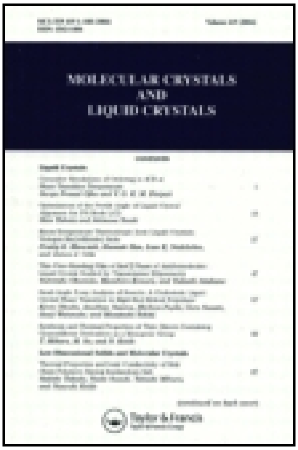

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Thermochromism of N-Triphenylmethylsalicylideneimine Activity of the Trans-Open Enol Conformer at Low Temperature

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Thermochromism of *N*-Triphenylmethylsalicylideneimine Activity of the Trans-Open Enol Conformer at Low Temperature

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N-triphenylmethylsalicylideneimine (MS1) represents a reversible thermal and photo-coloration system. The initial stage of the system studied was defined by means of X-ray structure analysis. Crystal structures were done at 295 and 230 K, taking into account the results of differential scanning calorimetry; basing on the DSC measurements, a pseudo-first order phase transition at 241 K was identified. According to the analysis of the luminescence spectra of MS1, low temperature favors a benzenoid-type trans-enol open form of the molecule under study. However, after UV excitation, the photochemical reaction (proton transfer and/or photoisomerization) generates the quinoid form. So, thermochromy has been interpreted as due to geometry changes of a chelate ring, and creating an open enol molecular form rather than a shift of the tautomeric equilibrium benzenoid-to-quinoid form. Below 240 K, the light-induced generation of unstable photochromic species is manifested as the sample color change (colorless-to-orange). That newly created species is of a trans-keto-type isomer of MS1 molecule with breaking hydrogen bond, and the open trans-enol form existing in the ground state is a source of that orange species.

Keywords: *N*-triphenylmethylsalicylideneimine; phase transition; photochromism; photoluminescence; thermochromism

1. INTRODUCTION

N-triphenylmethylsalicylideneimine (MS1) is closely related to *N*-salicylidene methylamine, a model Schiff base, the simplest

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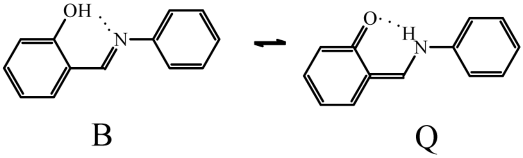
molecule of that family possessing a hydrogen OH…N bridge. The reversible solid-state coloration of that type system was first observed by Senier and his coworkers [1] and widely discussed by Schmidt and others [2]. The photo- and thermochromic behaviors of Schiff bases have been the subject of immense interest for more than four decades [3–5]. A variety of hypotheses were put forward to account for the reaction, because the photocoloration could be produced in solid state, as well as in rigid glasses at spectroscopic dilution [6,7]. However, the explanation based on intermolecular effects can be ruled out. The application of flash techniques has permitted the analysis of similar but transient phenomena in the fluid medium [8]. The femtosecond study of the dynamics of the excited state, proton transfer, and relaxation processes was also done [9]. The interesting theoretical approach how the photochromic transient is created was done by Zgierski et al. [10]. Generally, a much more attention was focused on the photochromism of Schiff bases than on the thermochromism. According to Schmidt's results of anils, thermochromy has been interpreted as due to a shift of the tautomeric equilibrium (benzenoid-quinoid), as is presented in the scheme below:



However, the results of our low-temperature photoluminescence study of MS1 in the frozen n-alkane matrix leads to the claim that there exists an open form (rotamer) of the molecule, already in the ground state. This is crucial for the explanation of deactivation channels of the original form in the excited state, particularly in the rigid matrix [11]. This is why we focused once again the attention on the temperature modification of the structure and photoactivity of this compound.

