Tautomerism Phenomenon of Pyrazolo[3,4-b]quinoline: Spectroscopic and Quantum Mechanical Studies

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Tautomerism of pyrazolo[3,4-b]quinoline (PQ) was studied using electronic absorption and emission spectroscopies in various polar and nonpolar solvents. The absorption spectra of the tatutomers were modeled, and the respective bands were assigned using ab initio quantum mechanical calculations. Temperature-dependent absorption spectra showed the dynamic equilibrium of the two species, which were observed only in aliphatic solvents. The anomalous relative populations of the tautomers were explained by the stabilizing effect of the specific PQ−hydrocarbon interactions. Excited-state intramolecular proton transfer (ESIPT) was proposed to explain the measured fluorescence spectra. Hydrogen bonds that are formed in methanol and benzene were shown to strongly influence the nature of both the absorption and emission spectra.

Introduction

Pyrazoloquinolines constitute an important group of compounds, whose derivatives find numerous practical applications. Two basic structures in this group are pyrazolo[4,3-c]quinoline and pyrazolo[3,4-b]quinoline. Derivatives of the first group have found applications in pharmacology, mainly as selective antagonists for adenosine receptors.[1,2] Derivatives of the latter are used as luminescent and electroluminescent materials.[3] Some PQ derivatives fluoresce with very high quantum efficiencies (over 90%), and their emission occurs in the color range from blue[4] to green.[5] This property makes the compounds of this group very good candidates for the production of organic light-emitting diodes (OLEDs).[6] Some PQ derivatives containing both electron-donor and -acceptor moieties show a strong dependence of their emission on the polarity and viscosity of the environment because of intramolecular charge transfer. They have been applied as fluorescent molecular probes in microenvironment characterization.[7,8]

Both pyrazoloquinoline structures are formally made up of quinoline and pyrazole rings attached in the c or b position. The proximity of nitrogen atoms in the PQ molecule enables proton transfer between these positions and can lead to tautomerism in the pyrazol ring. The phenomenon of proton transfer is under intensive theoretical and experimental study mainly because of its significance in biological systems.[9−12] However, unlike in most widely studied heterocycles,[13] proton transfer in PQ cannot proceed via formation of hydrogen bonds and stable five- or six-membered cycles. To the best of our knowledge, proton transfer in such heterocyclic systems containing two nitrogen atoms in the 1 and 2 positions has not yet been studied by electronic spectroscopies.

To date, different derivatives of PQ have been intensively investigated, whereas the parent compound has been studied rather poorly. Further improvement of the design of PQ derivatives requires more information on the electronic and optical properties of the parent PQ compound. Electronic absorption studies of PQ have already been undertaken,[14,15] but because of the limited experimental data and poor quantum mechanical methods used (semiempirical), the tautomerism phenomenon and possible excited-state intramolecular proton transfer (ESIPT)[16,17] were omitted and not addressed at all. Determination of the mechanism of proton transfer in both the ground and excited states via either intramolecular (ESIPT) or intermolecular fashion is important in explaining many enzymatic reactions and mutation mechanisms. Thus, with its unique structure and properties, PQ might become a novel model compound for these studies.

Computational and Experimental Details

All quantum mechanical computations were carried out using the Gaussian 03 program.[18] Full optimization of the geometries of 1H-pyrazolo[3,4-b]quinoline (1H-PQ) and 2H-pyrazolo[3,4-b]quinoline (2H-PQ) was performed by density functional theory (DFT) with the aug-cc-pVDZ basis and application of the hybrid B3LYP potential.[19] Computations of the singlet-state energies (first 50 states) were carried out in the same basis with the identical hybrid potential by time-dependent DFT (TD−DFT) theory.[20] The influence of solvents was taken into account in the computations using the polarizable continuum model (PCM)[21] with the following values of the dielectric constant (ϵ): benzene, $\epsilon = 2.23$; cyclohexane, $\epsilon = 2.02$; *n*-octane, $\epsilon = 2.00$; and methanol, $\epsilon = 32.63$.

