

A distortion of the aromatic character of 7-azaindole in solid-state after its N7 protonation: linear polarized IR-spectroscopy of embedded chemicals in nematic host

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Abstract The effect of N7 protonation on the IR-spectroscopic characteristics in solid-state and aromatic character of 7-azaindole (7AI) are elucidated by means of linear-polarized IR-spectroscopy of oriented colloids in nematic host. A comparison between the data of neutral and protonated form of 7AI is done. The experimental data are supported by theoretical ab initio ones and experimental UV-spectroscopic measurements.

Keywords 7-Azaindole · IR-LD spectroscopy · Solid-state · Protonation effect · Quantum chemical calculations · UV-spectroscopy

Introduction

7-Azaindole (7AI, Scheme 1(1)) is an important bicyclic aza-aromatic molecule. It is with an isoelectronic structure of purine and has a close relationship with the nucleic bases adenine and guanine [1]. 7AI can create two hydrogen bonds by donating the pyrrole proton and accepting a proton at the pyridine nitrogen [2] and can form a stable dimeric form (Scheme 1(2)), which has received a considerable attention since has been recognized as a simple model for the hydrogen bonded base pair of DNA [3]. It could provide information on the possible role of tautomerism in mutation as well [3]. As far as the protonation processes play an important role in whole of the living organisms it is reasonable to understand as well the relationship structure-spectroscopic properties in 7AI. So, in

this work, we are reported the effect on N7 protonation in 7AI (Scheme 1(4)) on the IR-spectroscopic characteristics of the systems by means of solid-state linear polarized (IR-LD) spectroscopy of oriented colloids in suspension of nematic host. A comparison with the characteristics of neutral 7AI is done under the same orientation conditions. Quantum chemical calculations are performed with a view to predict the vibrational characteristics of N7 protonated form of 7AI. In addition the performed UV-experiments supported the conclusions, which are done about the aromatic character distortion of the 7AI after N7 protonation. The role of the protonation on the N_{py}-nitrogen on the IR-spectroscopic data of substituted pyridines has been intensively studied during last decade [6–10], due to the heterocyclics play an important role as template moieties in the design on new organic materials with nonlinear optical properties [6–10].

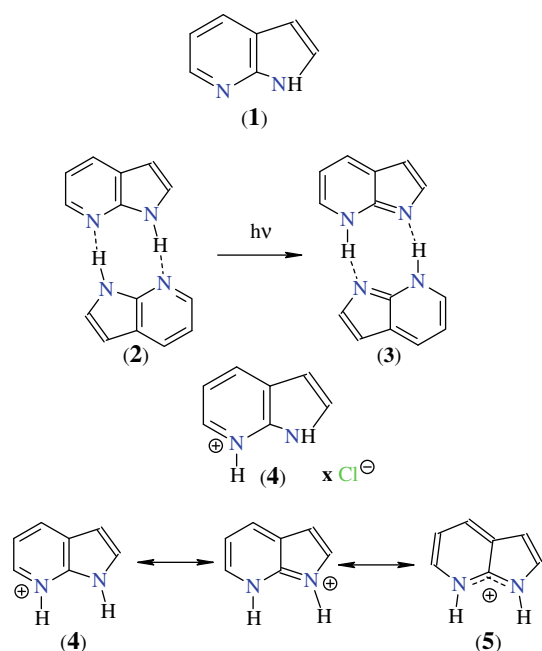
Experimental

Materials and methods

1H-Pyrrolo[2,3-b]pyridine (7-azaindole) was purchased from Sigma–Aldrich (Germany).