In the molecular system under study, three phenyl rings substitute hydrogen atoms of methyl group. The general molecular view of MS1 according to the scheme R1–C=N–C–R2 gives opportunity to distinguish three main units: phenolic (R1 = C_6H_4–OH), flexible central (–C=N–C–), and bulky one (R2 = –C(Ph)$_3$). Each unit participates in a different manner in the photo-induced rearrangement. The phenolic unit with the –OH group is crucial for the photochemical transformation, especially in the intramolecular proton transfer reaction in the excited state. The central –C=N–C– flexible fragment governs conformational changes in the ground as well as in excited electronic states. Moreover, in the crystal lattice, its own activity seems to be also important. A spatial bulky substituent, close to the nitrogen atom, acts as a moderator of molecular flexibility that balances the changes in temperature and energy excitation.

That new fashion makes completely different spectral characteristics of MS1 in relation to the model Schiff base. The molecule under study exhibits specific solvatochromy. Moreover, MS1 in polar and non-polar solvents, similarly to deep-yellow crystals of that compound, exhibits strong luminescence at ambient as well at low temperatures [12]. Temperature is an important factor which modifies the photochromic behavior and promotes the manifestation of thermochromism [13]. Photocoloration at low temperature is a reversible reaction.

Basing on the results of photoluminescence spectra at an ambient and low temperatures supported by infrared spectra, calorimetric measurements, and X-ray structural analysis presented here, we have postulated the following: 1 – Thermochromism is due to the geometry change of a chelate ring, which causes the creation of an open trans-enol form in the low-temperature range. A thermally driven transformation of the type ‘benzenoid-quinoid form’ of MS1 is less probable because of the generation of OH rotamer form at low temperatures; 2° – Temperature limit for that process correlates well with the phase transition temperature; 3° – Photocolored (orange) unstable species, which is created at low temperatures only, is a trans-keto isomer, as was proposed for anils. The trans-enol open form existing in the ground state is the source of that orange individuality. The barrier of the fading reaction cannot be interpreted as a simple one-step keto-enol-type isomerization process.

2. RESULTS AND DISCUSSION

The IR Spectrum

MS1 molecule (Figure 1) belongs to the intramolecular hydrogen bonded system with OH…N hydrogen bridge. The high-frequency

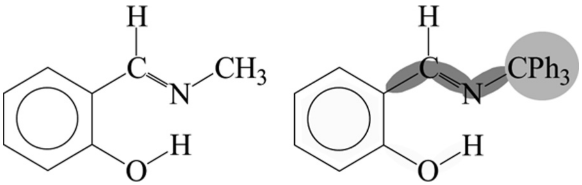


FIGURE 1 *N*-salicylidene methylamine, SmA and *N*-triphenylmethylsalicylideneimine, MS1.

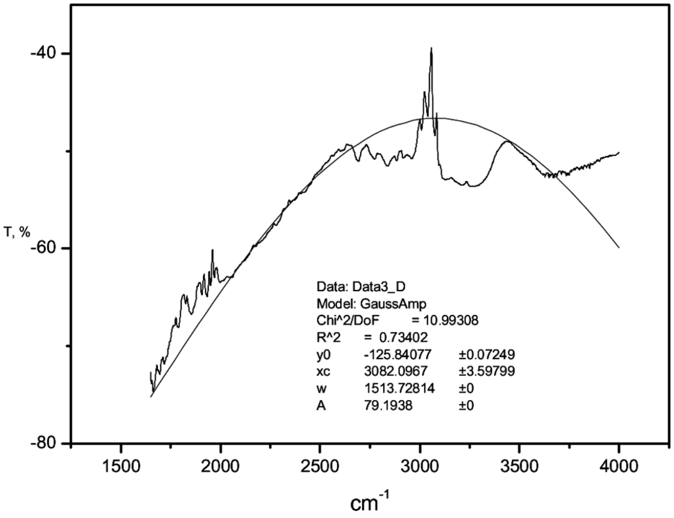


FIGURE 2 High frequency ranges of the IR spectrum of MS1 and a KBr pellet.

(4000-1500 cm^{-1}) range of the spectrum is shown in Figure 2. The important feature of the infrared spectrum is the absence of the band corresponding to the free OH stretching vibration expected over 3600 cm^{-1} (Fig. 2). Instead, the broad OH band with maximum ca. 3100 cm^{-1} related to the OH…N bond is visible. This proves that the OH group in the solid state is totally engaged in the intramolecular hydrogen bond, which is exactly the same as observed in the simplest Schiff base with intramolecular hydrogen bond [14]. The hermetic nature of that OH … N intramolecular hydrogen bond was confirmed theoretically [12].