Spectrophotometric-grade solvents, namely, benzene, cyclohexane, *n*-octane, and methanol, from Aldrich were used in the experiments. PQ was synthesized using the method reported by Gupta at al.[22] Steady-state fluorescence measurements were performed using an SLM Aminco 8100 spectrofluorimeter equipped with a thermostated cuvette holder and a low-temperature accessory for measurements in liquid nitrogen (77 K). The concentration of the PQ solutions was in the range of 0.01 mM to ensure that the optical density was below 0.1 at

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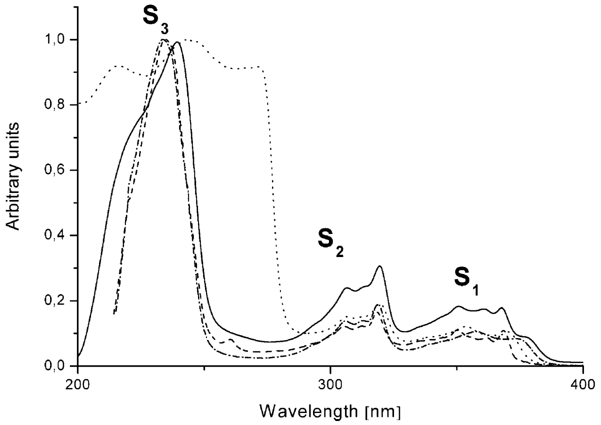


Figure 1. Electronic absorption spectra of PQ in cyclohexane (— — —), *n*-octane (—), benzene (• • •), and methanol (— • — • —).

TABLE 1: Peak Positions in the Absorption Spectra of PQ in Polar and Nonpolar Solvents

	absorption wavelengths (λ, nm)			
	cyclohexane	*n*-octane	benzene	methanol
S_3	234.8	240.0	242.0	233.8
S_2	305.4	305.0	306.0	305.8
	313.4	313.0	312.0	312.8
	318.4	320.0	320.0	318.8
S_1	336.4	–	340.0	–
	350.2	350.0	354.0	357.6
	362.0	360.0	364.0	–
	368.6	368.0	370.0	373.8
	–	378.0	–	–

the excitation wavelengths. The resolution of both the emission and excitation spectra was 1 nm. All spectra were corrected for the instrumental response. UV/vis absorption studies were carried out using an HP 8452A diode-array spectrophotometer equipped with temperature-control accessories. The resolution of the spectra was 2 nm.

Results and Discussion

Absorption Spectra. The spectral properties of PQ depend strongly on the nature of the solvent (vide supra), but in both polar and nonpolar solvents, electronic absorption spectra display three characteristic bands (see Figure 1 and Table 1). The most intense band lying between 200 and 250 nm was assigned as S_3, and two other bands lying in the ranges 280–330 nm and 330–380 nm were denoted as S_2 and S_1, respectively.

Formally, one can distinguish two subsystems in the PQ molecule: pyrazole and quinoline. Upon comparison of the absorption spectra for quinoline and PQ in cyclohexane (Figure 2), a very good concordance of the peaks positions in the 300–320 nm range can be observed. For quinoline, the matching maxima appear for the wavelengths $\lambda_{max}(S_2) = 305$, 311, and 319 nm, which differ from the positions of similar peaks in PQ spectrum by only about 1 nm. This suggests that the S_2 band can be attributed to the $\pi \rightarrow \pi^*$ transition in the quinoline ring of PQ. The position of the maximum of the S_3 band [$\lambda_{max}(S_3)$= 232 nm in cyclohexane] suggests that it might come mainly from the electronic $\pi \rightarrow \pi^*$ excitation localized on the pyrazole ring (λ_{max}= 210 nm, data not shown), given that the corresponding maximum for quinoline is located at much longer wavelength (λ_{max}= 275 nm). The S_1 band cannot be assigned to a localized excitation in any subsystem of PQ; yet, later analysis of the influence of solvents on this state shows that the band might, to a large extent, be the result of excitation of the pyrazole ring. Other types of excitations, in particular, $n \rightarrow \pi^*$, in the measured spectrum of PQ were not observed. This type of excitation does not appear in the spectrum of quinoline,[23] whereas for pyrazole, the band with a maximum at about 270 nm is assigned to the $n \rightarrow \pi^*$ transition.[24,25] Even if such a transition were possible in the PQ molecule, it would be very weak, appearing in the range of the $\pi \rightarrow \pi^*$ excitations and very likely covered by them.

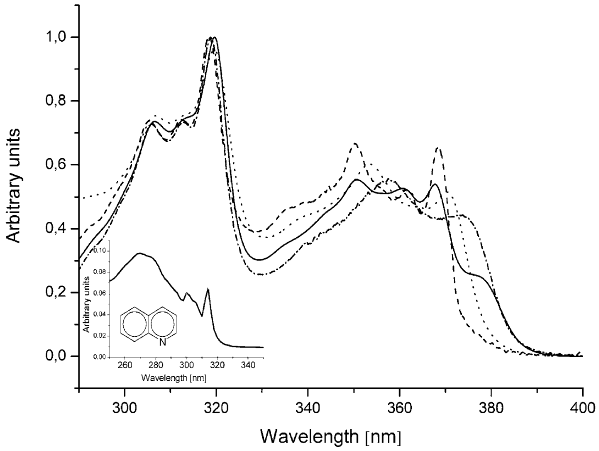


Figure 2. Electronic absorption spectra of PQ in cyclohexane (— — —), *n*-octane (—), benzene (• • •), and methanol (— • — • —) for the S_2 and S_1 states. Inset: Absorption spectrum of quinoline in cyclohexane.