Conventional and polarized IR-spectra were measured on a Thermo Nicolet OMNIC FTIR-spectrometer (4000–400 cm⁻¹, 2 cm⁻¹ resolution, 200 scans) equipped with a Specac wire-grid polarizer. Non-polarized solid-state IR spectra were recorded using the KBr disk technique. The oriented samples were obtained as a colloid suspension in a nematic liquid crystal ZLI 1695. The theoretical approach, experimental technique for preparing the samples, procedures for polarized IR-spectra interpretation and the validation of this new linear-dichroic infrared (IR-LD)

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Scheme 1 Chemical diagram of 7AI (1), structure of the dimers in ground (2) and excited state (3) as well as N7 protonated form (4)

orientation solid-state method for accuracy and precision has been presented. The influence of the liquid crystal medium on peak positions and integral absorbances of the guest molecule bands, the rheological model, the nature and balance of the forces in the nematic liquid crystal suspension system, and morphology of the suspended particles also been discussed [4–10]. The application of colloid suspensions in nematic liquid crystal host contribute to the facile IR-spectroscopic and structural elucidation of embedded solid particles. Such an approach was demonstrated in a series of papers, dealing with the characterization of inorganic compounds and glasses and, also, organic and coordination compounds. It was found, that a partial orientation (15–20%) of suspended particles, which was adequate for recording reasonable linearly polarized IR-spectra could be achieved. The procedure was conducted as 5 ± 1 wt% from a given solid compound of average particle size within 0.3–0.9 μm were mixed with nematic liquid crystal substance (ZLI 1695, ZLI 1538 or MLC 6815), which was appropriate for IR spectroscopy studies. The resulting slightly viscous suspension was then phase-pressed between two KBr-plates. Their surface was processed by subsequent “rubbing” in one direction with fine sandpaper (C800, size 5 μm) before use. Both the KBr-plates and the pressed suspension were then processed by 100 times repeated mutual “skidding”, with the average velocity of 3 $\mu\text{m/s}$. The optimum cell thickness was 100 μm . The validation of the orientation solid-state method for accuracy and precision, the influence of the liquid crystal medium on peaks positions and integral

absorbencies of the bands of the guest molecule were given. Moreover, the rheological model, the nature, and the balance of forces, acting on the nematic liquid crystal suspension system as well as the mathematical model, and morphology of the suspended particles were also discussed.

The positive ESI mass spectra were recorded on a Fisons VG autospect instrument employing 3-nitrobenzylalcohol (Sigma-Aldrich) as the matrix.

Ultraviolet (UV) spectra were recorded on Tecan Safire Absorbance/Fluorescence XFluor 4 V 4.40 spectrophotometer operating between 190 and 900 nm, using solvent water in concentration of $2.5 \cdot 10^{-5}$ M (0.0921 cm quartz cells).

Quantum chemical calculations are performed with GAUSSIAN 98 program packages [11]. The output files are visualized by means of the ChemCraft program [12]. The geometries of the protonated form of 7AI were optimized at second-order Moller–Pleset perturbation theory (MP2) and 6-311++G** basis set. Molecular geometries of the studied species were fully optimized by the force gradient method using Bernys’ algorithm. For every structure the stationary points found on the molecule potential energy hypersurfaces were characterized using standard analytical harmonic vibrational analysis. The absence of the imaginary frequencies, as well as of negative eigenvalues of the second-derivative matrix, confirmed that the stationary points correspond to minima of the potential energy hypersurfaces. The calculation of vibrational frequencies and infrared intensities were checked to establish which kind of performed calculations agree best with the experimental data. So, the MP2/6-311++G** data are presented for above discussed modes, where a modification of the results using the empirical scaling factor 0.8929 is made to achieve better correspondence between the experimental and theoretical values. The UV spectra of (4) in the gas phase and in water solution are obtained by CIS/6-311++G** and TDDFT calculations.

The thermal analyses were performed in the 300–500 K region on a Differential Scanning Calorimeter Perkin-Elmer DSC-7, and a Differential Thermal Analyzer DTA/TG (Seiko Instrument, model TG/DTA 300). The experiments were carried out with scanning rate of 10 K/min under an argon atmosphere.