The Differential Scanning Calorimetry

In this section, we present the existence of a phase transition of MS1 which was performed by the DSC technique in the temperature range 77–470 K. The results of DSC measurements are presented in Figure 3. As the insert, the thermogram shows the enlarged endothermic peak about 241 K of the lambda-type, with the enthalpy $\Delta H = 0.35\,J/g$. The endothermic peak effectively corresponds to a drop of the color (yellow) intensity of the crystal observed by using the microscopic technique. When the temperature increases, the colorless sample recovers its yellow color again with the 1.5 K temperature hysteresis. The melting point is well defined at $T = 467.1\,K$ with $\Delta H = 100.0\,J/g$.

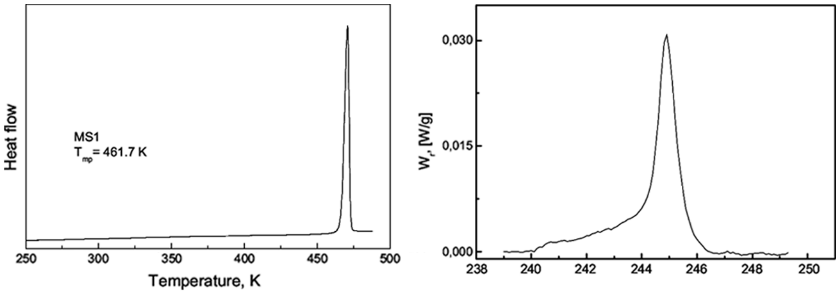


FIGURE 3 DSC runs of MS1 with heating speed 1 K/min. The melting point (on the left) and the lambda-type plot of phase transition (on the left) are shown.

The X-ray Data

Taking into account the results of differential scanning calorimetry, the crystal structure was done at 295 and 230 K. A drawing of the molecular structure of MS1 with the atomic and ring description scheme as well as the packing diagram are shown in Figure 4a and 4b. The inequality of the two C−C−O angles as well as a shortening of the C−O bond length of the frame of a phenolic ring is in accordance to the proper values specified for *ortho*-substituted phenols with intramolecular hydrogen bond [15]. The exocyclic C6–C7 bond distance compares well with the values reported for the corresponding bond in salicyl acid [16]. However, it is shorter than that fixed for thermochromic *N*-5-chloro-salicylideneaniline [17]. In contrast to the last mentioned compound and salicylaldehyde azine [18] or *ortho*-di-substituted aromatic compounds [19], the values of valence and exocyclic

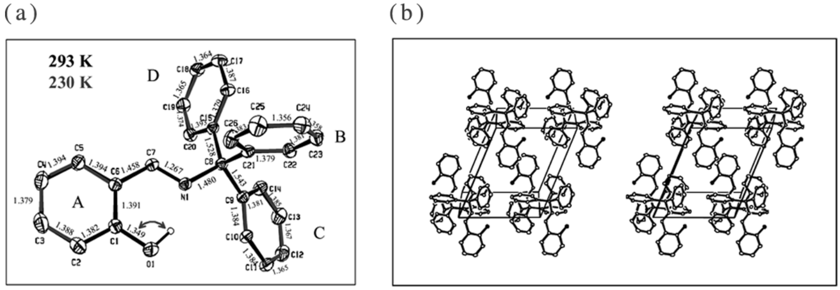


FIGURE 4 A-ORTEPII drawing of MS1 ($C_{26}H_{21}NO$, MS1). Displacement ellipsoids are drawn at the 20% probability level; H atoms were omitted for clarity. Red colored line points out the bond and angle changes at 230 K. B-Packing diagram (stereoview) of MS1; as above H atoms are also omitted.