Assignment of the Spectra to PQ Tautomers. As presented schematically in Figure 3, the PQ molecule could theoretically exist in two tautomeric forms: 1H-PQ and 2H-PQ. (The structure with the hydrogen atom attached to the nitrogen at position 9 is energetically unfavorable, as verified by calculations.[26]) The electronic absorption spectra were calculated for both forms in polar and nonpolar solvents and compared to the measured spectra. The computations of the first 50 excited states for both forms are presented in Figure 3 for two example solvents: cyclohexane and methanol. The results of vertical energy computations for the excited states of both PQ tautomers in the selected solvents are presented in Table 2. Only the absorption bands between 225 and 410 nm whose oscillator strengths (*f*) exceeded 0.005 were considered.

The calculations show qualitatively that the spectrum of 2H-PQ is red-shifted in all three bands compared to that of 1H-PQ disregarding the solvent. The most indicative is the shift in S_1 band, but the difference in relative intensities of the transitions within the S_3 band is also significant. In particular, except for the strong transition in the S_3 band for both tautomers, there is also another weak transition, which appears at shorter wavelengths for 2H-PQ than for 1H-PQ. These main observations were later used for the assignment of the specific bands to the respective tautomers and the resolution of the measured spectra.

The calculations also indicate that the ground-state energy is lower for 1H-PQ.[26] In such a case, the form prevailing in solution should be 1H-PQ. However, the difference amounts to only about 8 kcal/mol (3000 cm^{-1}), and it also enables the 2H-PQ tautomer to be populated in solution, as specific solute–solvent interactions can greatly affect the equilibrium of the two tautomeric forms.

The experimental spectra presented in Figures 1 and 2 show that the S_1 band is most sensitive to the nature of the solvent used. For aliphatic solvents such as *n*-octane and cyclohexane, whose dielectric constants are very similar, very similar spectra should also be expected. Nevertheless, a few significant differences point to a specific interaction between PQ and

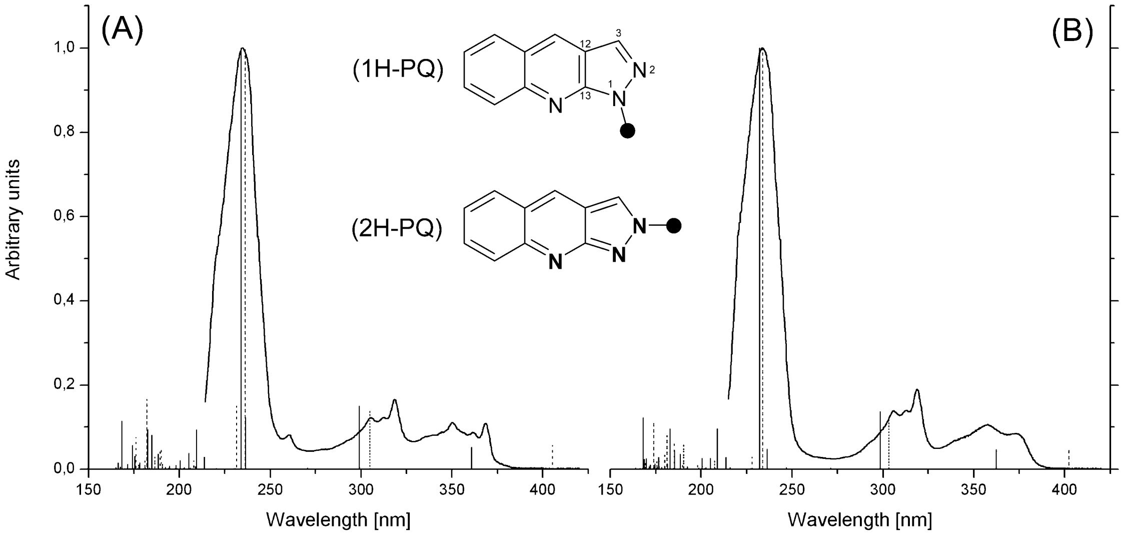


Figure 3. Comparison of experimental and theoretical electronic absorption spectra of PQ in (A) cyclohexane and (B) methanol. Two tautomeric forms: 1H-PQ (—) and 2H-PQ (• • •) were assumed for the calculations.

