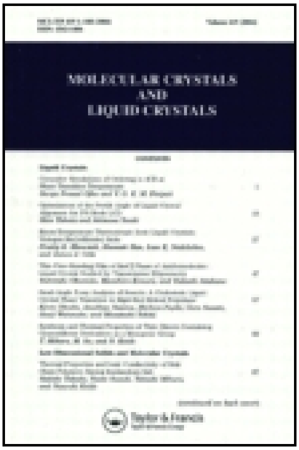

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Solid State Photochromism and Thermochromism of N-(5-Bromosalicylidene)-2-Phenylethylamine

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SOLID STATE PHOTOCHROMISM AND THERMOCHROMISM OF N-(5-BROMOSALICYLIDENE)-2-PHENYLETHYLAMINE

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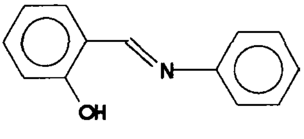
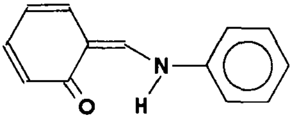
Abstract The title compound exhibits in its crystalline state both photochromic and thermochromic properties. The crystal structure shows that the salicylaldimino part is planar to permit *enol* - *keto* isomerization and thus thermochromism. Moreover, the crystal packing permits *the cis* - *trans* isomerization of the *keto* species to form the photoproduct.

INTRODUCTION

Three molecular species are involved in the thermochromism and photochromism of anils: the *enol* form (1) , the *cis-keto* form (2) that is involved in the thermochromic crystals and the *trans-keto* form (3) resulting from the *cis* by *cis-trans* isomerization about the C = N bond , thus stabilizing the photoproduct in the photochromic crystals[1,2].



(1)



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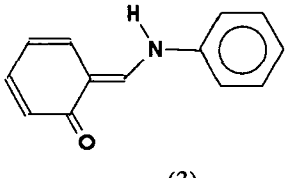

(3)

It is supposed that the non planarity of the molecules is a determining factor for the photochromic behavior. The close packing of planar thermochromic molecules prevents the *cis-trans* isomerization[3] and therefore deprives the crystal of photochromic properties. In the present contribution we examine the properties and the structure of N-(5-bromosalicylidene)-2-phenylethylamine (Figure 1) resulting from the thermochromic N-5-bromosalicylideneaniline by the addition of two methylene groups.

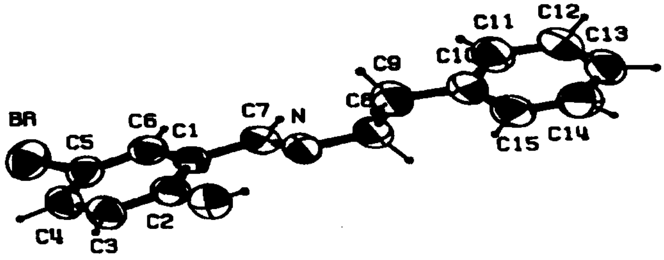

FIGURE 1 ORTEP drawing of the molecule showing the geometry and atom labelling.

EXPERIMENTAL

The title compound was prepared by condensation of 5-bromo- 2-hydroxybenzaldehyde and 2-phenylethylamine in ethanol. The photochromic and thermochromic properties of the compound were examined in thin polycrystalline films. These films were prepared from the melt between two optical quartz plates under pressure and their quality was examined under a polarizing microscope. The absorption spectra were recorded with a Cary-17 or Varian Techtron 635 spectrophotometers using a Dewar vessel with quartz windows.

Single crystals were grown by diffusing methylcyclohexane in a CCL_4 solution of the substance. Crystallographic data were collected from a well-formed prismatic crystal (0.88 x 0.20 x 0.04 mm) mounted along its longest axis. One octant of data ($2.0 < 2\sigma < 140.0$) was collected on a Syntex $P2_1$ diffractometer at 22° C with Ni filtered CuKα radiation, θ - 2θ scan mode with scan range 1.8° plus α_1 -α_2 divergence in 2θ and scan rate 1.0 - 10.0°. 2624 reflections were measured of which 1874 with $F > 5\sigma F$ were concidered as observed. Data were corrected for Lorentz, polarization and absorption effects. The diffraction conditions (hkl: h+k=2n, h0l: l=2n) and the monoclinic symmetry indicated the space group C2/c. The unit cell parameters are : a = 19.8864(1), b = 5.7218(3), c = 23.9916(1)Å, α =96.805(2)°, V = 2710.7(1)Å^3, Z = 8, Dx = 1.42, Dm =1.41 g cm^{-3} . The density was measured by flotation in aqueous $ZnCl_2$. The structure was solved and refined with SHELX76 [4]. Refinement was carried out by full matrix weighted least squares ($\Sigma w(Fo - Fc)^2$ minimized, $w = 1/\sigma F^2$). Best E map (E>1.2) revealed only the bromine atom out of 18 non-hydrogen atoms. The additional 17 atoms were found from difference maps.

