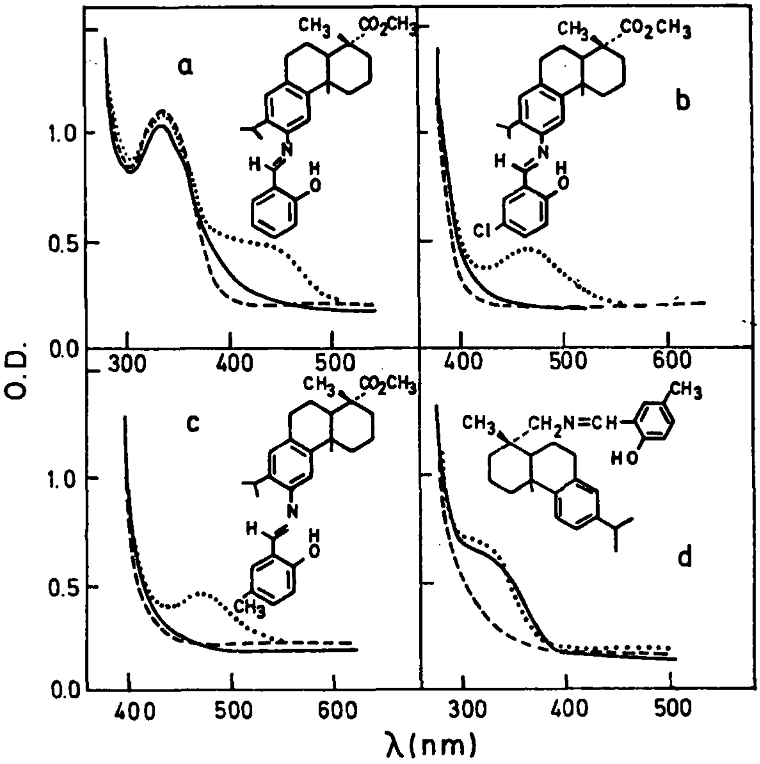


FIGURE 1. The absorption spectra of crystalline films of the indicated compounds at room (full lines) and low (broken lines) temperature; the dotted lines are after UV irradiation at low temperature.

RIGID GLASSES

Experiments in the rigid state were conducted with solutions of EPA at liquid nitrogen temperature and with PMMA at room temperature and at liquid nitrogen temperature. The results may be summarized as follows:

(i) photocolouration in rigid glassy solutions of the examined compounds occurs only at liquid nitrogen temperature. In the case of EPA, the effect is reversed when the rigid solution softens and in PMMA when the sample is warmed up.

(ii) the compounds, thermochromic or photochromic in the crystalline state, are all photochromic in rigid glasses.

(iii) in the absence of the ortho-OH group from the salicylaldehyde moiety (compound 6) or when the C = N bridge is saturated (compound 7), photochromism is not observed. Fig. 2 shows the results in PMMA for compounds 2 and 4.

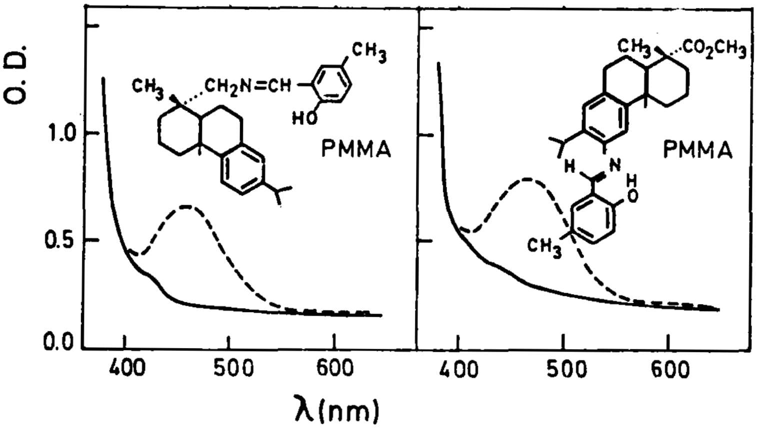
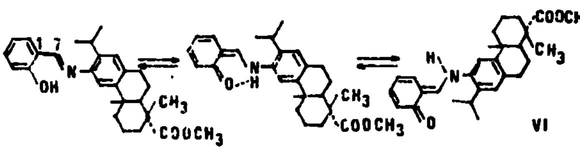


FIGURE 2. Absorption spectra of the indicated compounds at liquid nitrogen temperature (full lines) and after UV irradiation at the same temperature (broken lines)

DISCUSSION

By comparing our findings with those of salicylideneanilines we notice two substantial differences. First, we now have compounds which are both photochromic and thermochromic, and second, in the bridge compounds elongated by addition of the $-CH_2-$group, we do not have exclusively photochromic compounds as in salicylideneanilines[3], but thermochromic/photochromic and thermochromic as well. This is an indication that the structural requirements for salicylideneanilines, planarity with short interplanar distances of the order of 3.5Å for thermochromism and nonplanarity with interplanar distances more than 4.5Å for photochromism, are not enough to explain present results as was also found for some salicylideneaminopyridines[12]. Therefore either there are structures which permit the simultaneous appearance of photochromism and thermochromism or the planar structures in the present case are also "open" with interplanar distances more than 4.5Å and therefore permit rotations, analogous to those shown in Eq. 2, which produce photoproducts of the "keto" form VI. These structures have to await X-ray three-dimensional analysis.



VI

(2)

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