TABLE 2: Computed Energies (Expressed in Absorption Wavelengths) of Vertical $\pi \rightarrow \pi^*$ Transitions and the Respective Oscillator Strengths for 1H-PQ and 2H-PQ in Selected Solvents

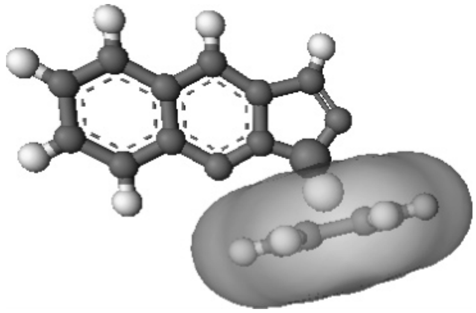
	cyclohexane		*n*-octane		benzene		methanol	
state	λ (nm)	f	λ (nm)	f	λ (nm)	f	λ (nm)	f
				1H-PQ				
S_3	233.8	1.352	233.7	1.365	234.7	1.191	232.2	1.404
S_3	236.4	0.166	236.3	0.148	236.7	0.353	236.3	0.066
S_2	298.9	0.203	298.9	0.201	299.3	0.218	298.4	0.192
S_1	360.7	0.071	360.6	0.070	361.3	0.074	362.2	0.066
				2H-PQ				
S_3	231.4	0.216	231.4	0.231	231.4	0.139	228.0	0.045
S_3	236.3	1.435	236.1	1.417	237.2	1.534	233.8	1.532
S_2	304.7	0.201	304.6	0.198	305.0	0.215	303.3	0.184
S_1	405.2	0.081	405.1	0.081	405.8	0.085	402.1	0.075

n-octane (vide infra). In benzene, despite the comparable dielectric constant, a significant red shift of the vibrational structure appears with some broadening of the band. For methanol, there is a further red shift and the loss of the vibrational structure of the band.

The S_2 band, regardless of the type of solvent, undergoes only slight changes, which suggests an insignificant influence of the environment on the $\pi \rightarrow \pi^*$ transition in the quinoline ring. Similarly, the S_3 bands in the spectra in cyclohexane and methanol are symmetrical and differ only slightly in the position of the maximum (see Figure 1). The spectrum in benzene is distorted below ca. 280 nm because of the superposition of the solvent band in that area.

Interestingly, a considerable asymmetry of the S_3 band appears in *n*-octane solution that might be caused by a different population of the tautomers compared to the situation in the other solvents. Taking into account the calculated relative intensities of the transitions in the S_3 band (see Figure 3 and Table 2) and comparing them with the measured spectrum, one can conclude that the population of 2H-PQ tautomer is larger in *n*-octane than in the other solvents studied. Yet, the most pronounced change is observed for the S_1 band, for which an entirely new band/shoulder appears at 378 nm. This observation is also consistent with the higher population of the 2H-PQ tatutomer, for which the S_1 band should be red-shifted compared to that of 1H-PQ (see calculations). Unlike in 1H-PQ form, the double bonds in the 2H-PQ molecule appear alternately, and there is no possibility of delocalizing those bonds within the quinoline ring. Treating that structure formally as a polycyclic system and comparing it with the $(CH{=}CH)_7$[23] molecule, for which the absorption band appears at $\lambda = 374$ nm provides additional support for the assignment of the mentioned PQ band ($\lambda = 378$ nm) to the 2H-PQ tautomer.

SCHEME 1: Possible Structure of the Hydrogen-Bond Complex between PQ and Benzene



Also, the observed small red shift of the S_2 band in *n*-octane compared to the other solvents indicates the presence of the 2H-PQ tatutomer rather than a solvatochromic shift (compare the theoretical spectra in Figure 3). All of the above-mentioned conclusions indicate the significant population of the 2H-PQ tautomer only in *n*-octane solution, whereas in the other nonpolar solvents (cyclohexane, benzene), the tautomeric equilibrium is strongly shifted toward 1H-PQ. We proposed to explain this phenomenon by specific PQ−octane interactions that stabilize the 2H-PQ form (vide infra).