angles are changed insufficiently. The C7=N bond length is in an excellent agreement with the value given by Levine [20] for the pure carbon–nitrogen double bond. Intramolecular interatomic distances in the hydrogen bridge formed at the central molecular part are $r(\mathrm{O}\ldots\mathrm{N}) = 2.574(2)$ Å, $r(\mathrm{OH}\ldots\mathrm{N}) = 1.71(4)$ Å; and the $\angle\mathrm{C{-}O{-}H}$ angle is equal to 105(2)°. At 230 K, these values are equal 2.576(2) Å, 1.70(2) Å, and 104(1)°, respectively. The interatomic distances in the hydrogen bridge strongly suggest that the intramolecular H-bonded form dominates in the crystal. Its geometry indicates a relatively strong character of the H-bond. The phenolic fragment together with the six-membered chelate ring is coplanar. The above-presented data enhance the idea of molecular conformation changes essential for the photochromic behavior discussed in the frame of the proton transfer reaction.

Other main X-ray results are summarized as follows. The inductive effect of bulky –C(Ph)$_3$ substituent is an origin of the distinct elongation of the N1−C8 bond length with respect to the same bond length of N-5-chlorosanicylidene-aniline molecule [17]. The dihedral angle between the plane of the phenolic fragment of MS1 and the phenyl rings of the spatial –C(Ph)$_3$ moiety are equal to 84.0(2)°, 39.9(2)°, and 68.5(2)° for $\angle AB$, $\angle AC$, and $\angle AD$, respectively. After decreasing the temperature, new angle values were specified as equal to 83.77(5)°, 40.06(8)°, and 68.05(6)°, respectively. The intermolecular H-bond was excluded by the fact that the interplanar distance equals 6 Å. The arrangement of MS1 in the lattice is presented in Figure 4. The molecular pairs are in antiparallel orientation. Due to the non-planarity of the molecule, the characteristic packing of flat molecules with a 3.4-Å distance between planes was not observed. In this respect, MS1 differs from other thermochromic *o*-hydroxy anils, e.g. *N*-5-chlorosalicylidene-aniline. It is interesting to note that the phenyl ring denoted as *A* in Figure 4 has no respective counterpart(s) in the distance less than 5.3 Å. Details corresponding to non-bonded nearest-neighbor interatomic distances point out that, in the case of the phenolic fragment of MS1 molecule, the interatomic distance $\mathrm{C}(2)\ldots\mathrm{C}(2)^{i}$ (symmetry code) $(i = 1-x, 1-y, 1-z)$ of the closest rings fixed to 3.412(4) Å ($\angle\mathrm{C}(3)\text{–}\mathrm{C}(2)\text{–}\mathrm{C}(2)^{i} = 92.25(16)^\circ$ and $\angle\mathrm{C}(1)\text{–}\mathrm{C}(2)\text{–}\mathrm{C}(2)^{i} = 111.88(17)^\circ$) is in agreement with the interplanar distance of the thermochromic compound.^{17} In the frame of the C(Ph)$_3$ moiety, the mode of contact between two antiparallel molecules is equal to 3.648(3) Å for the $\mathrm{C}(22)\ldots\mathrm{C}(23)^{ii}$ $(ii = \bar{x}, \bar{y}, 3-z)$ distance. The same value is for the $\mathrm{C}(23)\ldots\mathrm{C}(22)^{ii}$ one, and there is the shortest contact between $B\ldots B'$ phenyl rings. But in the frame of $C\ldots C'$ phenyl counterparts, the value of the closest $\mathrm{C}(12)\ldots\mathrm{C}(13)^{iii}$ $(iii = \bar{x}, 1-y, 3-z)$ inter-atomic distance is greater than that of $B\ldots B'$ one and equals 3.863(4) Å.

Lowering the temperature results in geometry changes which are focused mainly on the angle relations in chelate six-membered rings. Hindered librations causes irregular changes of the single and double bonds of all phenyl rings. However, in general, the temperature changes of all the detected parameters including a crystal packing are not greater than those which would be expected from the normal thermal coefficient of expansion.

Thermochromism

Thermochromism is a characteristic feature of MS1 molecule. Yellow crystals of the compound change color to the white. Bleaching is the thermally driven reaction and is clearly observed using the microscopic technique below ambient temperature. Only one color transformation was observed, till down to 77 K. The temperature limits for that process correlate well with the phase transition temperature of 241 K. Taking into account the results of X-ray structural analysis, thermochromism have been explained as the geometry change of a chelate ring which causes the transenol open form creation, not as the benzenoid-quinoid transformation. The scheme proposed is shown in Figure 5.

