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Photochromism and thermochromism of solid *trans*-*N*,*N*′-bis-(salicylidene)-1,2-cyclohexanediamines and *trans*-*N*,*N*′-bis-(2-hydroxy-naphylidene)-1,2-cyclohexanediamine

Eugene Hadjoudis[a,1], Aliki Rontoyianni[b], K. Ambroziak[c],
Teresa Dziembowska[c], Irene M. Mavridis[a,*]

[a] *Institute of Physical Chemistry, National Center for Scientific Research "Demokritos", P.O. Box 60228, Aghia Paraskevi 15310, Greece*
[b] *Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, P.O. Box 64004, 157 10 Zografou-Athens, Greece*
[c] *Institute of Chemistry and Environmental Protection, Technical University of Szczecin, Al. Piastów 42, 71-065 Szczecin, Poland*

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Abstract

The photochromic and thermochromic properties of *trans*-*N*,*N*′-bis(salicylidene)-1,2-cyclohexanediamine (**1**), *trans*-*N*,*N*′-bis(3,5-dichloro-salicylidene)-1,2-cyclohexanediamine (**2**), *trans*-*N*,*N*′-bis(3,5-di-*t*-butyl-salicylidene)-1,2-cyclohexanediamine (**3**) and *trans*-*N*,*N*′-bis(2-hydroxy-naphylidene)-1,2-cyclohexanediamine (**4**) were investigated by UV and fluorescence spectroscopies in the crystalline state at various temperatures and the molecular structures of **2** and **4** were determined by single-crystal X-ray diffraction. The existence of the two Schiff base groups on a single molecule does not seem to differentiate the chromobehavior of the present compounds (except possibly for **3**) with respect to the usual Schiff bases of salicylaldehyde. It is suggested that for this class of compounds also, what determines the thermochromic behavior is the enhanced basicity of the nitrogen atom, due the absence of π,π- and *n*,π-conjugation with an aryl ring bound to it. The role of the crystal structure in this case is important only in so far as it affects the electron density on the nitrogen atom. Photochromism, however, is structure dependent and requires space for the generation of the photoproduct that involves *cis* to *trans* isomerization in the excited state.

Keywords: Photochromism; Thermochromism; Tautomerism; Anils; Structures

1. Introduction

Compounds presenting photochromism, a reversible color change brought about in at least one direction, by the action of electromagnetic radiation, attract considerable attention from various fields of chemistry, physics and material science as potential candidates for practical applications. Since long time, the Schiff bases of salicylaldehyde with aromatic amines (anils or *N*-salicylideneaniline derivatives) are recognized as such compounds, which undergo enol–keto tautomerism and present common features in their structures and reaction mechanisms [1]. The tautomerism involves proton transfer from the hydroxylic oxygen to the imino nitrogen atom that occurs intramolecularly via a six-membered ring (Scheme 1), with the keto species showing bathochromically-shifted spectra. However, this light induced tautomeric reaction does not always take place in the crystalline state, since the rules governing the photo-equilibrium are not determined only by purely chemical factors but depend on the crystal structure as well [2]. On heating, the anils that are not photochromic in the crystalline state develop a spectrum closely resembling the spectrum of the colored photochromic solid, thus they are thermochromic. In crystalline *N*-salicylideneanilines photochromism and thermochromism were found to be mutually exclusive properties. Structural studies have shown [1–3] that in thermochromic anils, the molecules are essentially planar exhibiting intermolecular $\pi\cdots\pi$ interactions ("closed structures") with short inter-planar distances (3.5 Å). In contrast, photochromic anils are not planar in the crystalline state, the aniline ring being rotated about the N–C bond by ∼50°, consequently, the molecular packing does not have the characteristic aryl-to-aryl close contacts of

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[*] Corresponding author. Tel.: +30-210-650-3793; fax: +30-210-651-1766.
E-mail address: mavridi@chem.demokritos.gr (I.M. Mavridis).
[1] Co-corresponding author.

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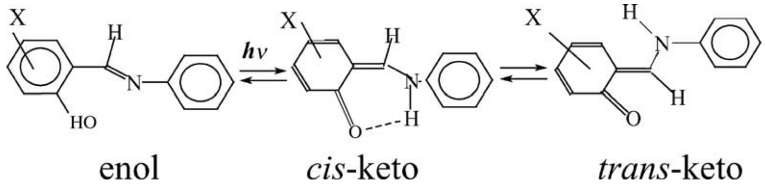
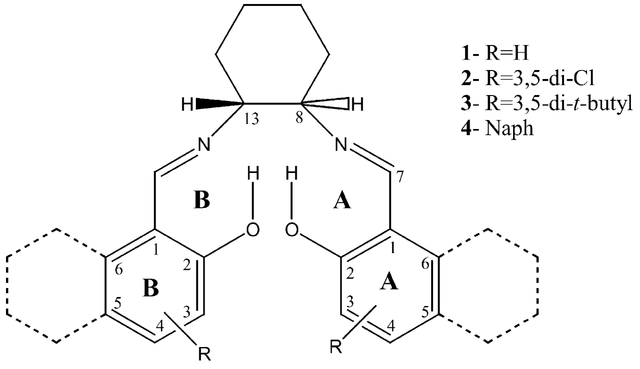


Scheme 1.

planar conjugated molecules, i.e. it has an "open structure" [4]. These results, together with fluorescence data led to the interpretation that thermochromism is due to the tautomeric equilibrium from the colorless enol to the *cis*-keto form in the ground-state, whereas photochromism is due to the transformation of the enol to the *trans*-keto form (via a *cis*–*trans* isomerization process) in the excited state, according to Scheme 1. Later on, it was shown that the close plane-to-plane packing, and hence molecular interactions in the solid state, is not a prerequisite of thermochromism, since non-planar Schiff bases, as *N*-salicylidene–benzylamines, where a spacer CH_2 group was placed between the aldimine and phenyl groups, exhibit thermochromism in addition to photochromism [2,5–8]. This has been attributed to the high electron density on the lone pair of the imino nitrogen, due to the disruption of conjugation with the phenyl ring of benzylamine.