The elemental analysis was carried out according to the standard procedures for C and H (as CO_2 , and H_2O) and N (by the Dumas method).

Synthesis

The 7-azaindolum hydrochloride was synthesized by mixing of 0.1321 g 7AI and 5 ml water solution of HCl with concentration 1 M under continuous stirring and heating at 40 $^\circ\text{C}$ for 1 h. A colourless polycrystalline

sample was obtained from the resulting solution after 2 days. The product was filtered off and dried under air. (Found: C, 54.39; H, 4.55; N, 18.13; $[C_7H_7N_2Cl]$ calcd.: C, 54.38; H, 4.56; N, 18.12%). The most intensive signal in the positive ESI mass spectrum is that of the peak at m/z 119.27, corresponding to the singly charged cation $[C_7H_7N_2]^+$ with a molecular weight of 119.15. The TGV and DSC data in temperature range of 300–500 K show an absence of the included solvent molecules in the polycrystalline 7-azaindolum hydrochloride.

Result and discussion

The non-polarized IR- and difference IR-LD spectra of 7AI oriented as a colloid suspension in nematic host are depicted in Fig. 1. As can be seen a significant degree of orientation of the solid particles are obtained [13–20]. It is valid for the protonated form of the 7AI (see Fig. 4(2)). The polarization IR-spectroscopic data of 7AI oriented as single crystal technique has been reported [21]. However, the isolation of suitable and with high quality crystals of the 7AI hydrochloride (Scheme 1(4)) does not be successful and the application of single crystal X-ray diffraction or different polarization methods for direct orientation of the single crystal, which is a limitation. The precise and adequate interpretation of the IR-spectroscopic characteristics and corresponding changes as a result of N7

protonation require both the neutral and protonated form of 7AI to be elucidating at equal experimental conditions. For these reasons we are presented the IR-LD spectroscopic data of oriented colloid suspensions in nematic host, technique, which is applicable for solids independently of their crystalline or amorphous character [13–20].

As a first step of our investigations we are performed an experimental assignment of the IR-characteristic bands of the neutral 7AI by means of reducing-difference procedure for polarized IR-spectra interpretation, which is appeared a unique method for experimental assignment of the IR-bands [13–20]. In our case we are compared our polarized experimental data with those obtained by detail theoretical analysis, previously reported in [21, 22]. Like other heterocyclics [23], studied by polarization IR-spectroscopy, 7AI is a C_s system and IR-bands are assigned to in-plane (a') and out-of-plane (a'') modes. The transition moments of the first one can be disposed along or perpendicular to main symmetry axis and are eliminated at different dichroic ratio. For these reasons the elimination of the band at 1600 cm^{-1} (a') leads to disappearance of series of a' bands at 1330 , 1284 , 1066 and 900 cm^{-1} (Fig. 2(2)). The application of the reducing-difference procedure to the band at 1583 cm^{-1} leads to vanishing of the bands at 620 , 563 and 428 cm^{-1} belonging to a' symmetry class as well (Fig. 2(3)). The a'' maxima at 800 , 767 , 725 , 605 cm^{-1} are eliminated at equal dichroic ratio (Fig. 2(4)). The obtained data correlated remarkable well with theoretically