The microscopic observations at room temperature were carried out using an Olympus microscope BX60 with CCD color camera IKEGAMI ICD-803D, a fluorescence unit with mercury burner USH102D (Ushio Electric, excitation 360/370 nm), and a DELL OptiPlex GX1 PC.

Luminescence. The steady-state corrected emission spectra of a crystalline sample were recorded with a Hitachi F-4500 Fluorescence Spectrophotometer using a right-angle setup with excitation at 31250 cm^{-1} (320 nm) and 24390 cm^{-1} (410 nm), respectively. Low temperature luminescence measurements were done using an Oxford Instruments cryostat mounted inside a HITACHI F-4500 apparatus.

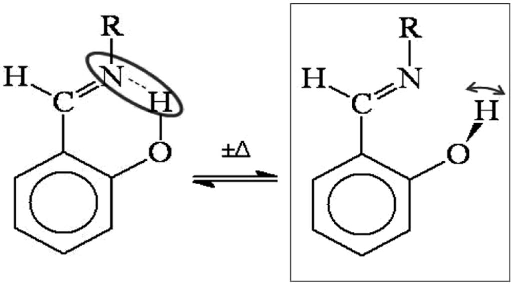


FIGURE 5 Molecular scheme of the open trans-enol and closed form of MS1.

The fluorescence and the fluorescence excitation spectra were recorded at 77 K and 300 K using the steady-state technique. The same spectra of a quickly frozen (77 K) sample were recorded dynamically in the 77 → 300 K temperature range. The room-temperature spectra were done with the same apparatus in a standard quartz cell. At room temperature, the deep-yellow crystals of this compound are strongly fluorescent after UV excitation. The microscopic pictures of the non-luminescent and luminescent materials are presented in Figure 6.

Two examples of the temperature evolution of the luminescence spectrum of the proton-transferred form of solid MS1 at a low temperature are shown in Figure 7. The $^1(\pi,\pi^*)$ excited singlet state of the enol form is an active state in the phototransformation process.

Using the standard Marquardt-Levenberg method for non-linear curve fitting, the fluorescence band of a solid sample of MS1 presented in Figure 7 was resolved to three components: 490-nm (20410 cm^{-1}), 510-nm (19600 cm^{-1}), and 540-nm (18520 cm^{-1}) one. The separation was conducted by assuming the Gaussian band shape. The envelope of the broad band luminescence is in excellent agreement with experimental data for all curves fitted. The temperature evolution of each *sub*-band fixed was done in the temperature range 77–300 K. Only two examples of the emission band are presented in Figure 7. There is a relation between these components, probably the same as proposed for the multicomponent fluorescence of *N*-salicylideneaniline [7,21]. Plots of the intensity changes and the peak positions of the fluorescence *sub*-bands measured as a function of temperature presented in [13] confirmed that suggestion.

The excitation fluorescence spectra of a solid sample of MS1 at 77 K monitored at 520 nm are presented in Figure 8. The accumulation of the photocolored form registered after different times of irradiation

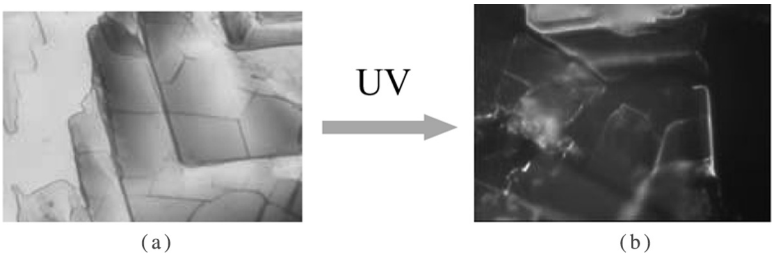


FIGURE 6 Microphotographs of the room temperature of a thin crystalline sample of MS1 (a) before excitation and (b) green-yellow luminescenu after UV excitation.