Continuing our studies on the relation between the Schiff base geometry in the crystalline state and photochromism and/or thermochromism, we report presently on double Schiff bases (di-Schiff bases), in which the amine is the aliphatic *trans*-1,2-diaminocyclohexane, namely: *N*,*N*′-bis-(salicylidene)-1,2-cyclohexanediamine (**1**), *N*,*N*′-bis(3,5-di-chloro-salicylidene)-1,2-cyclohexanediamine (**2**), *N*,*N*′-bis-(3,5-di-*t*-butylsalicylidene)-1,2-cyclohexanediamine (**3**) and *N*,*N*′-bis(2-hydroxy-naphylidene)- 1,2 - cyclohexanediamine (**4**) (Scheme 2). According to the known cases, it is expected [6–8] that all compounds should exhibit thermochromism, irrespective of the molecular packing, whereas photochromism should depend on the crystal structure, i.e. on the ability of the independent moieties to perform the required conversion from *cis*- to *trans*-keto form (Scheme 1). The fact that the molecules are double Schiff bases was the initial motivation for the study, since the two active moieties may behave independently depending on their different crystalline environment and resulting in dual behavior from species such as enol–enol, enol–*cis*-keto (or *trans*-keto), *cis*-keto–*trans*-keto, etc. Comparison of the chromobehaviour of **1**–**4** is expected to shed more light on how the microenvironment in the crystal, affects photochromism and/or thermochromism.



Scheme 2.

2. Experimental

2.1. Preparation of compounds

Compounds **1**, **2** and **4** were prepared by condensation of the appropriate salicylaldehydes or 2-hydroxynaphthalene-1-carbaldehyde, respectively with racemic *trans*-1,2-cyclohexanediamine in ethanol, as described previously [9]. *N*,*N*′-bis(3,5-di-*t*-butyl-salicylidene)-1*R*,2*R*-(−)-1,2-cyclohexanediamine (**3**), was purchased from Strem Chemicals Inc. and used with no further treatment.

2.2. Thin films

The polycrystalline thin films of the compounds were obtained by slow cooling from the melt between two optical quartz plates under pressure. The quality of the films was examined under a polarizing microscope.

2.3. Instrumentation

The absorption and fluorescence spectra were obtained on a JASCO V-5600 spectrophotometer and a JASCO PTL-396S spectrofluorimeter, respectively. Polarized spectra were recorded using a Barr and Strout polarizer. Steady state photochemical experiments employed a 200 W high pressure Hg lamp with Corning glass filters. The IR spectra were taken in the form of KBr pellets with a Bruker Equinox 55/S FT-IR spectrometer.

2.4. X-ray diffraction

Single crystal X-ray diffraction data of racemic *trans*-*N*,*N*′-bis-(3,5-dichloro-salicylidene)-1,2-cyclohexanediamine ($C_{20}H_{18}O_2N_2Cl_4$) (**2**) and racemic *trans*-*N*,*N*′-bis(2-hydroxy-naphylidene)-1,2-cyclohexanediamine ($C_{28}H_{26}O_2N_2$)

Table 1
Crystal data and structure refinement for compounds **2** and **4**

	Compound **2**	Compound **4**
Empirical formula	$C_{20}H_{18}O_2N_2Cl_4$	$C_{28}H_{26}O_2N_2$
Formula weight	460.16	422.51
Crystal system, space group	Triclinic *P*-1	Monoclinic, *C*2/*c*
a (Å)	10.862(6)	20.44(3)
b (Å)	11.184(7)	9.532(19)
c (Å)	17.985(10)	22.83(4)
α (°)	89.841(16)	90.00(0)
β (°)	86.060(17)	91.06(4)
γ (°)	101.154(17)	90.00(0)
V (Å^3)	2138(2)	4449(14)
Z, calculated density (Mg m^{-3})	4, 1.429	8, 1.256
Absorption coefficient (mm^{-1})	5.186	0.627
F (0 0 0)	944	1776
Crystal size (mm)	0.5 × 0.35 × 0.25	0.5 × 0.125 × 0.125
2θ range for data collection (°)	5–117	8–117
No. of reflections collected/unique	5937/5937	3258/3162
Data/restraints/parameters	5937/0/649	3162/0/387
Goodness-of-fit on F^2	1.082	1.124
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0624$, $wR2 = 0.1599$	$R1 = 0.0584$, $wR2 = 0.1448$
R indices (all data)	$R1 = 0.0679$, $wR2 = 0.1679$	$R1 = 0.0630$, $wR2 = 0.1510$
Largest differences peak and hole (e Å^{-3})	0.619 and −0.489	0.322 and −0.451

(**4**) were collected at room temperature with Cu Kα radiation by the θ–2θ scanning method on a Syntex diffractometer equipped with Rigaku rotating anode and graphite monochromator. The data were corrected for Lorentz and polarization effects. X-ray data and refinement details are summarized in Table 1. The structures were solved by direct methods, and refined by full-matrix least squares based on F^2s with SHELXL [10]. Anisotropic refinement was applied to non-hydrogen atoms. H-atoms were found from difference Fourier maps. In compound **2**, both protons involved in the intramolecular H-bonds, are located unambiguously on the oxygen atoms (Table 2), whereas in **4** they are closer to the imine-N-atom (Table 2) but exhibit rather long N–H distances. Therefore, it was considered that the structure consists of a mixture of enol and keto tautomers and idealized H-atoms were placed on the O- and N-atoms, respectively. This model was refined accordingly and the refinement converged to keto/enol ratios of 72 and 48% for the two Schiff base moieties A and B of **4**.

3. Results and discussion

The atom numbering of the studied compounds **1**–**4** is depicted in Scheme 2. Selected bond lengths and angles are shown in Table 2.