Hydrogen atoms were similarly located at the end of anisotropic refinement. The final R = 0.0440, Rw = 0.0536. Maximum and minimum values in the final difference-electron-density map were 0.20 and 0.25 eA^{-3} respectively.

RESULTS

N-(5-bromosalicylidene)-2-phenylethylamine in the crystalline state exhibits both photochromic and thermochromic behaviour. Thus, at room temperature its absorption spectrum has a thermochromic band with a maximum around 420 nm which disappears on cooling at liquid nitrogen temperature (thermochromism). Subsequent uv irradiation at liquid nitrogen temperature results in the appearence of a new , structured band (photochromism) with a maximum around 450 nm and a shoulder at 510 nm (Figure 2).

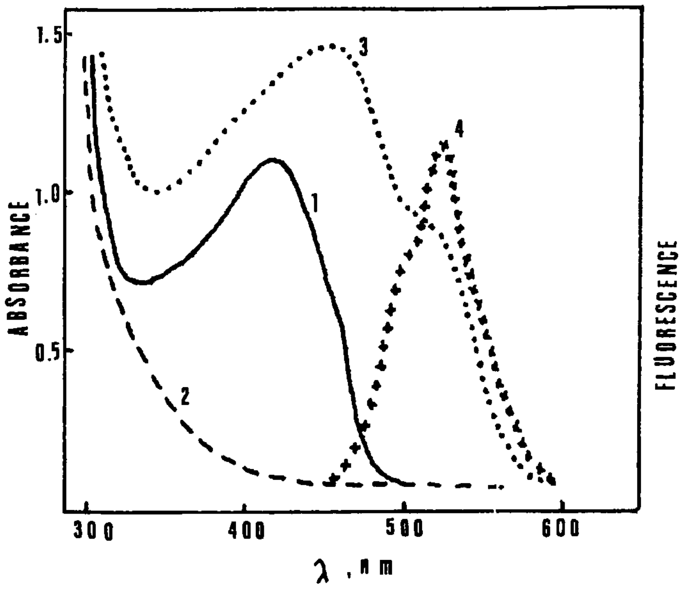

FIGURE 2. Absorption and fluorescence spectra of the title compound in thin polycrystalline film: 1) at room temperature 2) at liquid nitrogen temperature 3) after irradiation with 365 nm light at liquid nitrogen temperature 4) the fluorescence spectrum at room temperature.

It should be noted that the photochromic band decreases as the irradiation temperature increases and it is barely observed at room temperature. The absorption spectrum returns to the initial one on standing in the dark at room temperature. The polycrystalline film of this compound shows fluoresence at room temperature and in this respect it is similar to the crystalline thermocromic N-5-bromo-salicylideneaniline and in general N-salicylidene-anilines[2].

The geometry of the molecule as determined by the crystal structure is given in Table I.

TABLE I Molecular geometry.

(a) Bond lengths (Å)

C(1)-C(2)	1.394(5)	C(13)-C(14)	1.367(7)
C(1)-C(6)	1.394(5)	C(14)-C(15)	1.360(6)
C(1)-C(7)	1.464(5)	C(3)-H(C3)	0.91(4)
C(2)-C(3)	1.399(5)	C(4)-H(C4)	0.98(5)
C(2)-O	1.351(5)	C(6)-H(C6)	0.97(3)
C(3)-C(4)	1.380(6)	C(7)-H(C7)	1.08(5)
C(4)-C(5)	1.366(6)	C(8)-H1(C8)	1.05(5)
C(5)-C(6)	1.374(5)	C(8)-H2(C8)	1.13(4)
C(5)-Br	1.900(4)	C(9)-H1(C9)	1.00(8)
C(7)-N	1.260(5)	C(9)-H2(C9)	1.10(9)
C(8)-C(9)	1.511(6)	C(11)-H(C11)	0.89(6)
C(8)-N	1.470(5)	C(12)-H(C12)	1.06(4)
C(9)-C(10)	1.514(6)	C(13)-H(C1)	1.02(6)
C(10)-C(11)	1.376(6)	C(14)-H(C14)	1.01(5)
C(12)-C(13)	1.378(7)		