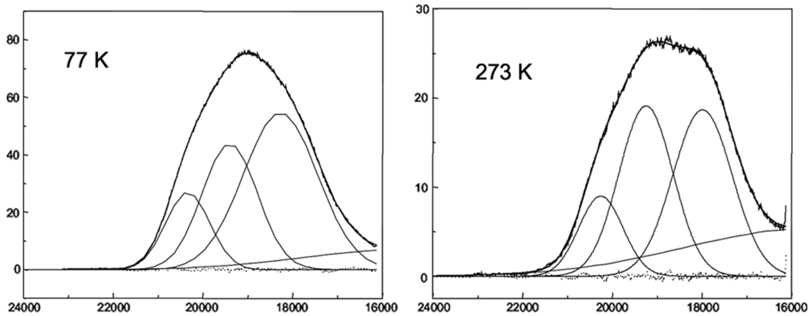


FIGURE 7 Two examples of the temperature evolution of the PT luminescence band of MS1 in solid state (energy excitation = 31250 cm^{-1}, wavelengths are in cm^{-1}, intensity – in arbitrary units).

is clearly seen in the figure. The luminescence behavior of MS1 can be explained basing on the four-level scheme presented in Figure 9.

Upon the irradiation with ultraviolet light, a proton transfer occurs in the excited electronic singlet state (ESIPT). The fluorescence spectrum is highly Stokes-shifted in relation to the energy excitation corresponding to the first absorption band. In the next step, in the excited state, after the photoisomerization (PhI) process, a colored metastable species is formed and accumulated. Unfortunately, it

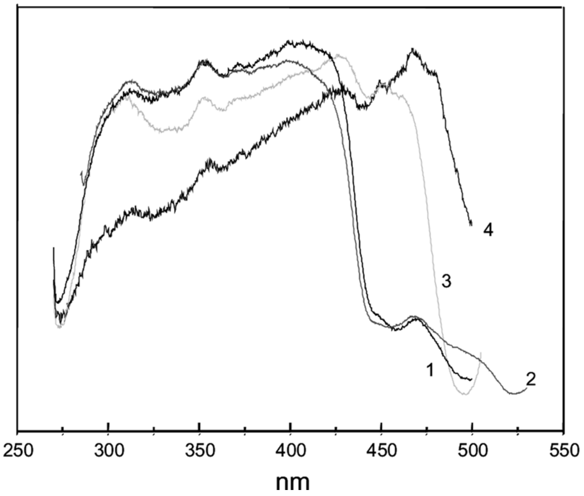


FIGURE 8 Fluorescence excitation spectra of MS1 at 77 K monitored at 520 nm after different times of irradiation of a solid-state sample: 1–immediately, after fast freezing; 2–after 2 min; 3–30 min; 4–60 min of UV exposure.

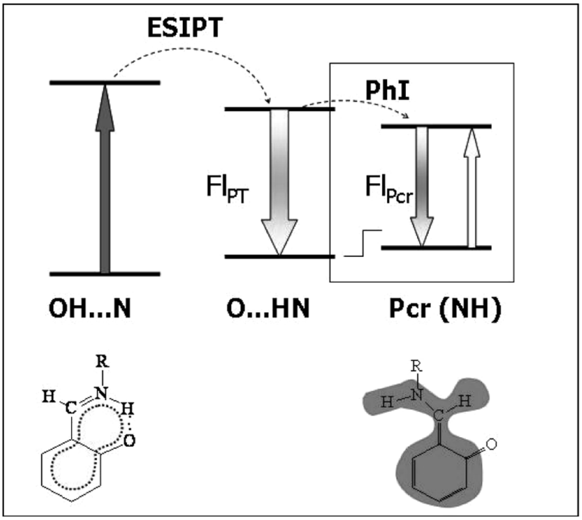


FIGURE 9 Multilevel scheme of the low temperature creation of the photochromic form of MS1.

cannot be isolated as a chemical entity, while it was detected by using the excitation emission spectra technique (cf. Fig. 8). The photocolored species match the geometrical isomers of the thermochromic species. The main thermochromic band of MS1 was observed at 480 nm. The same peak position is identified in the absorption spectra of thermochromic anils and Schiff bases [2]. It is important to note that the luminescence of the enol form of MS1, the mirror-image to the first absorption band, was not detected [13].