Similarly, the previously mentioned anomalies of the PQ spectrum in benzene can be explained by the specific solute−solvent interactions. Thus, broadening of the S_1 band in benzene solution compared to the behavior in cyclohexane solution could be caused by the formation of a hydrogen bond between the proton from the NH bond of the pyrazole ring (see Scheme 1) and the delocalized electrons of the benzene ring.[27,28]

Differences in solvent polarities might also partially explain the observations, but theoretical calculations performed for those solvents do not sufficiently support the observed shifts. The vibrational structure of the spectrum is not well-resolved in benzene solution as a result of hydrogen bonds, which might

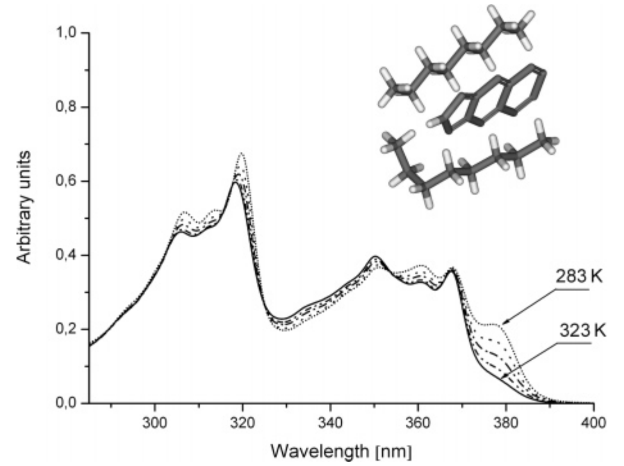


Figure 4. Temperature-dependent electronic absorption spectra of PQ in *n*-octane. Inset: One possible *n*-octane−2H-PQ complex structure.

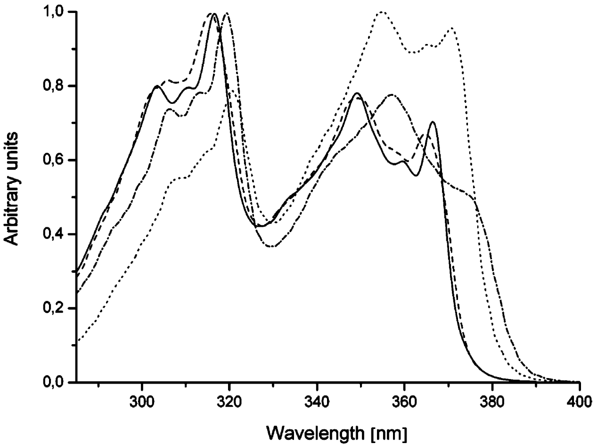


Figure 5. Fluorescence excitation spectra of PQ in cyclohexane (— — —), *n*-octane (—), benzene (• • •), and methanol (— • — • —) for an emission wavelength of 400 nm.

limit vibrations of the pyrazole ring in PQ molecule. Whereas one hydrogen bond affects the vibrational structure in benzene solution, in methanol, two bonds might be involved and be reflected in the experimental spectrum (see Figure 2). The postulated hydrogen bonds do not significantly influence the S_2 band, which was assigned previously to the quinoline subsystem in the PQ molecule.

Temperature-Dependent Absorption Spectra. Temperature-dependent absorption studies performed in *n*-octane in the range of 283−323 K show that, upon lowering of the temperature, the intensity of the shoulder at $\lambda = 378$ nm increases significantly, and the other peaks of the S_1 band also change moderately (see Figure 4). The temperature-dependent spectra show the thermodynamic equilibrium of only two forms of PQ, as can be concluded from the existence of the isosbestic points.

In the S_2 band, the intensities of the vibrational progression rise as the temperature is decreased, and all of the maxima shift toward lower energies. A small red shift is also observed for the S_3 band, accompanied by growth of the shoulder on the left-hand side of the band (data not shown). Taking into account the above-mentioned observations and the simulated spectra for both PQ tautomers (see Figure 3 and Table 2), one can conclude that the population of the 2H-PQ form (red-shifted spectrum) increases as the temperature of the PQ solution in *n*-octane is decreased.

According to theoretical calculations of the ground states of the PQ tautomers, we should rather observe a counter effect: the population of 1H-PQ should increase with decreasing temperature. The observed inversion might be induced by specific solvent−solute interactions (see Figure 4, inset) that favor the 2H-PQ tautomeric form over 1H-PQ and lead to the formation of a solvent cage around the former molecule. The rotational mobility of the *n*-octane chains slows as the temperature is decreased, and the stabilizing effect increases. As the temperature is increased, the enhanced mobility of *n*-octane is sufficient to destroy the weak specific interactions, and the previously blocked proton in position N2 becomes free to transfer to the energetically favored position N1.

The temperature-dependent absorption studies carried out in cyclohexane, benzene, and methanol did not reveal a similar phenomenon, whereas in *n*-hexane, a similar effect was observed, although definitely weaker than that in *n*-octane. These observations support the mentioned hypothesis about the stabilization of the 2H-PQ structure by specific interactions with *n*-octane molecules. Cyclohexane, despite having a similar dielectric constant, does not have any stabilizing effect, and *n*-hexane molecules seem to be to too short to effectively stabilize 2H-PQ. Thus, not only the linear structure but also the size of the solvent molecules that fits the size of the solute are important.