3.1. Solid-state IR

In the IR spectra of the studied compounds **1**–**4** a very broad weak absorption in the range of 2250–3200 cm^{-1} is observed, characteristic of Schiff bases with a medium strength intramolecular hydrogen bond and large amplitude of the OH vibration or proton transfer equilibrium [9,11]. For compounds **1** and **3**, this absorption with maximum at about 2700 cm^{-1} is assigned to νOH stretching vibration. For compound **2**, the maximum is shifted toward 2600 cm^{-1}, according to the increasing strength of the OH $\cdots$ N hydrogen bond. For compound **4**, where movement of the proton towards the N atom is possible, the absorption observed at higher wave numbers was assigned to the OH and NH stretching vibrations. The coexistence of both enol and keto tautomers for this compound is confirmed by the comparison of the imine bond absorption region at ∼1630 cm^{-1}. Further evidence for the latter stems from the stretching vibrations of the skeleton NH–C=C–C=O at about 1535 and 1510 cm^{-1}, which are absent in the three other di-Schiff bases [11]. Fig. 1 shows the IR spectra of **1** (a) and **4** (b) for reasons of comparison.

3.2. Chromobehavior of the compounds

The screening for photochromic and thermochromic properties of polycrystalline powders of **1**–**4** showed that **1** exhibits both photochromism and thermochromism, **2** only thermochromism, **3** both photochromism and thermochromism and **4** thermochromism. These results are also confirmed by using thin polycrystalline films of the compounds as described below.

3.2.1. *N,N′-Bis-(salicylidene)-1,2-cyclohexanediamine (**1**)*

The light yellow color of a thin polycrystalline film of **1**, at room temperature changes to white at liquid nitrogen temperature. The color turns back to the original light yellow when the temperature is raised to room temperature indicating that crystalline **1** is thermochromic. On the other hand, the compound exhibits fluorescence. Thus, by irradiating thin films with ultraviolet light (365 nm) a weak yellow emission appears, which, at liquid nitrogen temperature turns to strong yellow-green. By irradiating the light yellow thin film with 365 nm light for 10 min at room temperature, the color changes to orange. When the light is switched off, the color turns back to light yellow, but the orange color remains for sufficient time for its spectrum to be recorded (Fig. 2). However, photochromism is not observed at liquid nitrogen temperature, where only a strong yellow-green fluorescence (max ∼510 nm) is observed. The latter is a mirror image of the long wavelength absorption band (max ∼430 nm) thus showing that it originates from this band. This is in agreement with the excitation spectrum, which reproduces the same absorption band. Fig. 2 shows the above behavior. Therefore, **1** is both photochromic and thermochromic and the photoproduct is relatively stable at room temperature, in contrast to *N*-salicylideneanilines, for which lower

Table 2
Some characteristic distances and angles

	1 [12]	**2**		**3** [19]	**4**
		I	II		
Bond distances					
C1A–C2A	1.416	1.416	1.404	1.414	1.413
C1B–C2B	1.406	1.403	1.401	1.403	1.406
C1A–C6A	1.393	1.392	1.389	1.404	1.449
C1B–C6B	1.391	1.392	1.393	1.416	1.442
C1A–C7A	1.449	1.448	1.465	1.462	1.424
C1B–C7B	1.452	1.453	1.458	1.452	1.433
C2A–C3A	1.385	1.391	1.389	1.401	1.426
C2B–C3B	1.382	1.386	1.389	1.410	1.428
C3A–C4A	1.371	1.367	1.373	1.406	1.346
C3B–C4B	1.371	1.378	1.372	1.416	1.339
C4A–C5A	1.374	1.383	1.384	1.405	1.421
C4B–C5B	1.380	1.372	1.378	1.404	1.421
C5A–C6A	1.378	1.367	1.371	1.373	1.419
C5B–C6B	1.387	1.371	1.378	1.374	1.422
OA–C2A	1.347	1.331	1.341	1.364	1.307
OB–C2B	1.348	1.334	1.344	1.362	1.325
OA–H(OH)	1.077	0.828	0.695	0.991	1.52 (0.82)[a]
OB–H(OH)	1.110	0.676	0.869	1.037	1.70 (0.82)[a]
NA–C7A	1.275	1.279	1.266	1.270	1.290
NB–C7B	1.271	1.273	1.270	1.270	1.290
NA–C8	1.462	1.453	1.467	1.476	1.464
NB–C13	1.470	1.456	1.468	1.484	1.457
NA–H(OH)	1.658	1.855	1.979	1.675	(2.368)[a]
NB–H(OH)	1.635	1.970	1.851	1.645	(1.835)[a]
NA–H(NA)					1.184 (0.86)[a]
NB–H(NB)					1.068 (0.86)[a]
OA···NA	2.602	2.565	2.589	2.603	2.541
OB···NB	2.604	2.570	2.595	2.603	2.555
Bond angles					
C2A–C1A–C7A	121.2	120.1	120.3	121.1	118.8
C2B–C1B–C7B	121.4	120.1	120.9	121.9	119.0
C6A–C1A–C7A	120.7	120.1	119.5	119.3	121.4
C6B–C1B–C7B	120.3	120.4	119.1	118.3	121.3
C6A–C1A–C2A	117.9	119.7	120.2	119.5	119.6
C6B–C1B–C2B	118.4	119.5	119.9	119.9	119.6
OA–C2A–C1A	120.1	121.4	122.1	119.4	122.1
OB–C2B–C1B	120.9	122.4	121.5	119.4	122.0
OA–C2A–C3A	120.1	121.0	119.9	120.1	118.6
OB–C2B–C3B	119.0	119.6	119.7	120.1	118.3
NA–C7A–C1A	123.2	122.1	122.0	123.8	123.1
NB–C7B–C1B	122.6	121.7	122.1	123.4	123.6
C7A–NA–C8	118.7	119.3	119.0	118.6	121.6

[a] Hydrogen atoms placed at calculated positions.

temperatures are usually required to stabilize the photoproduct, i.e. −131 °C for 2-chloro-*N*-salicylideneaniline [1].