The fact that the proton return from the nitrogen atom to the oxygen atom in the final photocolored form is strongly hindered shows that an additional process must be present to cause some stabilization of the NH configuration. That feature was also distinguished for N-salicylideneaniline mixed crystals [7]. The back reaction is a rather purely thermal pathway, and a rearrangement from the NH (orange) to OH (yellow) form without ‘white color’ step as the temperature increases was observed.

The absence of photochromy at room temperature might have been due to the thermal rate of fading is too high to permit coloration as in salicylaldehydes [2].

Taking into account the results of our recent papers [11–13], there are two ground-state forms of MS1 in the crystal: the trans-enol (closed) ‘yellow form’ active at ambient and higher temperatures and the trans-enol (rigid, closed) ‘white’ one at lower temperatures. The

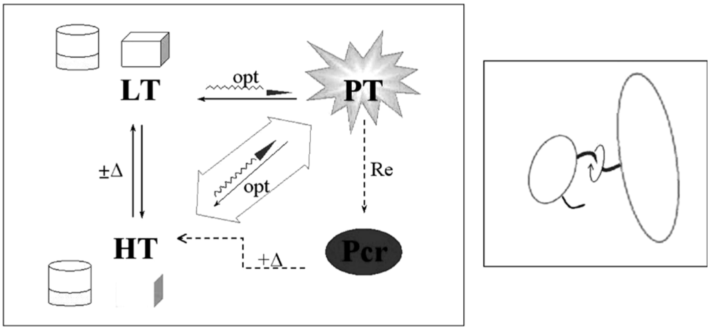


FIGURE 10 General scheme of the rearrangement of MS1 in solution as well as in solid state. Legend: LT, HT – low and high temperature conditions, opt – optical transition, PT – proton transfer, Re – rearrangement in excited state, Pcr – photochromic form. On the right: scheme of the molecular bicycle-pedal motion.

term *trans*- is concerning in relation to the phenyl ring and bulky substituent. The temperature manipulation gives rise to the interconversion of closed ↔ rigid open forms, as is shown in Figure 5. Taking into accounts the ambient and low temperature spectral behavior, the general scheme of the rearrangement is shown in Figure 10, with 'visualization' of the bicycle pedal motion active in the molecular rearrangement, as was suggested in [22] and documented in [23].

3. CONCLUSIONS

Taking into account the results of X-ray analysis, IR spectrum, and the photoluminescence as well as fluorescence excitation spectra of MS1 in the crystalline state and in the frozen n-alkane matrix together with temperature dependence of the emission, the main conclusions are as follows. Contrary to the Schiff base as well as anil model compounds, the non-planar molecule, *N*-triphenylmethylsalicylideneimine in the solid state at low temperatures, represents simultaneously a photochromic- as well as thermochromic-type material. Temperature is the easy way for modeling the spectral features of the molecule under study. Low temperature favors the benzenoid *trans*-enol open form of MS1. However, the photochemical reaction in an excited state (proton transfer and/or photoisomerization) prefers the molecular quinoid form.

Thermochromy acts as the reversible feature, and it was explained due to geometry changes of the chelate ring, which causes the *trans*-enol open form creation. The phase transition temperature is well correlated with the temperature limit of the color change of the molecule under study from the yellow to the white.

The absence of photochromy near room temperature is due to the influence of the temperature factor. The temperature limit is a restriction, where the thermal rate of fading is too high to permit coloration. Spectral changes result in the temperature lowering, and UV irradiation was interpreted in terms of a drastic rearrangement in the central part of the molecule. The barrierless excited state intramolecular proton transfer process following photoisomerization operates as a starting point of the MS1 color form creation. Moreover, this photochemical reaction coupled with thermochromic processes makes the rearrangement cycle, as a whole, reversible.

Species rigid under low-temperature conditions and the open-form species promote the nonradiative deactivation channel of the excited state.

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