(b)Bond angles (^{o})

C(2)-C(1)-C(6)	119.5(3)	C(8)-C(9)-N	109.9(3)
C(2)-C(1)-C(7)	120.9(3)	C(8)-C(9)-C(10)	110.5(3)
C(6)-C(1)-C(7)	119.4(3)	C(9)-C(10)-C(11)	120.5(4)
C(1)-C(2)-C(3)	119.4(3)	C(9)-C(10)-C(15)	122.0(4)
C(1)-C(2)-O	122.3(3)	C(11)-C(10)-C(15)	117.5(4)
C(3)-C(2)-O	118.3(3)	C(10)-C(11)-C(12)	121.7(4)
C(2)-C(3)-C(4)	119.6(3)	C(11)-C(12)-C(13)	119.2(4)
C(3)-C(4)-C(5)	120.7(3)	C(12)-C(13)-C(14)	119.6(4)
C(4)-C(5)-C(6)	120.5(3)	C(13)-C(14)-C(15)	120.5(4)
C(4)-C(5)-Br	120.6(2)	C(10)-C(15)-C(14)	121.3(4)
C(6)-C(5)-Br	118.8(2)	C(7)-N-C(8)	119.1(3)
C(1)-C(6)-C(5)	120.1(3)	C(2)-O-H(OH)	111(6)
C(1)-C(7)-N	121.8(3)		

c) Dihedral angles (^{o}) involving planes A B C. Planes A, B and C defined as : A (atoms C1, C2, C3, C4, C5 and C6), B (atoms C9, C10, C11, C12, C13, C14 and C15), C (C1, C2, C7, N, O and H (OH)).

The angle between A and B 17.8. The angle between A and C 3.5. The angle between B and C 15.5

DISCUSSION

A significant aspect of the problem of the photochromic and thermochromic anils is whether the molecular interactions in the crystal play a role in stabilizing the photoproducts or the crystal packing is important only in so far as it imposes constrains upon the molecules keeping them fairly rigid.

N-(5-bromosalicylidene)-2-phenylethylamine shows both photochromic and thermochromic properties (Figure 3). This is in contradiction to crystalline salicylideneanilines where thermochromism and photochromism are mutually exclusive properties [5]. The insertion of the two methylene groups in the bridge of the first gives the molecule the "open" crystal structure of photochromic molecules which permits *cis-trans* isomerization to take place[1] (Figure 3).

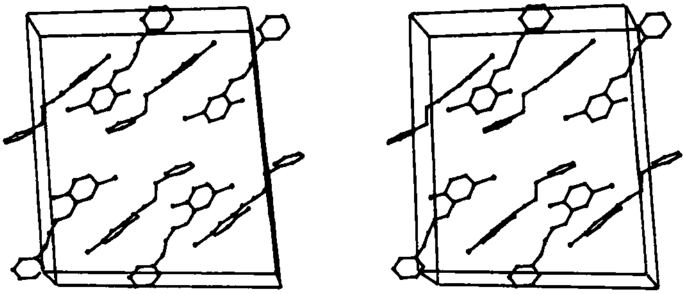

FIGURE 3 Stereoscopic diagram of the molecular packing as viewed along a axis.

On the other hand the molecule shows also thermochromism, a fact indicating that planarity of molecules and close packing of the molecular planes at 3.5A [6] is not necessary for appearence of the phenomenon. It has been suggested[7] that the principal difference between thermochromic and photochromic anils lies in the valence state of the nitrogen lone-pair. Its density is not diminished in the planar salicylideneanilines while it is in the photochromic non-planar ones in which it interacts with the aniline ring. However, in the non-planar N-(-5-bromosalicylidene)-2-phenylethylamine the aliphatic system $-CH_2-CH_2-$ blocks interaction of the nitrogen lone-pair with the phenyl rings thus leaving its density undimished and fully available for O-H...N hydrogen bonding and subsequent enol - keto tautomerization, hence thermochromism.

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