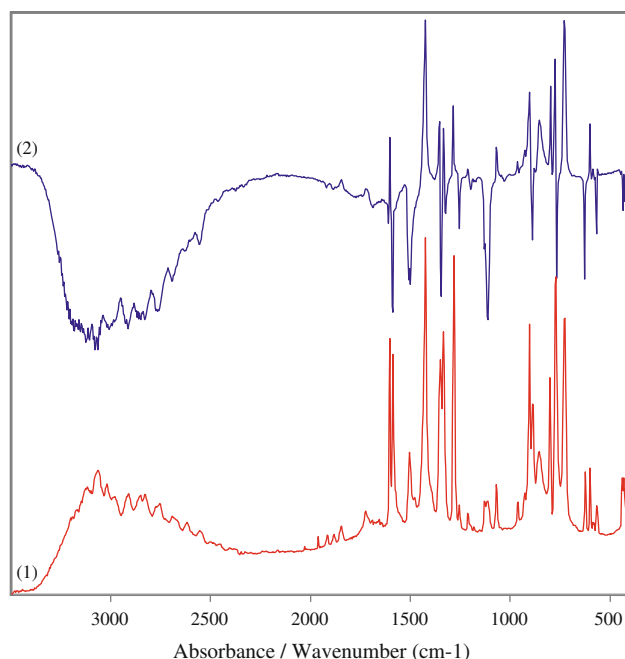


Fig. 1 Non-polarized IR-(1) and difference IR-LD (2) spectra of 7AI oriented as a colloids suspension in nematic liquid crystal

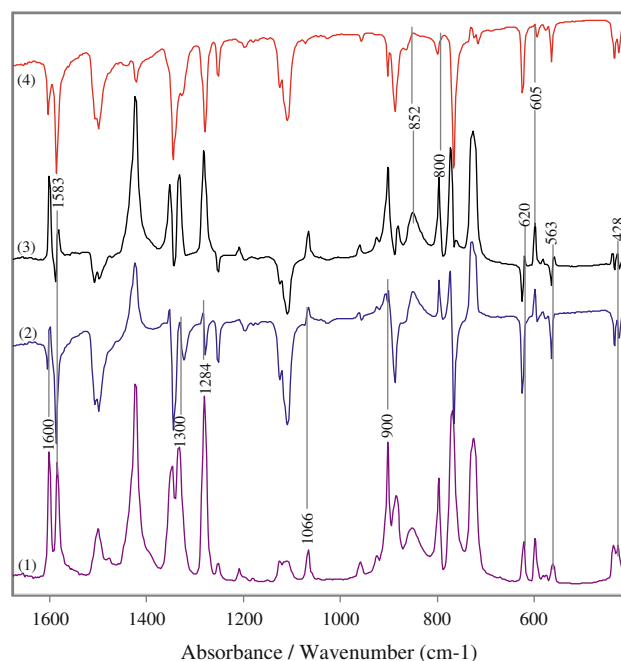
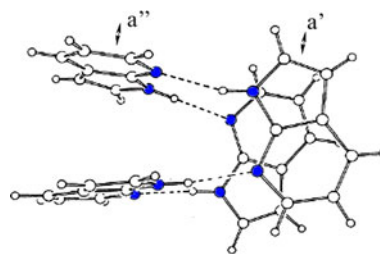


Fig. 2 Non-polarized IR-(1) and reduced IR-LD spectra of 7AI after elimination of the bands at 1600 cm^{-1} (2), 1583 cm^{-1} (3) and 852 cm^{-1} (4)

predicted values [21, 22]. During the last procedure also is eliminated the band at 852 cm^{-1} assigned to out-of-plane ν_{NH} mode of pyrrole ring. The obtained difference in this case of 415 cm^{-1} comparing both theoretical [23] and experimental value is explained with the participation of NH group in very strong intermolecular interactions of $\text{NH}\cdots\text{N}$ type, typical for 7AI in solid-state, where crystallographic data reported a stabilization of tetramer of the compounds studied [24]. The reported self-assembly [24] affected as well on the observation of the broad band within whole $3300\text{--}2700\text{ cm}^{-1}$, more typical for partially of full charged amines. The obtained values correlated well with the other reported theoretical data on 7-azaindole–water complex [25].

