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Spectroscopic characteristics of the micro-environmentally induced H-bond transformation in anil-type species: experimental and theoretical study

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Abstract The results of combined experimental and theoretical investigations of the spectral behavior of anil-type systems are presented. Two species: *N*-triphenylmethylsalicylidene imine (MS1) and *N*-salicylidene methylamine (SmA) were studied. The electronic (absorption, emission and excitation) spectra of MS1 at room temperature were investigated in pure isooctane as well as in acetonitrile and methanol solutions by the steady-state experiments. A mechanism of molecular processes in the ground and excited states in different microenvironments is also proposed. It includes formation of *intra*- and *intermolecular* hydrogen bonds, their role in stabilization of molecular conformations and conformation equilibria. The “solvent assisted” proton transfer reaction and rearrangement were modeled using complexes obtained by attaching methanol molecules to the species studied. The OH-rotamer of SmA was also considered. Infrared and Raman spectra were predicted for MS1 and SmA and compared with the experimental data. An analysis of fundamental vibration frequencies was carried out. Quantum chemical *ab initio* calculations at the HF/6-31G** level were performed for the species studied and their complexes. Chemical formula of anil-type compound: *N*-salicylidene methylamine (SmA), *N*-salicylideneaniline (SA) and *N*-triphenylmethylsalicylidene imine (MS1).

Keywords *N*-triphenylmethylsalicylidene imine · *N*-salicylidene methylamine · Luminescence · Proton

transfer · Fundamental vibration frequency · *Ab initio* method

Introduction

Anils characterized by the general structure displayed in Scheme 1 form a specific group of organic compounds that possesses the ability to form intramolecular hydrogen bonds [1, 2]. Rather complicated mechanisms of photochemical reaction in the solid state as well as in rigid solutions that involve a proton-transferred form and the creation of photoproduct(s) of side reaction(s) were a source of inspiration to many groups [3–8]. Among others, special attention was paid to the spectral features of *N*-salicylideneaniline (SA)-a model compound for modern organic photochemistry [9: Chap. 16, 10: Chap. 17]. As an *o*-hydroxy anil, the SA molecule exists in solution in two thermally interconverted forms [11, 12]. They are characterized by different long-wavelength absorption bands that lie in the near ultra-violet or the visible range of the spectrum. The type of anil and its concentration, the solvent, and the temperature determine the relative intensities of these two bands. A number of explanations of the nature of the visible absorption band have been put forward [13–18]. The SA molecule luminesces weakly in solution and the maximum of this single-band emission, which peaks at approximately $20,000\text{ cm}^{-1}$, is highly Stokes shifted in relation to the excitation energy [11]. The intensity of this emission, attributed to the proton-transferred form, increases with decreasing temperature. The results of time resolved fluorescence measurements, especially in polar protic solvents such as cyclohexanol, show that the fluorescence exhibits a biexponential decay in the picosecond range, which is independent of emission wavelength in the $20,400\text{--}17,500\text{ cm}^{-1}$ range. The two-component luminescence phenomenon was attributed to the existence of two solvated forms of anil in the excited state [19]. However, laser-induced fluorescence spectra

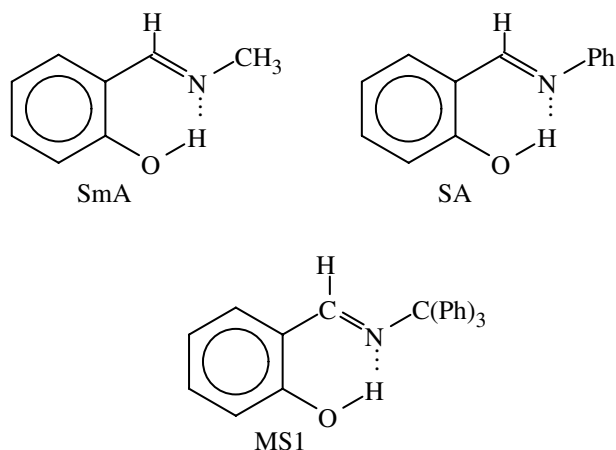
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of SA in CH_3CN obtained by the sequential two-step laser excitation [20] reveal another emission, red shifted with respect to the phototautomeric one and assumed to originate from the zwitterionic and photochromic forms. *Cis*-zwitterionic character of the photochromic transient in the SA molecule has been postulated [21]. However, this assignment proved to be controversial [22]. According to the model proposed, the zwitterionic structure for SA was characterized as a *cis*-configuration with respect to the $\text{C}=\text{N}$ bond in the central part of the molecule. As was proposed [23], more than one zwitterionic structure could be considered to explain of the time-resolved spectroscopic data. According to the results of resonance-Raman and NMR spectroscopic investigations [17], there is an equilibrium between the H-bonded benzenoid and the zwitterionic forms when tetrahydrofuran is chosen as solvent. A sub-microsecond time-resolved infrared study of SA in acetonitrile [22] provides the possibility to assign the $1,635\text{ cm}^{-1}$ fundamental vibration frequency as the $\text{C}=\text{N}^+$ stretch of the protonated Schiff base. Simultaneously, it should be noted that the $\text{C}=\text{N}^+$ and $\text{C}-\text{O}^-$ stretches are coupled through the delocalization of an electron in the OCCCN frame of the molecule [22]. According to Refs. [24, 25], the infrared band at $1,627\text{ cm}^{-1}$ could easily consist of the bands at $1,633$ and $1,616\text{ cm}^{-1}$ in the resonance Raman spectrum. These bands are assigned to the $\nu_{\text{C}=\text{NH}^+}$ and $\nu_{\text{C}=\text{N}}$ modes, respectively. These results were a stimulus to perform a comparison of the infrared spectra (calculated and obtained experimentally) of *N*-triphenylmethylsalicylidene imine and *N*-salicylidene methylamine molecules (hereafter abbreviated as MS1 and SmA, cf. Scheme 1). According to our knowledge, there are only a few papers on the electron spectroscopy of SmA [5, 26, 27]. The effect of H-bond formation on shift and intensity changes of NIR and MIR bands of SmA based on thin-film transmission spectra were discussed in Ref. [28]. However, the solvent effect and

temperature dependence of the Raman and absorption spectra indicate the existence of a tautomeric equilibrium for the enol and the protonated forms of SmA in methanol. The latter is more stable (by $0.85\text{ kcal mol}^{-1}$) than the former [26]. Moreover, the excited-state proton transfer reaction was not observed directly. The corresponding keto-tautomeric fluorescence was almost undetectable [27].