The structure of **1** in the crystalline state shows that the two aromatic rings form a dihedral angle of 56.5° and the compound is found in the enol form [12]. Its crystal packing is shown in Fig. 3. Molecular layers parallel to the *ac* plane are stacked along the *b*-axis. No π–π interactions are observed in the structure ($\pi \cdots \pi$ distances are more than 4.5 Å along the *z*-direction and more than 9.5 Å along the *x*-direction). However, the salicylaldimine moieties exhibit some close contacts (C···C distances 3.3–4.0 Å) with adjacent molecules. The closest distances correspond to C–H···O interactions involving the enolic oxygen atoms: $\mathrm{OA(I)} \cdots \mathrm{C3B(I')} = 3.32$ Å ($\mathrm{OA} \cdots \mathrm{HC3B} = 2.67$ Å) and $\mathrm{OB(I)} \cdots \mathrm{C7A(II)} = 3.42$ Å ($\mathrm{OB(I)} \cdots \mathrm{HC7A(II)} = 2.90$ Å). Molecular graphics program "O" [13] was used to see if it is possible to transform the *cis*-keto to the *trans*-keto form of the molecule in order to generate the photoproduct. Thus, a rotation of 180° around the C1–C7 bond (Scheme 2) was performed, during which the intermolecular distances of the salicylaldimine group atoms from their neighbor molecules were continuously measured. The rotation showed that except for one intermolecular C···C distance that reached the value of 2.7 Å, the rest remained

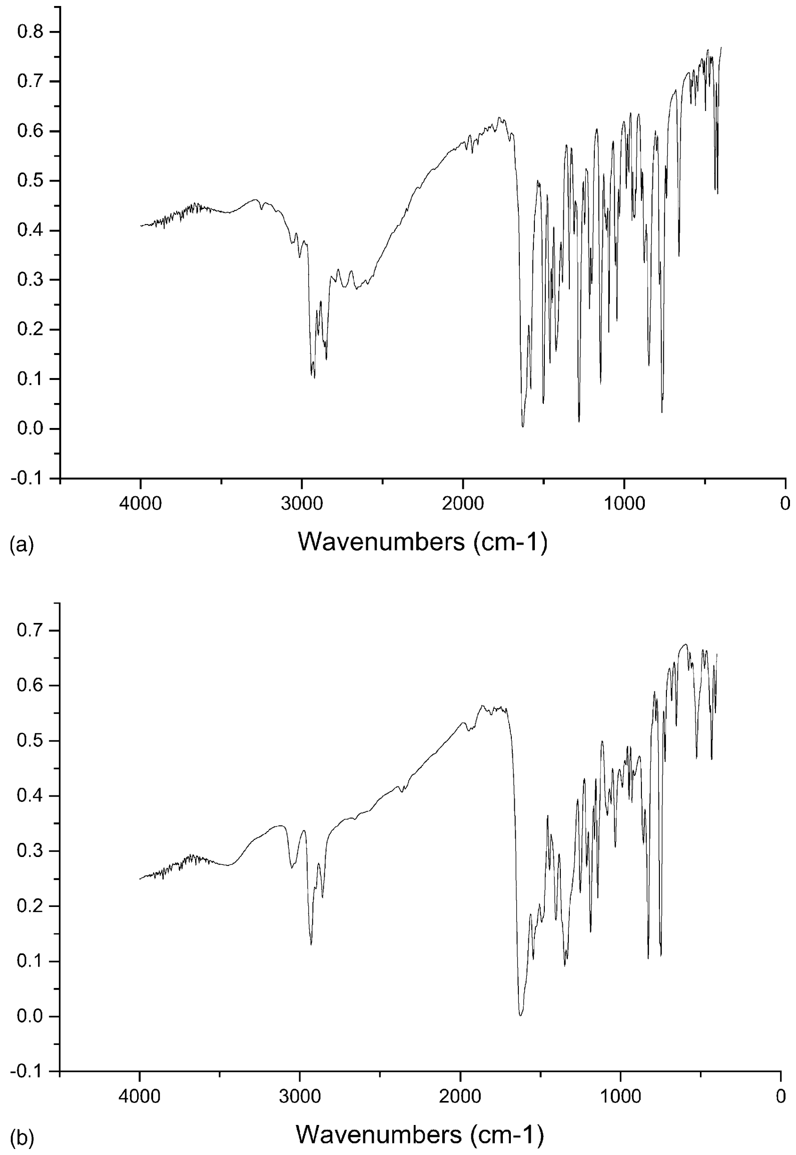


Fig. 1. FTIR spectra in KBr pellets of (a) **1** and (b) **4**.

within acceptable limits. This indicates that such a rotation of the phenyl ring in the crystal is not prohibitive. Moreover, if the mechanism for the generation of the photoproduct is not a rotation but a "pedal motion" of the imine bridge, as proposed recently [14], much less movement of the moieties that flank the bridge is required, therefore, such a motion is possible to occur in the crystal lattice of **1**.

3.2.2. *N,N′-Bis-(3,5-dichloro-salicylidene)-1,2-cyclohexanediamine (**2**)*

The yellow color of a thin polycrystalline film of **2** at room temperature changes to white at liquid nitrogen temperature. The color turns back to the original yellow when the temperature is raised back to room temperature. By heating the film above room temperature (below the mp) the color changes to orange. The color is restored quickly to its original yellow when the material is left to cool down to room temperature. UV-irradiation (365 nm) of the polycrystalline thin film at room or liquid nitrogen temperature does not result in any coloration of the compound but only to the generation of a yellow or strongly yellow-green fluorescence, respectively. Thus, crystalline **2** is a rather strongly thermochromic compound. Fig. 4 shows the above results. In this case also the fluorescence (max ∼530 nm) is a mirror image of the long wavelength absorption band (max ∼440 nm) showing that it originates from this band. This is in agreement with its excitation spectrum that reproduces the same absorption band as shown in Fig. 5 for emission of light at 525 nm. It should be noted, at this point that thermodynamic studies of the enol to *ci*s-keto equilibrium is unattainable in thermochromic compounds, since the population of the *cis*-keto species is very small, even at elevated temperature. Thus,