In all of the reducing procedure applied the elimination of the given bands are supported by the observation of the second pairs of maxima. As can be seen the elimination of the band at 1583 cm^{-1} , where about 620 cm^{-1} is eliminated a band and in parallel one peak at 624 cm^{-1} is obtained (Fig. 3). Last procedure leads to an elimination of the a'' band at 593 cm^{-1} as well (Fig. 3). As far as in the frame of one molecule the elimination of the a' and a'' maxima is impossible, because of these bands possess different symmetry classes and the corresponding transition moments



Scheme 2 Unit cell of 7AI [24]

are mutual perpendicular oriented. The reason for this result can be explained looking on the crystallographic data for 7AI [24]. The unit cell contains 8 molecules and four of them form tetrameric motif (Scheme 2) of approximately S_4 symmetry. In the frame of this tetramer the transition moments of the out-of-plane modes of two of the molecules can be co-linear disposed with corresponding in-plane modes of the neighboring molecules (Scheme 2).

The N7 protonation of 7AI leads to a dramatic change of the IR-pattern comparing the spectra in Figs. 1(1) and 4. The IR-spectrum of (4) is characterized with a pair of intensive and high frequency shifted bands at 1639 cm^{-1} and 1615 cm^{-1} , which are eliminated in different dichroic ratios (Fig. 5a). The protonation affected in

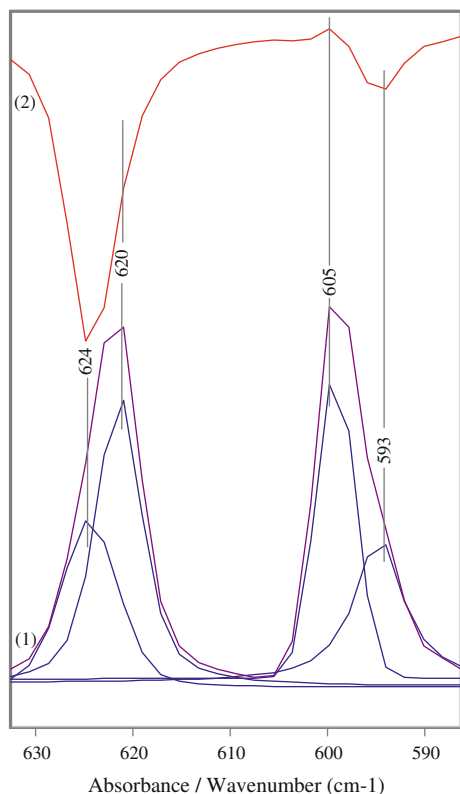


Fig. 3 Curve-fitted IR- (1) spectrum of 7AI within $630\text{--}580\text{ cm}^{-1}$ range and reduced IR-LD (2) one after elimination of the band at 1583 cm^{-1}

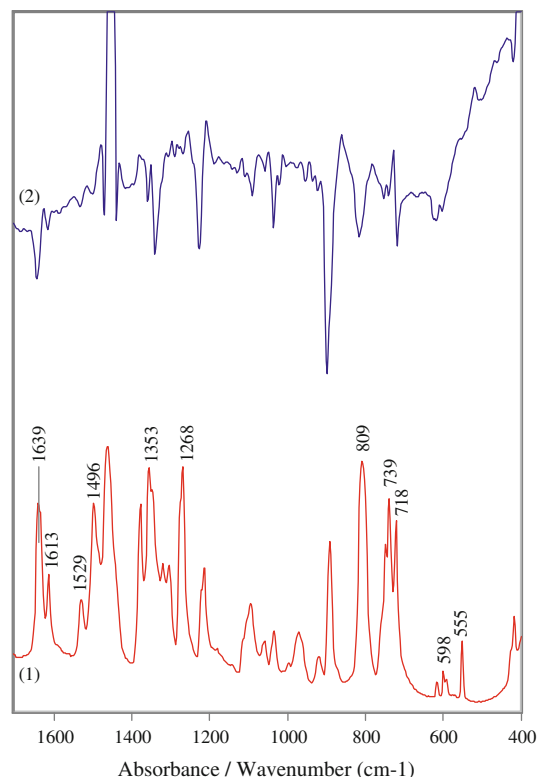


Fig. 4 Non-polarized IR-(1) and difference IR-LD (2) spectrum of protonated 7AI (4)