In this work, we focus our investigation on the spectral properties of MS1, the role of *intra*- and *intermolecular* hydrogen bonds, and their participation in the stabilization of molecular conformations. The function of bulky substituents connected to the nitrogen atom that acts as a moderator of spectral characteristics of the anil-type molecule studied is also established. Our discussion takes into account an analysis of the electronic absorption spectra, luminescence, excitation fluorescence and IR and Raman spectra of MS1 in nonolar, polar protic, aprotic and in mixed solvents. Additionally, because of the previously reported specific solvatochromy of MS1 [29], computer modeling of the micro-environmentally induced H-bond transformation is used to explain MS1's spectroscopic properties in polar media. The "solvent assisted" proton-transfer reaction and rearrangement were modeled using complexes obtained by attaching 1–4 methanol molecules to the SmA model molecule. The OH-rotamer of SmA was also considered. According to [30], in a hydrogen-bonded complex surrounded by solvent molecules, the solvent rearrangement must first proceed in order for the proton transfer to occur. The solvent largely determines the reaction coordinate and the reaction is governed by the activation free energy of this rearrangement, rather than by the height of the proton barrier. In the SmA case, the fundamental vibration frequencies for the molecule surrounded by polar solvent molecule(s) determined theoretically are reported and compared with the literature.



Scheme 1 Chemical formula of anil-type compound: *N*-salicylidene methylamine (SmA), *N*-salicylideneaniline (SA) and *N*-triphenylmethylsalicylidene imine (MS1)

Results

Absorption spectra

The room-temperature absorption spectra of MS1 in isooctane, acetonitrile, methanol and 2-propanol are shown in Fig. 1. In isooctane, the absorption band maximum (in cm^{-1}) and $\log \epsilon_{\text{max}}$ (in parentheses) are equal to $31,250\text{ cm}^{-1}$ (4.17) and $38,760\text{ cm}^{-1}$ (3.6), respectively. In both protic solvents, methanol and 2-propanol, apart from the two bands mentioned above, the spectrum contains an additional one, centered at $24,390\text{ cm}^{-1}$. The value of its absorbance is much lower than the former ones. In methanol, the values of the $\log \epsilon_{\text{max}}$ are equal to 4.17, 3.63 and 2.47, respectively. In pure acetonitrile, in the range $33,000\text{--}20,000\text{ cm}^{-1}$ the spectrum consists of a single absorption band. However, in the mixed acetonitrile-water solvent, the formation of a new absorption band in the visible range of the

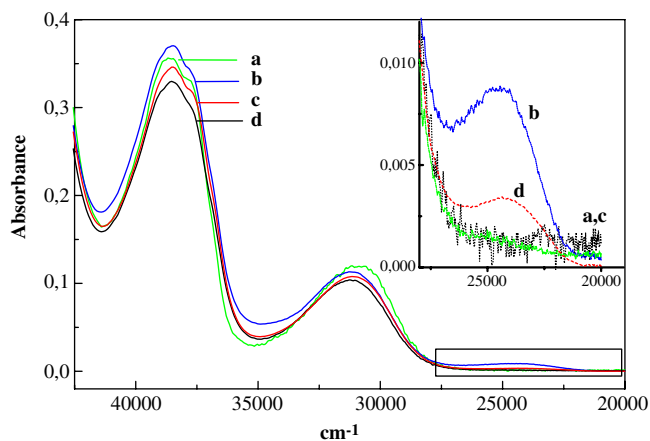


Fig. 1 Absorption spectra of MS1 in different solvents: (a) isooctan, (b) methanol, (c) 2-propanol, (d) acetonitrile ($T = 295 \text{ K}$, $c = 2.5 \times 10^{-5} \text{ M}$). Insert shows enlarged the VIS-range absorption spectra in vicinity of $25,000 \text{ cm}^{-1}$

spectrum (peaked at $24,690 \text{ cm}^{-1}$) is observed (cf. Fig. 2). The percentage concentration of water was in the range 1.5–40%. As shown in Fig. 2, the absorbance of this newly-created band increases as the hydrogen-bonding strength of the solvent is increased, at the cost of the band at $31,250 \text{ cm}^{-1}$. Also, absorbance changes measured in the visible and important ultra-violet peak mentioned above are shown. Both dependences are well fitted linearly.

The intensity of the absorption band and peak position is very sensitive to the nature of the solvent used. Figure 3 shows these characteristics for methanol, a polar protic solvent, upon addition of 0.1 M NaOH or 0.1 M HCl.