Other possible mechanisms to explain this phenomenon are less plausible. The tautomeric equilibrium is observed only in pure aliphatic solvents; addition of a small amount of methanol (0.1%) to an *n*-octane solution canceled this effect entirely, and the spectrum became identical to that in methanol. (Note that addition of water instead of methanol did not cause any changes. It is likely that water molecules are too polar and are therefore excluded from the solvation of PQ. As a result, they do not have the opportunity to form hydrogen bonds with PQ.) Thus, any possible traces of polar solvents in *n*-octane that could form hydrogen bonds and mediate tautomerization should be ruled out. Similarly, if dimers were populated in the system, one would expect dependence of the spectra on the concentration and some broadening of the bands, which also did not occur (as verified in the 0.001−0.1 mM range).

Fluorescence Spectra of PQ. Fluorescence spectroscopy was applied to further elucidate the system. The fluorescence excitation spectra were captured for different emission wavelengths in the range of 360−470 nm and temperatures between 283 and 323 K. For a given solvent, no significant dependence of the shape of the spectra on the emission wavelength and temperature was observed. These observations suggest that the fluorescence of PQ in solvents around room temperature is due to excitation of only one tautomeric form. There are no additional bands in the excitation spectra compared to the respective absorption bands, which rules out the formation of dimers or higher aggregates of PQ in its ground state. Selected excitation profiles for various solvents and an emission wavelength of 400 nm are presented in Figure 5. Table 3 summarizes the positions of the peaks in both the excitation and emission spectra of PQ.

For *n*-octane solution, in the temperature range of 283−323 K, the excitation profiles are in good agreement with the assigned absorption spectrum of the 1H-PQ tautomer: The band at 378 nm assigned previously to 2H-PQ (absorption spectrum) does not appear in the excitation profile disregarding the temperature and the emission wavelength. This observation can be explained by the much larger fluorescence quantum yield of the 1H-PQ tautomer compared to that of the 2H-PQ tautomer. The situation changes dramatically at liquid nitrogen temperature, 77 K (see Figure 6A). The excitation spectrum measured at this temperature is clearly red-shifted compared to that

TABLE 3: Peak Positions in the Emission and Excitation Spectra of PQ in Polar and Nonpolar Solvents

	cyclohexane	*n*-octane	benzene	methanol
	excitation wavelengths (λ, nm) ($\lambda_{em} = 400$ nm)			
S_2	305.8	303.0	307.4	306.4
	312.4	310.0	313.4	313.0
	319.0	317.0	320.6	319.6
S_1	336.4	−	−	−
	346.0	−	−	−
	350.8	349.0	355.4	357.4
	361.6	360.0	365.0	−
	368.6	366.0	371.0	374.2
	emission wavelengths (λ, nm) ($\lambda_{ex} = 345$ nm)			
	367.0	370.0	382.2	385.5
	374.5	376.0	394.8	402.0
	387.5	390.0		

obtained at room temperature fitting the absorption maxima of 2H-PQ that can be deduced from Figure 4. The band at 378 nm clearly dominates in the excitation spectrum measured at 77 K, suggesting a very high population of the 2H-PQ tatutomer at this temperature. The differences observed in the respective emission spectra (see Figure 6B) also support the postulated presence of the 2H-PQ form in the frozen matrix. The highest-energy peak ($\lambda_{em} \approx 370$ nm), which can be assigned to the 0−0 transition of the 1H-PQ tautomer, diminishes at 77 K, and the fluorescence from 2H-PQ seems to dominate. Interestingly, during prolonged irradiation at 77 K, the peak at 370 nm grows, which might be caused by ESIPT. This can be explained only if there is a barrier in the ground state that prevents 1H-PQ from going back to 2H-PQ, which is apparently the most stable form at low temperature. Nevertheless, precise assignments of the observed emission bands as well as the noticed photoinduced proton transfer require further detailed studies that are beyond the scope of this report. High-resolution fluorescence studies of PQ fluorescence in a Shpolskii[29] matrix are currently in progress.

For the remaining solvents, the S_2 and S_1 bands in the excitation spectra undergo virtually no shift compared to the respective absorption spectra. A significant relative intensity change is visible only in the spectrum recorded in benzene. In the absorption spectrum, the intensity of the S_2 band is greater than that of the S_1 band (see Figure 1), and the reverse effect is observed in the excitation spectrum (see Figure 5). The drop in fluorescence intensity might suggest competitive processes of quenching that are much faster in the S_2 than the S_1 state.