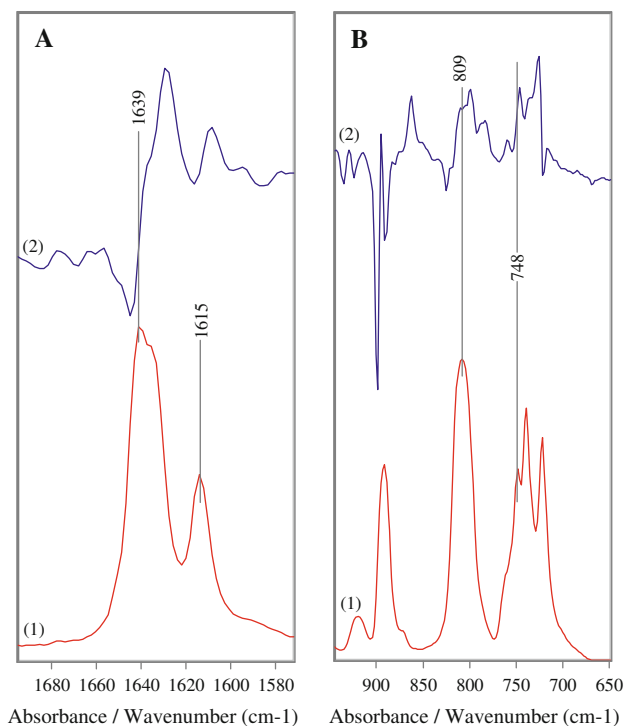


Fig. 5 Non-polarized IR-(1) and reduced IR-LD spectra (2) of (4) after the elimination of the band at 1639 cm^{-1} (a) and 809 cm^{-1} (b)

significant level the a'' bands, which are low frequency shifted and with different IR-spectroscopic pattern. As for example the a'' band at 767 cm^{-1} in 7AI is low frequency shifted with 19 cm^{-1} . The γ_{NH} is observed in (4) at 809 cm^{-1} , value with 50 cm^{-1} lower than corresponding one in (1). A direct proving of the assignment that is done follow from the obtained elimination of last two bands at equal dichroic ratio (Fig. 5b). Within whole $3300\text{--}2500\text{ cm}^{-1}$ are observed a broad band typical for $\nu_{\text{N+H}}$ stretching vibration.

The obtained changes in the IR-spectroscopic pattern of the protonated 4AI are similar to those of 4-aminopyridinium and 3,4-diaminopyridinium cations in solid state, where a quinoid like form is proved. For other substituted aminopyridinium salt the distortion of the aromatic character does not typical. The interesting here is that the N7 protonation affected on the aromatic character of the azaindole ring assuming a stabilization of the form (5) in Scheme 1. Probably the presence of the conjugated pyrrole ring to pyridine one leads to a possible charge redistribution and distortion of the aromatic character in this system. Moreover, a tautomerism (Scheme 1(2) and (3)), observing during the photochemical processes has been proved in the 7AI dimmers [26, 27].

Additional evidence of the assumption stated above follows by the obtained theoretical data about the electronic structure and IR-spectrum of N7 protonated 7AI (Fig. 6).