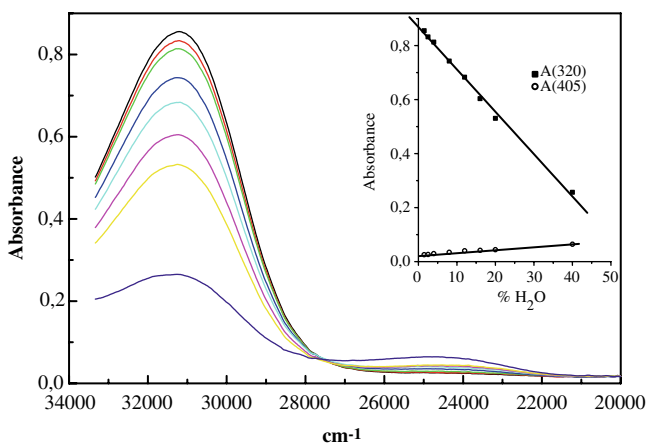


Fig. 2 Long wavelength part of absorption spectrum of MS1 in acetonitrile with a dash of water ($T = 295 \text{ K}$). The percentage contents of water (from top to bottom) is equal 1.5, 2.5, 4.0, 8.0, 12.0, 16.0, 20.0 and 40.0, respectively. Insert shows absorbance change as a function of water addition. Solid squares represent measurements at $\tilde{\nu}_{\text{max}} = 31,250 \text{ cm}^{-1}$ and open circle at $\tilde{\nu}_{\text{max}} = 24,900 \text{ cm}^{-1}$

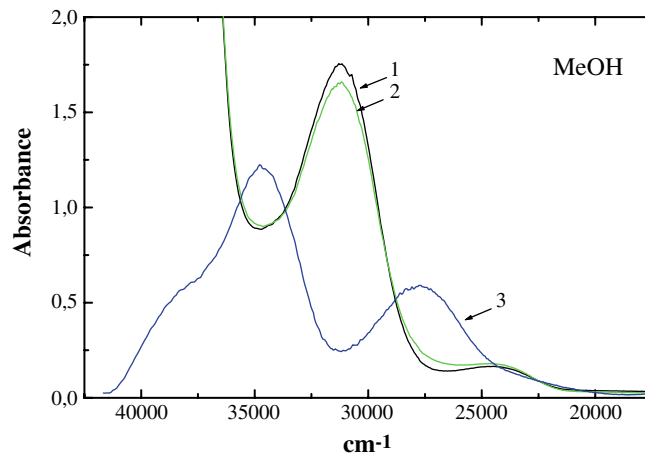


Fig. 3 The absorption spectra of *N*-triphenylmethylsalicylidene imine in methanol: 1-pure (neutral) methanol, 2-alkaline (MeOH + 0.1 M NaOH), 3-acidic (MeOH + 0.1 M HCl)

Fluorescence and fluorescence-excitation spectra

The fluorescence spectra of MS1 in isooctane and methanol at room temperature excited at $31,250 \text{ cm}^{-1}$ are shown in Fig. 4. The fluorescence in methanol mirrors visible and ultra-violet-range absorption bands, while the total detected emission in isooctane mirrors the UV band only. In isooctane, the values of the Stokes shift (related to the excitation energy) are equal to $5,600$ and $12,000 \text{ cm}^{-1}$ for emission in the blue range (F1, cf. Fig. 4) and the long-wavelength emission (F2, cf. Fig. 4), respectively. The values of the corresponding shifts in methanol slightly differ, and are equal to $7,150$ and $11,250 \text{ cm}^{-1}$, respectively.

The fluorescence-excitation spectra of MS1 in isooctane and in methanol, obtained in the $34,000$ – $23,000 \text{ cm}^{-1}$ range, are also shown in Fig. 4. As a result of monitoring the emission spectrum at the maximum of the F2 band, very well reflected absorption spectra were obtained in both solvents used.

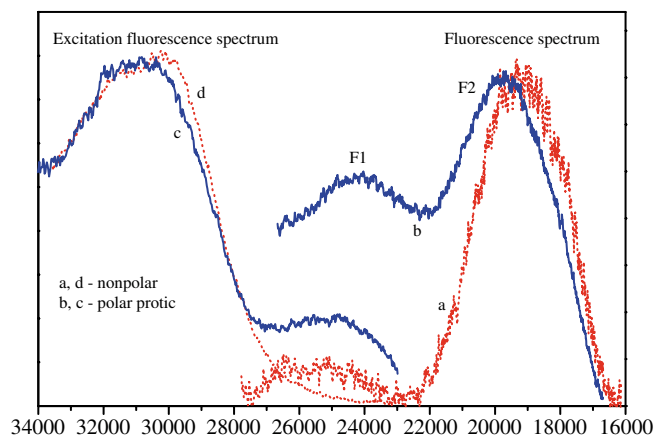


Fig. 4 Fluorescence excitation spectra (on the left) and fluorescence spectra (on the right) of MS1 in: a, d isooctane; b, c MeOH ($T = 295 \text{ K}$, excitation at $\tilde{\nu}_{\text{exc}} = 31,250 \text{ cm}^{-1}$, monitoring at $\sim 19,500 \text{ cm}^{-1}$)

Infrared and Raman spectra

The IR spectrum of MS1 in a KBr pellet at room temperature is shown Fig. 5a, b. The data are compared with fundamentals identified in the Raman spectrum of a crystalline sample of MS1 at room temperature as well as determined theoretically (Table 1, column 1–4). Quantum-chemical calculations were performed, based on the ab initio LCAO MO HF approach with the 6-31G** basis set, using the Gaussian98 package [31]. The proposed scaling factor of 0.8929 has been applied to the predicted harmonic vibrational frequencies in the present study [32].

In the spectra special attention was focused on the 3,700–3,200 and 1,700–1,600 cm^{-1} ranges due to possible intramolecular OH–N hydrogen bond and the fundamental vibration frequencies of the central R–C=N–R' chain, respectively. The typical remarkable feature of

the IR spectrum in the first range mentioned above is the absence of the band corresponding to the free OH stretching vibration expected over 3,600 cm^{-1} . Instead, a broad OH band related to the OH–N intramolecular hydrogen bond peaked at 3,450 cm^{-1} (the calculated value is equal to 3438.0 cm^{-1}) was observed. This proves that the OH group is engaged in intramolecular hydrogen bonds. It is very remarkable that this band is absent in the Raman spectrum.