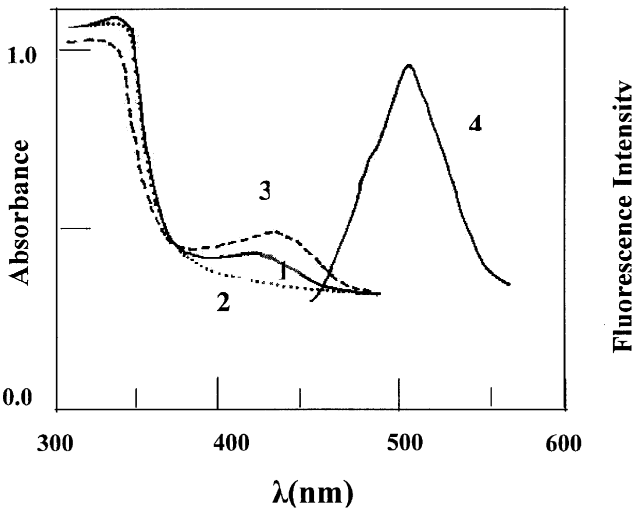


Fig. 2. Absorption and fluorescence spectra of a thin polycrystalline film of **1**: (1) at RT; (2) at liquid nitrogen temperature; (3) after irradiation with 365 nm light; (4) fluorescence at RT with exciting light 365 nm.

the thermal population of the *cis*-keto form of the strong thermochromic *N*-(5-chloro-salicylidene)aniline is approximately 5% at room temperature, whereas at liquid nitrogen temperature the conversion ratio is less than 10^{-4} [4].

Compound **2** crystallizes with two crystallographically independent molecules I and II in the asymmetric unit, which have similar bond distances and angles (Table 2). Table 2 also indicates that the enol tautomer is favored (as the bond distances C2–O1, C1–C7, C7–N, C1–C6, C2–C3 indicate). The salicylaldimine parts of each molecule show similar planarity. Dihedral angles between the aromatic ring and the plane through atoms C1, C2, C7, N, O are 11.21 and 3.81° for moieties A and B, respectively, of molecule I. The corresponding values for molecule II are 13.5 and 4.19°. The molecules are Y-shaped and the two salisylaldimine groups form dihedral angle of 52.3° in I and 53.7° in II. Di-Schiff base **2** has a very dense packing. Both salicylaldimino moieties A and B of each molecule exhibit $\pi \cdots \pi$ interactions (C···C distance = 3.5–3.6 Å) with corresponding salicylaldimino moieties of adjacent molecules on either side of it (Fig. 6). Thus, infinite lines of interacting A···A, B···B, A···A, etc. groups are formed, which develop into layers perpendicular to the *c*-axis. The overall packing (Fig. 7) consists of such layers of segregated molecules I or II alternating. The structure is very dense and does not permit the

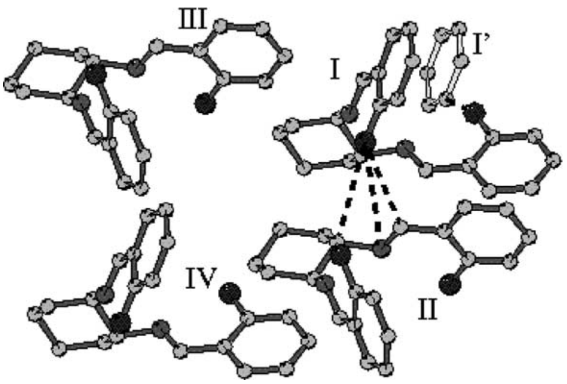


Fig. 3. Molecular packing of **1** perpendicular to *c*-axis. I–IV crystallographically independent molecules. I′ is the phenyl ring B of a molecule equivalent to I by translation along the *c*-axis.

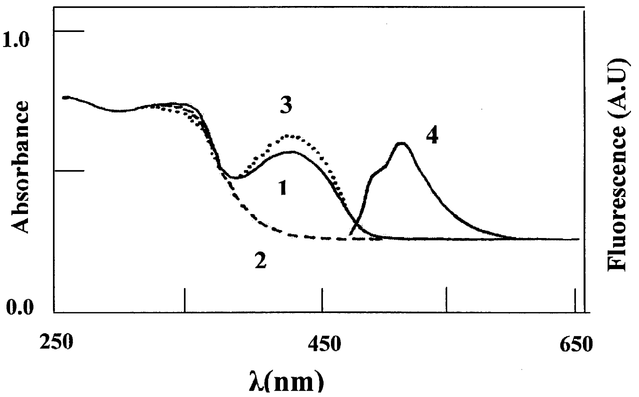


Fig. 4. Absorption and fluorescence spectra of a thin polycrystalline film of **2**: (1) at RT; (2) at liquid nitrogen *T*; (3) 20 °C above RT; (4) fluorescence at RT with exciting light 365 nm.

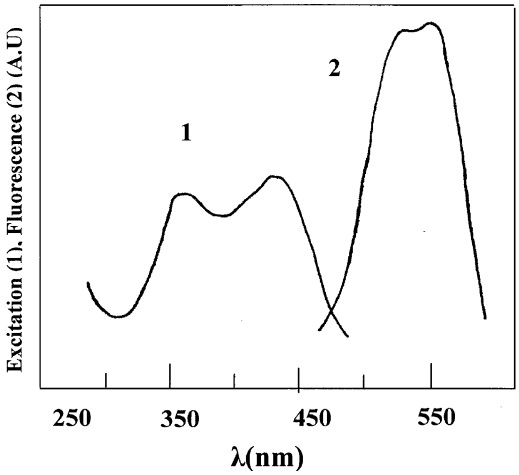


Fig. 5. Excitation (1) and fluorescence (2) spectra of a thin polycrystalline film of **2**. Observation at 525 nm for emission and exciting light 365 nm.

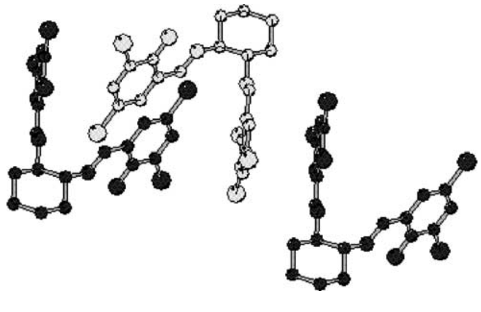


Fig. 6. Both salicylaldimino moieties A and B of each molecule (middle) exhibit $\pi \cdots \pi$ interactions with adjacent molecules.