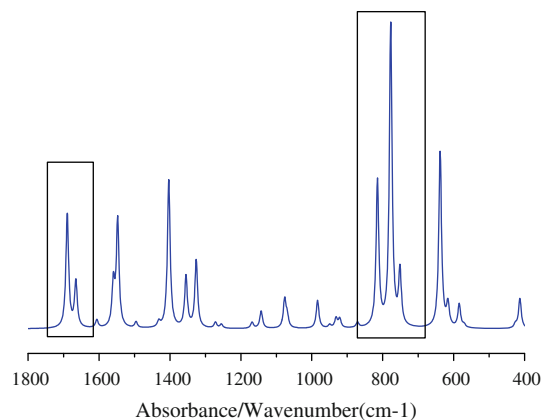
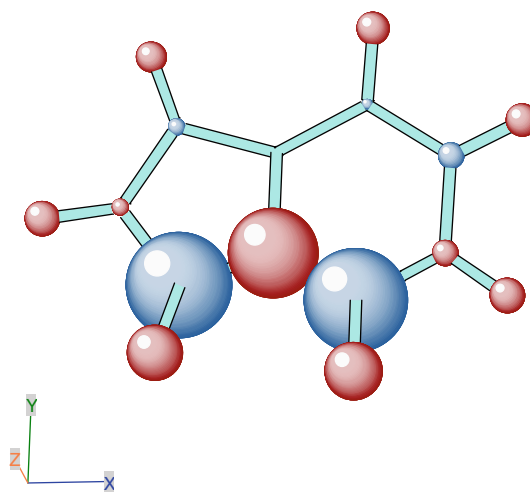