In the second range mentioned, the most prominent band detected at 1,623 cm^{-1} in the IR and Raman spectra corresponds to the R–C=N–R' flexible part of MS1 (the calculated value of this most intense frequency in the IR spectrum is 1688.9 cm^{-1}).

Calculations of the fundamental vibration frequencies active in IR and Raman spectrum of SmA as well as for SmA with 1–4 MeOH molecule(s) were carried out. The main modeled interacting systems include: pure SmA (OH–N) form, SmA (O–HN) tautomer, SmA (O–HN):2MeOH and SmA (OH)_{rot}:4MeOH. The last represents the SmA rotamer with a broken intramolecular hydrogen bond, but with an active solute-solvent intermolecular hydrogen bond. The IR and Raman spectra of the SmA model compound are shown in Fig. 6a–d and two examples of different structures calculated in Fig. 7.

In the case of SmA (OH–N) form, the value of the most intense fundamental vibration frequency is assigned to the OH mode and is equal to 3447.4 cm^{-1} , with an absolute IR intensity of 306.8. However, in the 1,700–1,600 cm^{-1} range, the fundamental vibration frequency of R–C=N–R' molecular fragment is also very prominent with 1718.6 cm^{-1} and an absolute IR intensity of 279.8 (256.3 for the Raman spectrum). The value of the same mode active in the IR spectrum of the SmA (O–HN) form is the strongest one and shifted to lower wavenumbers, and is equal to 1679.8 cm^{-1} (987.0). A new NH bending mode coupled with a ring out-of-plane mode was calculated at 1518.4 cm^{-1} (355.6). As expected, after binding the SmA (O–HN) form to two MeOH molecules, the mode of the R–C=N–R' molecular decreased to 1667.2 cm^{-1} and was still prominent, with a very high IR absolute intensity of 1268.4. The other high-intensity modes (absolute IR intensity in parentheses) are as follows: 3330.7 cm^{-1} (229.7) NH_{stretch}, 3505.6 cm^{-1} (688.7) OH_{stretch} ooph (in MeOH), 3555.2 cm^{-1} (547.5) OH_{stretch} iph (in MeOH).

When four MeOH molecules bind the SmA (OH–N) rotamer (cf. Fig. 7), the value of the fundamental vibration frequency of the strong R–C=N–R' mode does not change with respect to the data for the non twisted hydrogen atom of the O–H group of the SmA molecule. However, the series of very strong modes have characteristic intermolecular modes (absolute IR intensity in parentheses): 3477.6 cm^{-1} (829.1) OH → O (MeOH) 3562.8 (518.2) (H)O → OH (MeOH), 3650.0 (208.3) N → H(O) (MeOH), 3664.7 (218.1) (H)O → H(O) (MeOH).

In Table 1, the fundamental vibration frequencies (calculated and observed) of MS1 are compared with the

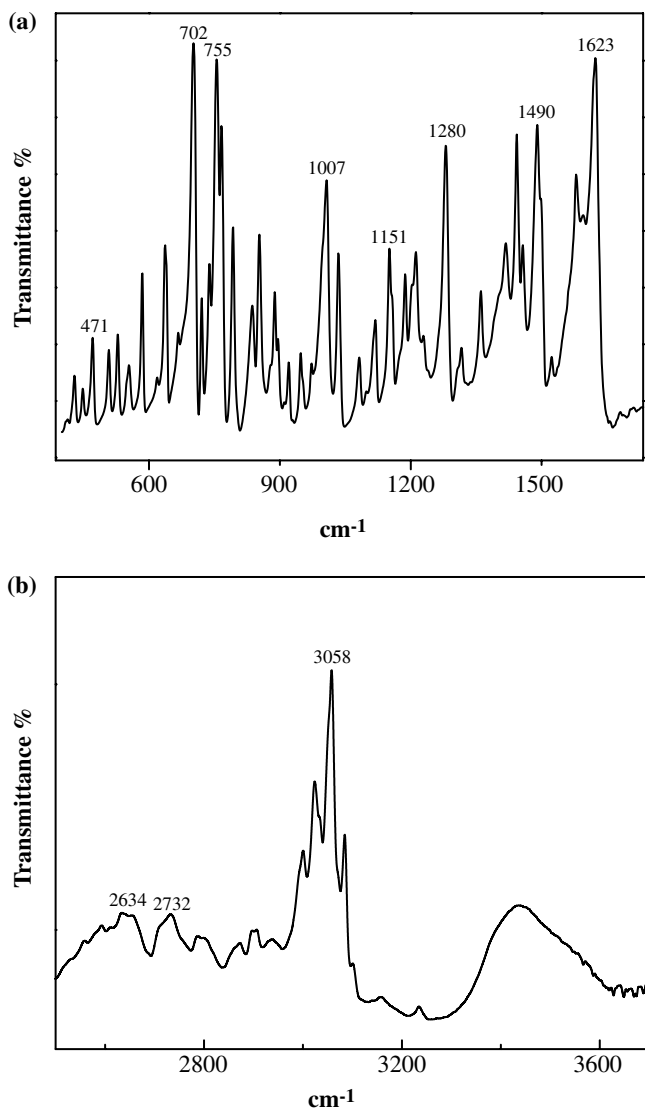


Fig. 5 The infrared spectrum of MS1 in KBr pellet: (a) 1,700–400 cm^{-1} and (b) 3,650–2,550 cm^{-1} range, respectively