Emission spectra of PQ in benzene and methanol solutions (Figure 7) are red-shifted compared to those measured in aliphatic solvents and lack clear vibrational structure. For polar solvents, the Stokes shift is equal to about 800 cm^{-1} (12 nm), and for nonpolar solvents, it amounts to about 140 cm^{-1} (2 nm). The insignificant value of the Stokes shift for nonpolar solvents shows that both the dipole moment of the excited state and the changes related to reorganization of the solvent cage after excitation are slight. In polar solvents, the formation of hydrogen bonds might have significant influence on the wavelength shift in the emission band. A complete description of the fluorescence response of PQ is the subject of further detailed studies as mentioned above.

Proton Transfer. On the basis of the performed computations, one can explain the observed tautomerization and mentioned ESIPT in a qualitative way.

To a first approximation, the wave functions of the excited states can be described with single-electron configurations. In Scheme 2, HOMO and LUMO molecular orbitals are presented for the two tautomeric structures of PQ.

As shown in the scheme, the calculated differences of the respective energies of the ground and excited states of the PQ tatutomers are not large. Calculations by Alkorta and Elguero[30] (DFT with B3LYP/6-31G* basis set) also showed that PQ1 has a lower ground-state energy than PQ2, but the energetic difference was larger than the value we calculated earlier[26] using the much larger aug-cc-pVDZ basis set. Apparently, the latter calculations are more precise because the separation of the ground-state energies of the tautomers must be rather small. As evidenced experimentally, even weak interactions of PQ with solvent molecules (octane) can invert the relative energy levels.

In the ground state of 1H-PQ, the electron density in the pyrazole ring is localized mainly on the N1 nitrogen atom and partially between the C3 and N2 atoms. The HOMO orbitals of the two tautomers are similar, but the 2H-PQ molecule contains a very acidic proton (low electron density on the N2 atom), which can be transferred from N2 to N1 with only slight reorganization of the electron density. Thus, the scheme qualitatively supports the observed stability of the 1H-PQ tatutomer and the possibility of ground-state proton transfer. As mentioned above, specific interactions of PQ with solvent molecules can lead to the inversion of the states, which is likely the case for *n*-octane.

Proton transfer between the excited states (LUMO orbitals) of the tautomers can be rationalized using similar arguments. The LUMO orbitals are similar, and thus, very little electron density repositioning would be associated with proton transfer between the excited states. Whereas the transfer from the acidic N1 position to the N2 atom should be favorable in a vacuum, the interactions with solvent molecules might change the direction of proton transfer. The calculated energy difference between the excited states is even smaller (1000 cm^{-1}) than that between the ground states (2900 cm^{-1}).

The presented qualitative model allows a coherent explanation of the experimental results, but further experimental and theoretical studies are required to address more quantitatively the postulated specific interaction of PQ with solvent molecules and the proposed ESIPT.

Conclusions

The tautomerism of the PQ molecule, which transfers a proton between two nitrogen atoms in adjacent positions, has been shown and studied for the first time. The phenomenon was evidenced only in linear aliphatic solvents (specifically, in *n*-octane), whereas in other hydrophobic media (cyclohexane, benzene), no effect was observed. The observations were explained by specific solvent−solute interactions that lead to the stabilization of the 2H-PQ tautomer, which is not populated in the other solvents.

The tautomeric equilibrium of PQ in *n*-octane was found to be temperature-dependent on the basis of electronic absorption spectra. Deconvolution of the spectra and assignment of the bands to the respective tautomers was accomplished using quantum-mechanical calculations. The computed excitation energies showed very good agreement with the experimental data for the most intense bands. Only the calculated energy of the S_1 band for 2H-PQ did not fit perfectly the experimental spectrum because of the applied continuum model, which did not take into account specific interactions between solute and solvent molecules.

The absorption and emission spectra in benzene were largely reminiscent of the spectra obtained in methanol despite the very