Fig. 6 Calculated IR-spectrum of N7 protonated 7AI

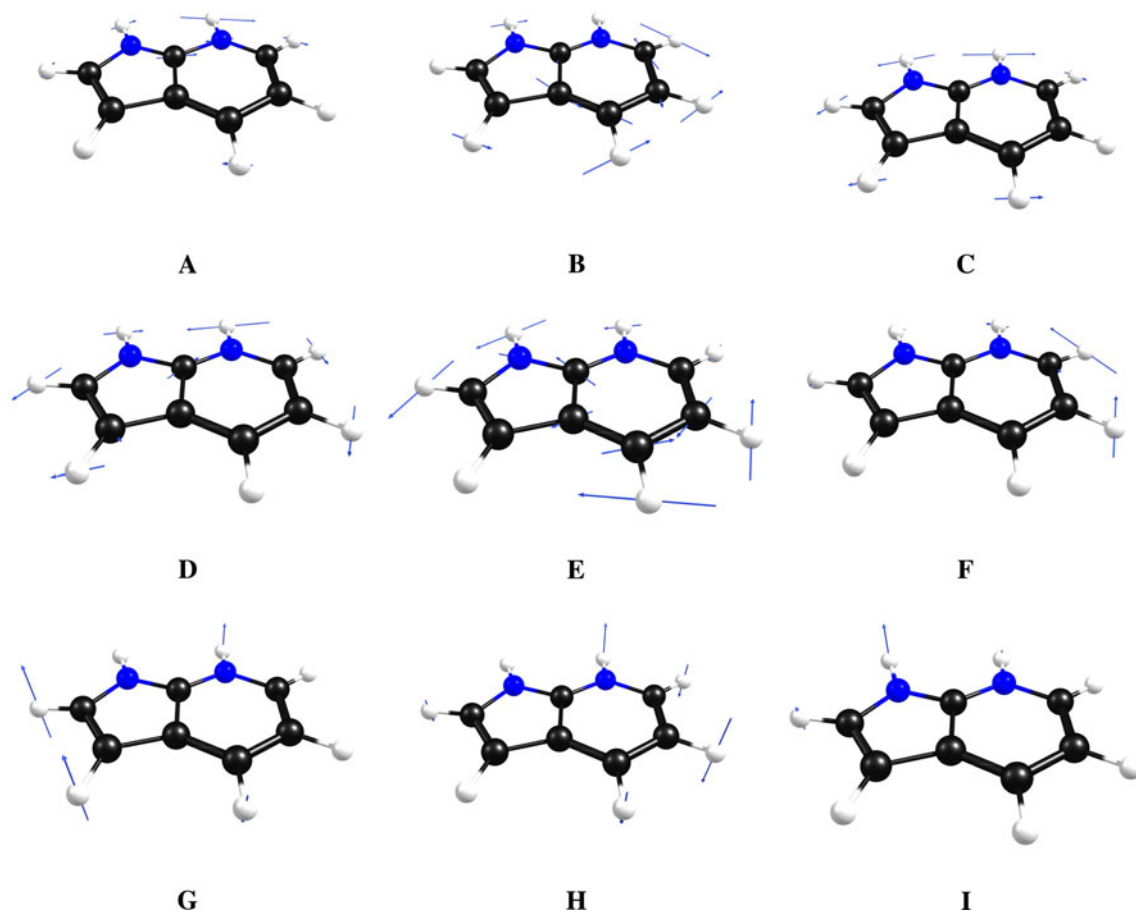


Scheme 3 Single atomic charges in N7 protonated 7AI

Comparing with the data of neutral 7AI, where have been calculated a values of $+1.2\text{ eV}$ of the single atomic charge of the both nitrogens, in the case of N7 protonated form we are obtained a values of $+2.42\text{ eV}$ (Scheme 3), which supported the form presented in Scheme 1(5).

The calculated IR-spectrum (Fig. 6) coincides well with the experimental IR-one of the N7 protonated 7AI (compare Figs. 4(1) and 6). The bands at 1640 and 1619 cm^{-1} belong to $\delta_{\text{N+H}}$ and azaindole a' modes (Scheme 4a and b). The other three bands at 1530 , 1500 and 1457 cm^{-1} are with combination character between δ_{NH} and a' modes (Scheme 4c–e). The bands at 750 , 735 and 720 cm^{-1} correspond to a'' modes (Scheme 4f–h), while the γ_{NH} is predicted at 815 cm^{-1} (Scheme 4i).

The UV-spectra of 7AI (Fig. 7(1)) and its N7 protonated form dissolved in water (Fig. 7(2)) show that the protonation leads to a partial distortion of the aromatic character of the 7AI molecule. A bathochromic shift of the band at 46.103 cm^{-1} and a hypochromic effect of the maximum at



Scheme 4 Selected transition moments in N7 protonated 7AI

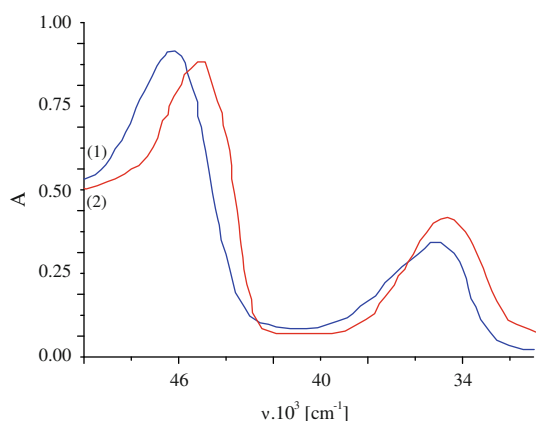


Fig. 7 UV-spectra of 7AI and its N7 protonated form in water

34.10^3 cm^{-1} are observed. The ϵ of the last band increase of the $7,924 \text{ l mol}^{-1} \text{ cm}^{-1}$ to $12,345 \text{ l mol}^{-1} \text{ cm}^{-1}$ after protonation. These data correlated well with theoretical calculated ones where a difference of the λ_{max} of 4 nm is obtained. In the cases of the pyridinium derivatives, where the aromatic character is keep after the protonation the UV-absorption bands are low affected depending the pH.

Conclusion

Polarized IR-spectroscopic study of oriented solids as a suspension in nematic host, theoretical quantum chemical calculations and UV-spectroscopy on the 7-azaindole and its N7 protonated form is performed. The following essential conclusion is done. In solid-state the N7 protonation leads to a partial distortion of the aromatic character of the 7-azaindole ring. This phenomenon can be explain with the presence of the conjugated pyrrole ring to the pyridine one, because of our previous studies on the different substituted pyridines, only in the case of 4-amino-pyridine and 3,4-diaminopyridine, the N_{py} protonation leads to a stabilization of the quinoid like form.

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