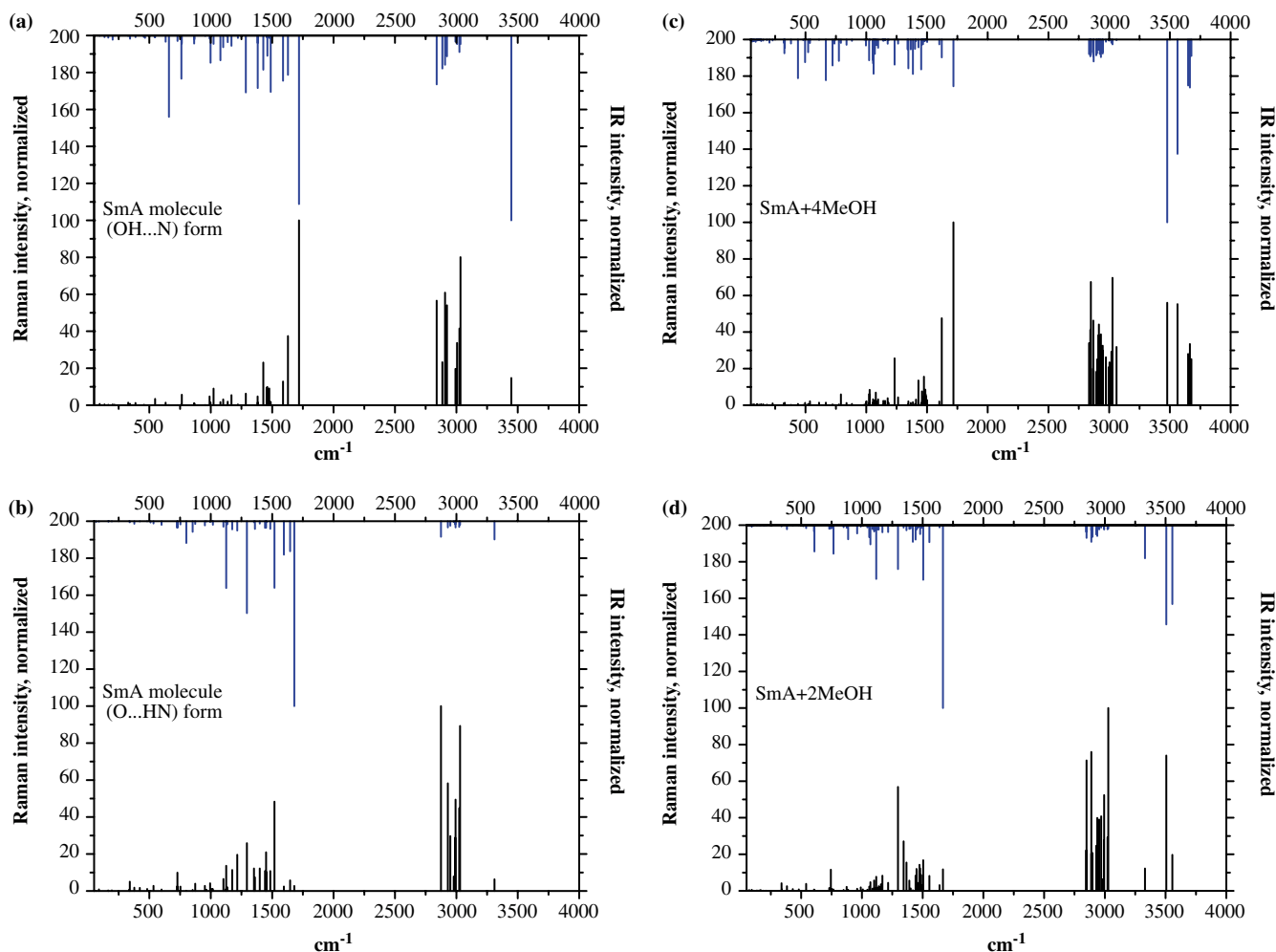


Fig. 6 The calculated fundamental vibration frequencies of SmA and SmA bound by methanol molecules, active in IR (*on the top*) and Raman (*on the bottom*) spectra: (a) SmA (OH–N) form, (b) SmA (O–HN) form, (c) SmA (OH)_{rot}:4MeOH system, (d) SmA (O–HN):2MeOH system

corresponding data of the IR and Raman spectra of SA and SmA obtained by other authors. The assignments of fundamentals given in the last column of the Table 1 have been supported using visualization of the calculated fundamentals by MOLDEN and IR and Raman spectral studies of SmA and SA molecules in different matrices and temperatures [17, 22, 24, 26].

Discussion

The MS1 molecule with the R1–C=N–C–R2 bond arrangements could be analyzed as a model system with three distinct units: phenolic (R1 = C₆H₄–OH), flexible central (–C=N–C–) and bulky (R2 = –C(Ph)₃). Each unit participates in the photoinduced rearrangement in a different manner. The phenolic unit with the –OH group is crucial for the photochemical transformation [1], especially in the excited state intramolecular proton transfer reaction. A spatial “heavy” substituent close to

nitrogen atom acts as a moderator of molecular flexibility that balances the changes in temperature and energy excitation. Moreover, in the crystal lattice, its own activity seems to be also important.¹ The central –C=N–C– flexible fragment governs conformational changes in the ground as well as in excited electronic states, as in the case of *N*-3,5-di-*tert*-butylsalicylidene-3-nitroaniline [8].

Based on the spectral behavior of MS1 in solutions of different type of polarity, ground state conformers are proposed in Scheme 2. According to this scheme, the (a) and (b) conformers: the *trans*-closed (OH) form and the *trans*-closed proton-transferred (PT) form, respectively, are active in polar protic solvents. The ground-state-proton transfer reaction leads to the PT form, which is stabilized by the polar protic environment. The bulky substituent moderates flexibility of the central part of the molecule, even at room temperature. Additionally, it acts as shield, facilitating formation of the intramolecular hydrogen bond [18, 29]. The (c) and (d) conformers

¹It is out of question that in the solid state, according to our X-ray analysis as well as NMR data MS1 molecule represents *trans*-closed form with clear shift of hydroxyl proton to nitrogen atom (interatomic distances: $r(\text{OH}–\text{N}) = 1.71 \text{ \AA}$, $r(\text{O}–\text{N}) = 2.57 \text{ \AA}$).