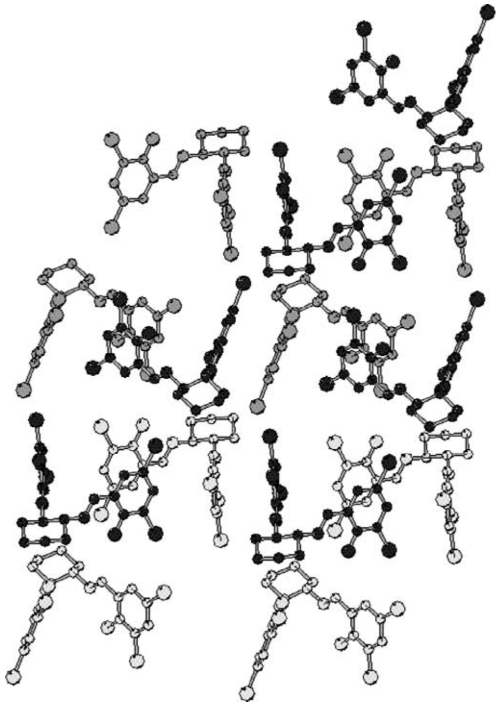


Fig. 7. Molecular packing of **2** perpendicular to *a*-axis.

needed movements for the *cis*-keto to *trans*-keto isomerization, which is consistent with the fact that the compound does not exhibit photochromism.

*3.2.3. N,N′-Bis-(3,5-di-t-butyl-salicylidene)-1,2-cyclohexanediamine (**3**)*

The light yellow color of a thin polycrystalline film of **3** at room temperature changes to white at liquid nitrogen temperature (Fig. 8). The color turns back to its original light yellow when the temperature is raised back to room temperature, indicating that the compound is thermochromic. At room temperature and under UV-irradiation (365 nm) the color of the compound changes to orange, whereas it turns back to its original color when the light is switched off, thus indicating that **3** is also photochromic. Irradiation of the film at liquid nitrogen temperature does not bring any color change but only appearance of yellow-green fluorescence. However, upon irradiation at a higher temperature (193 K) the color changes to orange thus, it seems that a "working range" for photochromism exists as observed in *N*-salicylideneaniline [15]. The fluorescence of **3** is structured and, unlike in compounds **1**, **2** and **4**, it extends from about 400 to 600 nm divided into two well-separated regions 400–475 and 475–600 nm. Fig. 8 shows the above results. The photoproduct of di-Schiff base **3** presents higher stability at room temperature than **1**, most probably because of the bulky *tert*-butyl substituents, therefore, its spectroscopic observation is easier [16]. Following the drop of the absorption intensity at the maximum of the photochromic band (∼450 nm), a half-life of 4 min is measured at 25 °C. A characteristic property of **3** is the complete separation of the *cis*-keto form, with maximum at about 350 nm, from the *trans*-keto form with maximum at about 450 nm, in contrast to **1** (Fig. 2), in which the two bands have maxima at nearly the same wavelength, as it is also the case in the majority of anils (i.e. *N*-salicylidene–benzylamines) [8,17].

Another important property of **3** is that the emission spectrum, shown in Fig. 8, is greatly affected by the exciting wavelength, indicating that there is more than one emitting species present and this explains the observed extended spectrum. Fig. 9 shows this effect. In order to elucidate the origin of this fluorescence (Fig. 8) the excitation spectra (Fig. 10) were examined. These indicate that the fluorescence originates from excitation spectra with maxima at about 370 and 460 nm. The curves are not corrected for incident-light intensity and thus exaggerate the yield, especially in the long wavelength band of the spectrum [18]. The first emission band (max ∼425 nm) corresponds to the end outset of the absorption band (shown in Fig. 8) of the *cis*-keto form (∼375 nm) and the second (max ∼550 nm) most probably to

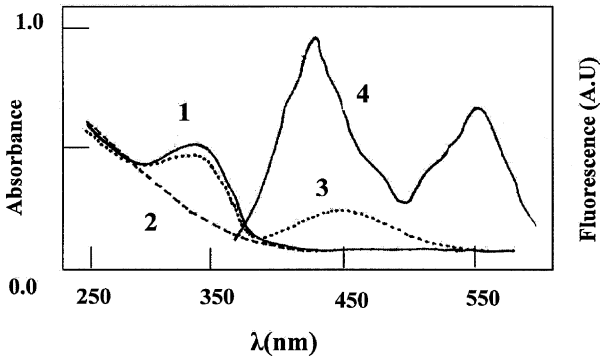


Fig. 8. Absorption and fluorescence spectra of a thin polycrystalline film of **3**: (1) at RT; (2) at liquid nitrogen *T*; (3) after irradiation with 365 nm light; (4) fluorescence at RT with exciting light 313 nm.

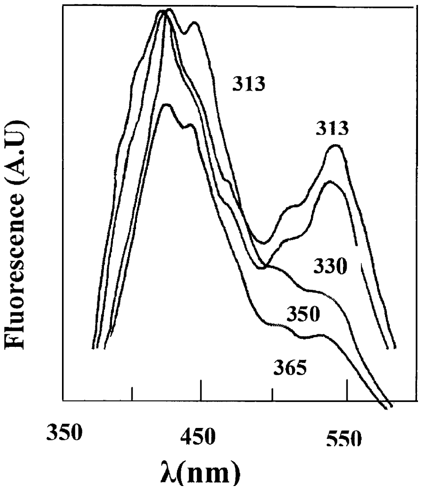


Fig. 9. Variation in the shape of emission spectrum of a thin polycrystalline film of **3** with the wavelength of the exciting radiation.