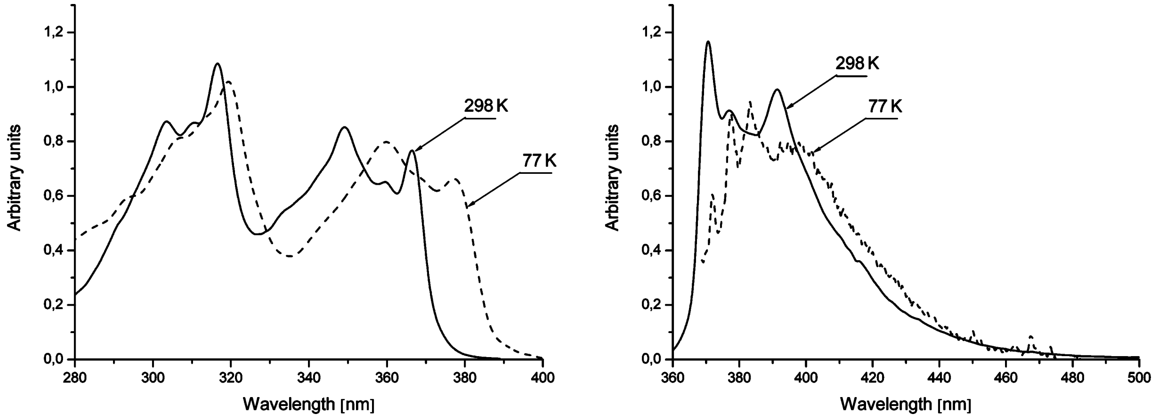


Figure 6. (A) Excitation ($\lambda_{em} = 430$ nm) and (B) emission ($\lambda_{ex} = 350$ nm) spectra of PQ in *n*-octane solution at 298 K and in frozen *n*-octane matrix at 77 K.

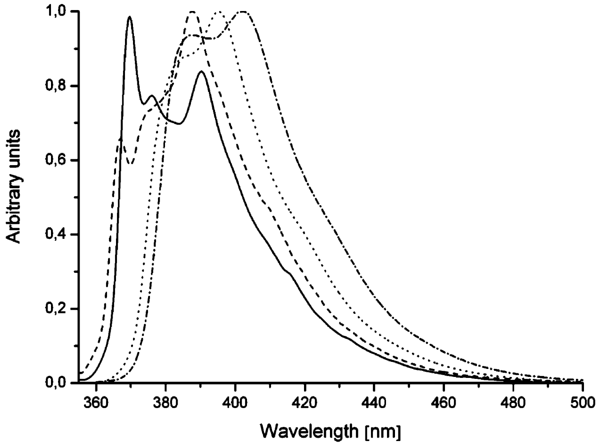
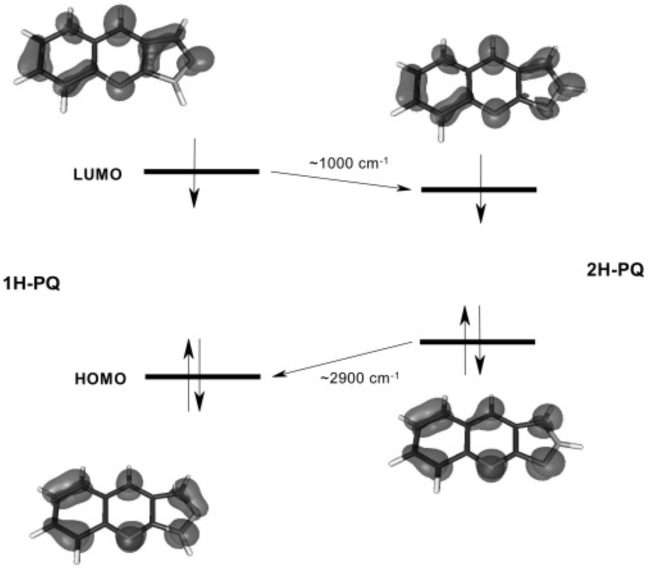


Figure 7. Fluorescence emission spectra of PQ in cyclohexane (— — —), *n*-octane (—), benzene (• • •), and methanol (— • — • —) solutions.

SCHEME 2: Energetic Scheme and Visualization of the HOMOs and LUMOs of 1H-PQ and 2H-PQ in a Vacuum



large difference in the dielectric constants of these solvents. Such a similarity of the spectra, in terms of the spectral shape and positions of the maxima, indicates the considerable influence of hydrogen bonds on the spectral properties of PQ in the studied solvents. A model system containing a hydrogen bond between benzene and the PQ molecule was proposed to account for this observation.

The fluorescence spectra of PQ showed that the emission at room temperature proceeds exclusively from the excited state of one tautomer, 1H-PQ, even in octane solution where the population of 2H-PQ in the ground state is significant. This observation implies the possibility of excited-state proton transfer (ESIPT) in the studied system. This was also evidenced by the increase of fluorescence intensity from 1H-PQ* after irradiation of 2H-PQ, which is the dominant tautomer at 77 K. The reported unusual photophysical properties of PQ are the subject of further studies using high-resolution fluorescence spectroscopy in Shpolskii matrices as well as low-temperature IR spectroscopy.

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