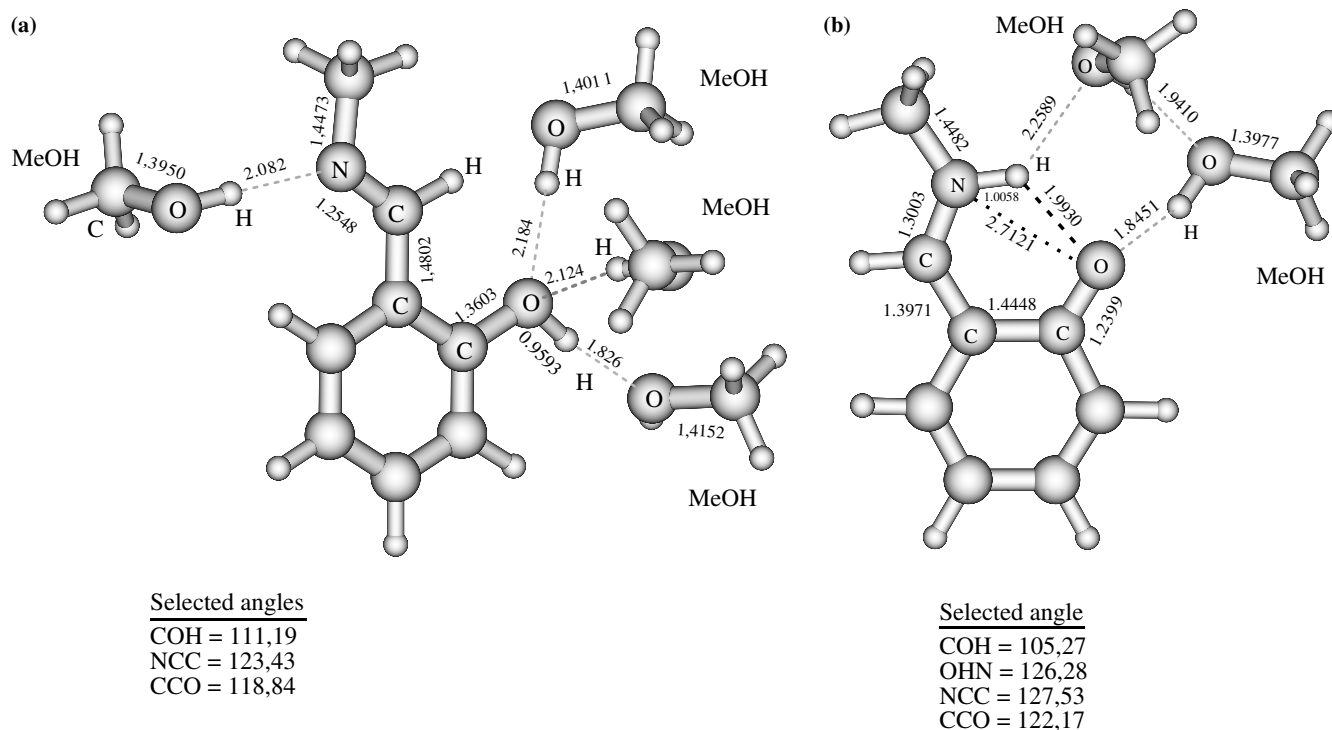


Fig. 7 The model SmA + MeOH molecular systems studied theoretically: (a) SmA (O–HN) form bonded by 2 MeOH molecules, (b) SmA (OH–N) rotamer bonded by four MeOH molecules. The intra- as well intermolecular selected distances (in angstroms) and selected angles are given

proposed in Scheme 2 are in equilibrium under the experimental conditions considered here, and both are called *trans*-open forms. These conformers can exist in the polar aprotic as well as in non-polar solvents. Each form could be stabilized by the (C(Ph)₃) spatial substituent. Additionally, in polar aprotic solvent, e.g., acetonitrile, the stabilization is caused by formation of a hydrogen bond (OH–N).

Taking into account the general pattern of absorption and emission spectra of MS1 in non-polar solvent, in the ground state the non-proton-transferred (non-PT) form dominates (cf. Scheme 2). However, in the excited singlet state both non-PT and PT forms are observed in the equilibrium. In protic solvent, methanol, the situation is quite different. In the ground state, the presence of both forms is detected, as in the case of the model anil. The character of the spectrum does not allow us to conclude in which way equilibrium is reached, but the existence of this ground state equilibrium is demonstrated by the absorption spectra in the mixed acetonitrile-water solvent, as was shown in Fig. 2. In a polar non-protic solvent, the non-PT form of MS1 exists in the ground state. The isobestic point at 27,000 cm⁻¹ indicates an equilibrium between the non-PT (*trans*-open) and PT forms in this medium [29]. The ground-state equilibrium between the open and the closed forms with intramolecular hydrogen bond of methyl salicylate was discussed in Refs. [33, 34]. The ratio of their relative concentrations depends on the nature of the solvent. In

the case of methyl salicylate, the lack of as flexible a part as in the case of MS1 causes stabilization of the open form by a hydrogen bond between solute and protic solvent [33, 34].