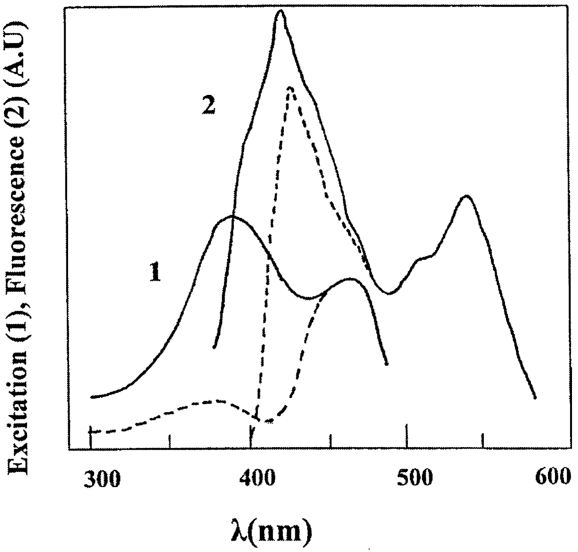


Fig. 10. Excitation and fluorescence spectra of a thin polycrystalline film of **3**. Excitation spectrum (1) recorded with observation at 512 nm (or 550 nm); fluorescence emission spectrum (2) recorded with excitation at 330 nm. The dotted lines depict the corresponding spectra with plane-polarized light.

a second *cis*-keto form, the absorption spectrum of which is difficult to be located convincingly with the present available data. Therefore, there could be two different *cis*-keto species fluorescing, i.e. coming from the two Schiff base moieties of **3**, which are nearly perpendicular to each other according to the crystal structure [19]. Additional evidence for the suggested assignment stems from the observation that plane polarized light affects (diminishes) only the excitation band with max ∼370 nm and the corresponding first part of the fluorescence (shown in Fig. 10). The affected curves of excitation and fluorescence are in a mirror image relation. An alternative explanation of the band with max ∼550 nm in Figs. 8–10 could be that the fluorescence originates from a *trans*-keto photochromic species with absorption maximum at 460 nm. However, fluorescence from the lowest $n,\pi*$ singlets of ketones is unusual, i.e. the one reported for the *N*-salicylideneaniline in stilbene and dibenzyl host crystals is exhibited at very low temperature (10 K) [20]. Whether the presence of the bulky *t*-butyl groups acting as “spacers” between molecules in the crystal might produce a similar behavior remains to be examined.

The molecular packing of di-Schiff base **3** [19], Fig. 11, consists of parallel molecules forming layers parallel to the *ac* planes, which stack in a head-to-head fashion along the *b*-axis. The closest intermolecular contact is observed between a hydroxyl O-atom and an adjacent cyclohexyl C-atom (O ··· C11 = 3.63 Å), all the rest intermolecular distances being longer than 3.8 Å. This is most probably due to the *t*-butyl groups that keep the molecules at a distance and permit amply the *cis*- to *trans*-keto isomerization, and therefore, the appearance of photochromism. Indeed, rotation of 180° around the C1–C7 bond performed with program “O” [13], as in the case of **1**, showed that the rotation is not hindered. Thermochromism on the other hand, is secured because of the enhanced basicity of the nitrogen atom as explained before.

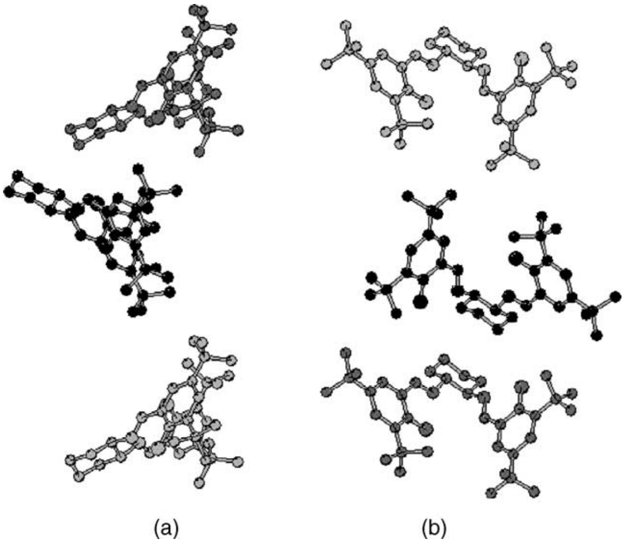


Fig. 11. Molecular packing along *b*-axis of **3** (a) perpendicular to *c*-axis; (b) perpendicular to *a*-axis.

3.2.4. *N,N′-Bis-(2-hydroxy-naphthylidene)-1,2-cyclohexanediamine (**4**)*

The deep yellow color of a thin polycrystalline film of **4** at room temperature changes to yellow at liquid nitrogen temperature. The color turns back to its original deep yellow color when the temperature is raised to room temperature again. By heating up the film of **4** from room temperature to mp, no change of color is observed. Under UV-irradiation at room temperature or at liquid nitrogen temperature, **4** shows yellow or yellow-green fluorescence, respectively, but no color change. The fluorescence is a mirror image of the long wavelength absorption band as in the case of the thermochromic **2**. Fig. 12 shows the behav-

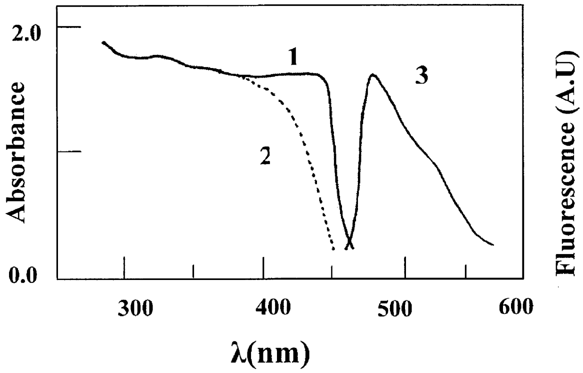


Fig. 12. Absorption and fluorescence spectra of a thin polycrystalline film of **4**: (1) at RT; (2) at liquid nitrogen *T*; (3) fluorescence at RT with exciting light 365 nm.

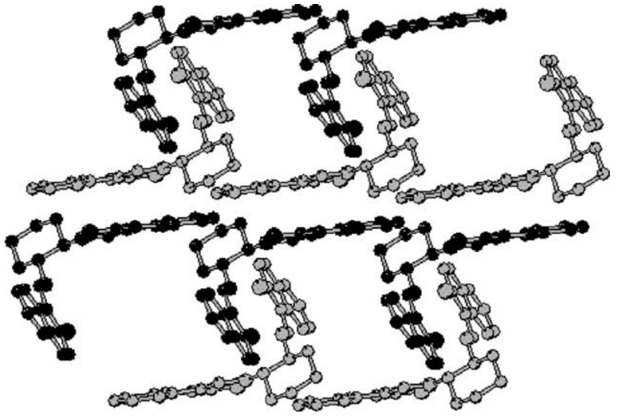


Fig. 13. Molecular packing of **3** perpendicular to the *b*–*c* direction.