Preliminary results of the theoretical treatment of the micro-environmentally-induced H-bond transformation indicate the existence of the two distinct energy minima in the non-solvated system. Besides the global minimum with the proton connected to the oxygen atom, also the 6.9 kcal mol⁻¹ less stable local minimum form with the proton transferred to the nitrogen atom exists. The energy barrier of this proton transfer is 9.7 kcal mol⁻¹ [29]. In alcoholic solvent, the results of the “solvent assisted” proton transfer and rearrangement of the initial intramolecular hydrogen bonded enol form are as follows. Binding 1–2 methanol molecules to the species investigated shifts this tautomeric equilibrium to form the proton-transferred structure, which is 2.5 kcal mol⁻¹ more stable than the structure with proton bound to the oxygen atom. However interactions with four methanol molecules are sufficient to form a stable non-cyclic structure of SmA, which is somewhat less stable than the fully solvated cyclic form.

Contrary to anils, *N*-triphenylmethylsalicylidene imine exhibits two-kinds of fluorescence at room temperature in all type environments used. Even in nonpolar solvent, a lack of the VIS absorption band breaks the spectral mirror symmetry. In isoctane at room temperature, no concentration dependence of the proton-transfer form fluorescence maximum peaking at ~20,000 cm⁻¹ was observed. The polarity of the solvent used, causes an increase in the quantum yield of fluorescence. This is the reason that in the emission spec-

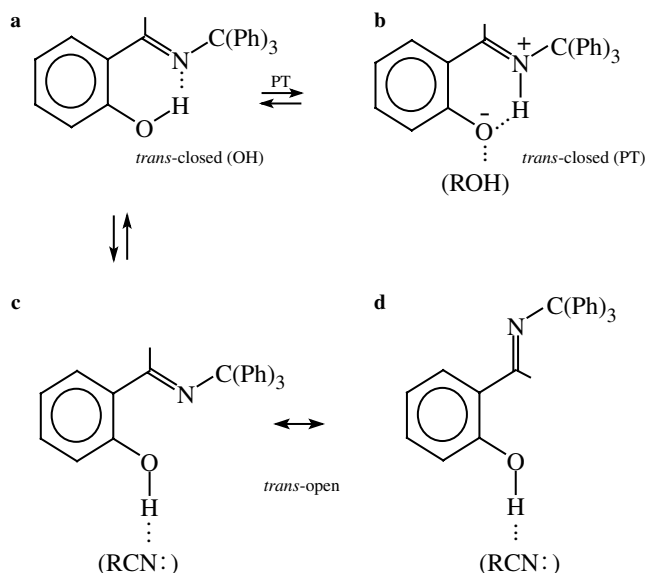
Table 1 The fundamental vibration frequencies (in cm^{-1}): a comparison of calculated and experimental data of MSI, SA and SmA molecules

| MSI | SA | | | SmA | | | Assignment | |
|--------|-----------------------|---------------------|----------------|-----------------|-----------------------|--------------------|------------|-------------------------------------|
| | IR ^a freq. | Calc. IR int. calc. | IR (in KBr) | R (solid state) | IR (solid state) [17] | IR (solution) [17] | | IR (solution) [21] |
| 994.0 | 72.43 | 1,007 s | 1,007 s | 999 vs | 1,008 | | | -CN (ip), ν_{12} |
| 1020.5 | 21.20 | 1,034 ms | 1,034 ms | 1,035 s | 1,038 | | | ν_{18a} , ring |
| 1078.9 | 49.37 | 1,082 mw | 1,082 mw | | | | | Ring |
| 1106.1 | 18.17 | 1,119 m | 1,119 m | | | | | Ring |
| 1158.3 | 16.38 | 1,151 m | 1,151 m | 1,151 m | 1,157 | 1,125 | 1,130 B | Ring |
| 1171.5 | 18.81 | 1,187 m | 1,187 m | | 1,194 | 1,145 | 1,151 A | CO, OH |
| 1199.1 | 8.71 | 1,211 m | 1,211 m | 1,206 m | 1,245 | 1,179 | | |
| 1209.9 | 2.84 | 1,228 w | 1,228 w | 1,228 m | | 1,239 | | |
| 1223.0 | 24.48 | | | 1,240 m | | | | |
| 1283.8 | 81.23 | 1,280 vs | 1,280 vs | 1,284m diff | | (1,263R) | 1,281 | 1,228 A, B 1,242 A, B 1,283 B |
| 1314.5 | 1.50 | 1,316 mw | 1,316 mw | 1,318 ms | 1,326 | | | C-O stretch |
| 1386.1 | 61.09 | 1,361 m | 1,361 m | | 1,366 | 1,319 | 1,318 A | ν_3 , CC, CO |
| 1389.9 | 47.98 | 1,418 m | 1,418 m | 1,410 m | 1,408 | 1,304 | 1,368 | def C=NH ⁺ stretch |
| 1440.3 | 38.81 | 1,443 vs | 1,443 vs | 1,444 diff. | | | | ν_{14} |
| 1461.4 | 33.20 | 1,456 m | 1,456 m | 1,459 ms | 1,462 | | | CH, CN |
| 1486.8 | 82.26 | 1,490 vs | 1,490 vs | | 1,490 | | | CH |
| 1490.0 | 2.91 | 1,497 sh | 1,497 sh | | | | | CC, CN |
| 1587.4 | 63.62 | 1,579 | 1,579 | 1,579 m | 1,577 | 1,459 | 1,460 | CH, OH, CN |
| 1598.4 | 5.53 | 1,594 w | 1,594 w | 1,595 w | 1,596 | 1,470 | 1,488 | CC stretch |
| 1629.4 | 72.05 | 1,623 vvs | 1,623 vvs | 1,622 vs | 1,621 | 1,477 | | Ring, CO |
| 1688.9 | 526.42 | | | | | 1,506 | 1,574 | Ring (ip), C=N stretch |
| 3007 | 7.315 | 3,000 | 3,000 | | | 1,538 | 1,594 | CC stretch, ring |
| 3024.1 | 34.83 | 3,024 | 3,024 | | | 1,650 | 1,620 | -C=N-(R) |
| 3026.0 | 25.15 | | | 3,048 sh | | | | CH ring |
| 3068.4 | 8.05 | 3,058 vs | 3,058 vs | 3,065 vs | | | | |
| 3098.6 | 10.66 | 3,084 | 3,084 | | | | | |
| 3476.0 | 470.20 | 3,438 ms diff. | 3,438 ms diff. | | | | | OH |

m medium, *w* weak, *vs* very strong, *sh* shoulder, *vvs* very very strong, *ms* medium strong

^aFundamental vibration frequencies selected in 3,500–1,000 cm^{-1}

^bA and B denote the value of the fundamental vibration frequency of the species absorbed at 300 nm and 400 nm, respectively (according to assignment of Lee Ho-hi and Kitagawa)



Scheme 2 Proposed ground state conformers of MS1 in solvents of different nature: (a) polar protic, *trans*-closed (OH) form; (b) proton transferred form, *trans*-closed (PT) form; (c, d) polar aprotic and nonpolar solvent *trans*-open form

trum, a high-energy visible band centered at $25,000\text{ cm}^{-1}$ is characterized as an extremely low intensity band in isoctane, while in polar solvent the luminescence was distinctly intensified. The energy difference of the peak positions of the F1 and F2 fluorescence manifested non-common solvent polarity dependence. F1 is blue shifted, and F2 moves to the red in isoctane, as compared to methanol. A similar shift is also observed in the absorption and fluorescence-excitation spectra monitored at the F2 maximum. However, similar observations were made for other anils. In the case of salicylideneaniline derivatives [13], a solvent dependence emission study leads to the conclusion that the shift of the emission maximum is a substituent effect and no general red shift occurs when going from a polar to a non-polar solvent. In the case of spectra, where the long-wavelength band is observable there is a reasonable overlap between this band and the F1 fluorescence. As a consequence, reabsorption of short-wavelength fluorescence occurs.

The IR and Raman fundamental vibration frequencies of the molecules under study are in good agreement with the corresponding data published in the literature [17, 22, 25, 26, 28]. The very strong band at $1,623\text{ cm}^{-1}$ (the calculated frequency values of two high-intensity mode at this range: $1,629$ and $1,688\text{ cm}^{-1}$) is highly mixed and assigned to a mode centered on the conjugated region $-\text{C}=\text{N}-\text{R}$ of the MS1 molecule. Our results are in agreement with Ledbetter's statement that the infrared band at $1,627\text{ cm}^{-1}$ probably consists of the bands at $1,633$ and $1,616\text{ cm}^{-1}$ in the Raman spectrum. In the case of other anils, these bands are assigned to $\nu_{\text{C}=\text{NH}^+}$ and $\nu_{\text{C}=\text{N}}$, respectively. The band of medium intensity at $1,579\text{ cm}^{-1}$ detected in the IR spectrum of

MS1 couples the ring in-plane and $\text{C}=\text{N}$ stretching modes. The $1,490\text{ cm}^{-1}$ mode could derive from the mode of *o*-substituted benzene and can be assigned to a ring mode coupled with the $\text{C}-\text{O}$ stretch. The $1,280\text{ cm}^{-1}$ band of very strong intensity in the IR, which is diffuse in the Raman spectrum, involves a mixture of CC and $\text{C}-\text{O}$ stretch modes. The $900\text{--}1,100\text{ cm}^{-1}$ region characterizes the out-of-plane $\text{C}-\text{H}$ wagging modes. However the strong intensity $1,007\text{ cm}^{-1}$ fundamental involving a $-\text{CN}$ in plane vibration was also observed (Table 1). In the case of $\text{SmA} + \text{MeOH}$ molecular systems, intensity enhancement of intermolecular $\text{OH} \rightarrow \text{O}_{\text{MeOH}}$ and the $\text{N} \rightarrow \text{H}(\text{O})_{\text{MeOH}}$ modes at $3,700\text{--}3,000\text{ cm}^{-1}$ was observed (Fig. 7). As detected for the MS1 molecule, in SmA molecular systems the deformation mode of the central CCNC molecular chain also represents high-intensity mixed mode in the $1,660\text{--}1,700\text{ cm}^{-1}$ range.

Conclusions

The investigated spectral properties of the MS1 strongly indicate that in solution this molecule exists in several forms, which can be interconverted in the absence of light by changing the polarity of the solvent.

Two types of fluorescence of MS1 were detected at room temperature. The excited state favors the proton transfer reaction, so even in non-polar solvents at room temperature well-marked emission peaking at approximately $20,000\text{ cm}^{-1}$ is observed. The *trans*-open and *trans*-closed forms were proposed in addition to the well-known proton transferred form to explain the MS1 spectral behavior in solvents of different polarity. The existence of different hydrogen-bonded forms was supported by the results of ab initio calculations. Interactions of the species investigated with methanol molecules shift this tautomeric equilibrium towards the proton-transferred structure, which is more stable than the structure with the proton bound to the oxygen atom. The interactions of methanol molecules with the rotameric form are sufficient to form a stable non-cyclic structure, which is somewhat less stable than the fully solvated cyclic form. Moreover, the central $-\text{C}=\text{N}-\text{C}-$ flexible fragment governs the conformational changes in the ground as well as the excited electronic states. A spatial "heavy" substituent close to the nitrogen atom acts as a moderator of molecular flexibility.

Computer modeling of the micro-environmentally induced H-bond transformation allows explanations of the spectroscopic properties of anil-type molecule in polar media. Further studies devoted to detailed elucidation of structure and hydrogen-bond interactions of *N*-triphenylmethylsalicylidene imine are in progress.

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