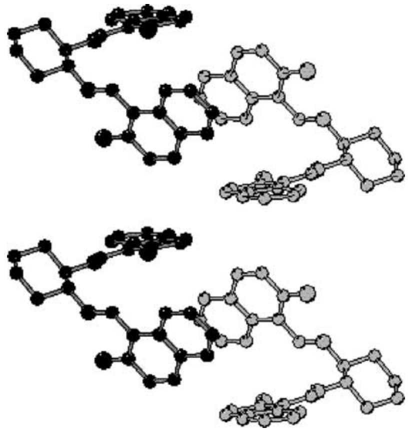


Fig. 14. Two pairs of Fig. 13 belonging to adjacent layers viewed from a direction perpendicular to *b*-axis.

ior of **4** described above, which is characterized as weakly thermochromic.

The molecular structure of **4**, as determined by single crystal X-ray diffraction, reveals that the molecule exists as a mixture of keto and enol forms. It has been mentioned in the experimental part that the proton atoms involved in the intramolecular H-bonds are located between the oxygen and nitrogen atoms (Table 2). This is an indication that both tautomers, ketoamine and enolimine, exist simultaneously in the crystalline state. By assuming (see Section 2.4) a model of such a mixture during the refinement process (H-atoms were placed at ideal positions with respect to O and N atoms and the occupancies of the resulting keto and enol forms were refined) ratios of keto/enol tautomers have been determined. Thus, the naphthaldimine moiety A has a keto/enol ratio of 72% and the corresponding B 48%. This is exemplified by the C(2)–O(1) distances, 1.307 and 1.325 Å for A and B, respectively, which compare to the ketoamine (1.277(2)–1.302(3) Å) and the enolimine (1.320(3)–1.323(3) Å) C–O bond distance of naphthaldimine derivatives, respectively [21]. The above accompanied by the lengthening of bonds, C1–C6, C2–C3 and C7–N as well as the shortening of bonds C3–C4 and C1–C7 suggest π-electron delocalization due to significant quinoid character of the naphthalene skeleton of both A and B moieties. Since there is no apparent reason for the differentiation of the two Schiff base moieties A and B as to their keto/enol ratio, it seems that the energy difference between the two forms is small and the equilibrium is affected by very subtle differences in their environment. The dihedral angle between the naphthalidene groups of the compound is 67.4°.

The packing of di-Schiff base **4** is almost as dense as that of **2**. It consists of layers almost parallel to the *bc* plane stacked along the *a*-axis (Fig. 13). Each layer is formed by antiparallel pairs of molecules interacting in a $\pi\cdots\pi$ fashion (distance 3.46 Å) via one of their naphthyl groups. The second naphthyl group of each molecule in the pair, forming the top and bottom of the layers, do not show $\pi\cdots\pi$ interactions with the corresponding naphthyl groups of adjacent layers but they exhibit several close contacts with them (C · · · C distances 3.42–3.98 Å) (Fig. 14).

4. Conclusions

All crystalline compounds **1**–**4** investigated exhibit thermochromism like the other Schiff bases of aliphatic amines [22], whereas two of them, **1** and **3**, exhibit additional photochromism. The weak thermochromism of di-Schiff base **4** presents the characteristics of the Schiff bases of 2-hydroxy naphthaldehyde that absorb strongly in the 400–500 nm range at room temperature but they are little affected by cooling [23]. The absorption maxima of the enol tautomers for all compounds are in the range 330–360 nm. Absorption maxima of the *cis*-keto or *trans*-keto of the di-Schiff bases **1**, **2** and **4** (420–470 nm) approximately coincide. Only in **3** the *cis*-keto absorption is completely separated from that of *trans*-keto. This difference, along with the observation that the emission spectrum of **3** is divided into two well-separated regions, may be attributed to the bulky *t*-butyl groups that act as “spacers” between molecules in the crystal. The latter emission might also be the only example among the four compounds, where the two salicylaldimine *cis*-keto forms show different behaviour i.e. different fluorescent maxima originating from the two groups at almost right angles to each other. In **1**, **2** and **4**, although the two active moieties are found in different environment in the crystal (especially **1** and **4**), the phenomenon of two well-separated fluorescent bands is not observed.

The crystal structures indicate that compounds **1**–**3** are in the enol form in the solid state, whereas in **4**, enol and keto forms coexist. This is in accordance with the photochemical results. The absorption spectra of compounds **1**–**3** (Figs. 2, 4, 8) indicate that these exist primarily in the enol form (the existence of a slight percentage of the *cis*-keto tautomer suggested by the absorption spectra as, i.e. ∼5% in the case of *N*-(5-chloro-salicylidene)aniline [4], cannot be detected by the X-ray experiment and cannot be ruled out). In contrast, **4** is present as an equilibrium mixture of tautomers with well-developed long wavelength absorption bands (Fig. 12). The latter is in agreement with the infrared results.

The appearance of thermochromism in this class of compounds as in other Schiff bases of aliphatic amines, supports the hypothesis that this property is due to enhanced basicity of the nitrogen atom of the aldimine bridge, because of the absence of π–π and n–π conjugation with an aromatic ring next to it, as it has been suggested before [2,22]. The crystal structure does not affect the thermochromic behaviour of the compounds. In contrast, crystal packing plays a crucial role in photochromism. The combination of dense crystal packing of di-anils **2** and **4** due to numerous $\pi \cdots \pi$ associations between the aromatic moieties and their lack of photochromism is in accordance with the hypothesis that generation of the photoproduct (*cis*-keto to *trans*-keto transformation) requires space and this is prohibited by the crystal lattice of **2** and **4**. Even if the mechanism of the photoproduct generation does not involves rotation of the salicylidene ring, as suggested by the majority of authors [16,24–27] but by a "pedal motion" of the bridge, as it has been proved recently [14] for *N*-(3,5-di-*tert*-butyl-salicylidene)-3-nitroaniline, the required concerted movements for this motion also would be impossible in the specific lattices.

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