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Hydrogen-Bonding-Induced Phenomena in Bifunctional Heteroazaaromatics

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ABSTRACT

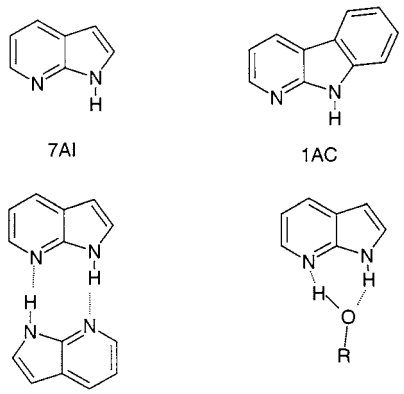
Ground and excited state processes induced by hydrogen bond formation are discussed for a family of heterocyclic compounds which possess both a proton donor (pyrrole NH group) and an acceptor (pyridine-type nitrogen). Excited state double proton transfer and rapid $S_0 \leftarrow S_1$ internal conversion are observed only for molecules capable of forming cyclic, multiply hydrogen-bonded complexes. If the 1:1 cyclic, doubly hydrogen-bonded solvate is present in the ground state, the phototautomerization occurs even in rigid solvents at low temperatures. Internal conversion process requires solvent rearrangement and, therefore, does not proceed in a rigid environment. Another type of fluorescence quenching was also detected, involving photoinduced electron transfer from an excited chromophore to an aromatic hydrogen-bonded acceptor, such as pyridine. In molecules consisting of proton donor and acceptor units linked by a single bond, syn−anti rotamerization caused by hydrogen bonding is observed.

Introduction

It is well-known that the formation of a hydrogen bond (HB) may lead to significant changes in chemical behavior. This is particularly true for the excited-state properties. For instance, diffusional limitations may prohibit a proton-transfer reaction to occur during the lifetime of the excited state, whereas such a process is possible for systems with preexisting intra or intermolecular hydrogen bonds. The phototautomerization phenomena have been discussed in numerous works[1−5] and remain subject of intense research.

A special case is provided by bifunctional molecules that can simultaneously act as HB donors and acceptors. For an appropriate position of both groups, if the HB partner is also bifunctional, it is possible to form HB networks, linking the donor and acceptor. A very well-known case is provided by 7-azaindole (**7AI**), a molecule which forms doubly hydrogen-bonded dimers or complexes with alcohols (Chart 1). Both types of structures undergo excited state double proton transfer (ESDPT) upon electronic excitation.[6,7] The photoreaction is accompanied by the appearance of a low-energy fluorescence band, assigned to the tautomeric species in which the proton is translocated from the pyrrole onto the pyridine nitrogen. Analogous behavior has been detected in a structurally similar 1-azacarbazole (**1AC**).[8−10] The mechanism of the ESDPT process is being heavily discussed, in particular the issue of stepwise versus simultaneous movement of the protons.[11,12] Dimers of **7AI** or **1AC** can also be considered important models of DNA base pairs, since tautomerization may play major role in mutagenesis.[13,14]

Chart 1. 7-Azaindole (7AI), 1-Azacarbazole (1AC), and Cyclic Dimers and Alcohol Complexes of 7AI



In this work, we describe ground and excited state phenomena induced by hydrogen bonding solvents in a series of bifunctional azaaromatic chromophores based on indole, pyrrole, pyridine, and carbazole units (Chart 2). Similarly to **7AI** and **1AC**, these molecules reveal ESDPT in the electronically excited state. However, the phototautomerization rates are completely different. The photoreaction occurs much faster than in **7AI** or **1AC**, due to what could have been considered a minor structural variation—three instead of two bonds linking the donor and acceptor nitrogen atoms. Moreover, various types of complexes are detected, of which one reveals ESDPT, while in the other forms the main channel of S_1 depopulation is a rapid internal conversion (IC) to the ground state.

In the compounds that consist of a HB donor and acceptor moieties linked by a single bond, syn−anti isomerization is possible. This phenomenon may be induced by dual HB formation, a process that can reverse the energy ordering of syn and anti forms. The rotamerization has important photophysical consequences, since the anti form cannot undergo fast depopulation processes, characteristic for the syn structure.

Finally, a phenomenon of photoinduced electron transfer promoted by HB formation with an azaaromatic proton and electron acceptor, such as pyridine, will be discussed.

Jacek Waluk was born in Warsaw, Poland, studied chemistry at Warsaw University, and received his Ph.D. in 1979 and D.Sci. in 1987 at the Institute of Physical Chemistry, Polish Academy of Sciences. Since 1991 he has been Head of the Photochemistry and Spectroscopy Laboratory of this institute and, since 2000, Professor of Chemistry at Cardinal Stefan Wyszyński University, Warsaw. His scientific interests include physical organic chemistry (proton and electron transfer, structure and reactivity of azaaromatics and porphyrin isomers, hydrogen bonding, conformational equilibria), spectroscopy and photophysics (electronic absorption/emission, IR/Raman, matrix isolation, linear and magnetic circular dichroism, time-resolved techniques), and theoretical chemistry. Dr. Waluk has visited at the Universities of Utah, Austin, Boulder, Copenhagen, Roskilde, and Berlin, the Colorado School of Mines, NREL. He has been the author or a coauthor of above 130 publications. In 2000 and 2002, he was elected Chairman of the European Photochemistry Association.

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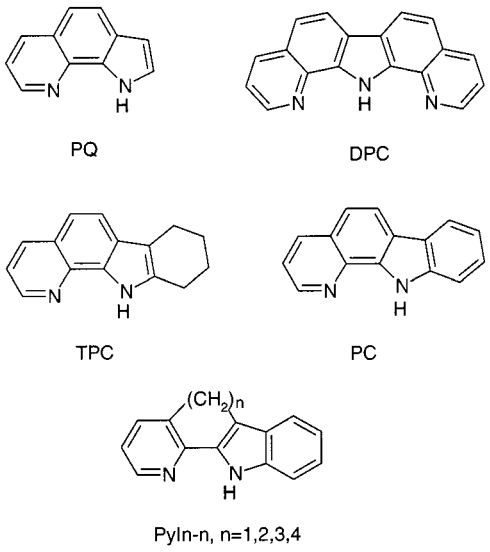
Chart 2. Examples of HB Donor−Acceptor Compounds: 1*H*-Pyrrolo[3,2-*h*]quinoline (PQ), Dipyrido[2,3-*a*:3′,2′-*i*]carbazole (DPC), 7,8,9,10-Tetrahydro-11*H*-pyrido[2,3-*a*]carbazole (TPC), 11*H*-Pyrido[2,3-*a*]carbazole (PC), and Methylene-bridged 2-(2′-pyridyl)indoles (PyIn-n)



This process is not specific for bifunctional molecules and was also detected for chromophores possessing only a donor NH group.

Excited State Double Proton Transfer

In nonpolar and polar aprotic solvents, all the molecules depicted in Chart 2 reveal intense fluorescence. In alcohols, the situation is completely different. The emission is weak; moreover, dual fluorescence is observed, as illustrated for dipyrido[2,3-*a*:3′,2′-*i*]carbazole (**DPC**) in Figure 1. The low-energy band, F_2, has been attributed to the tautomeric species, in which the proton has been shifted from the pyrrole onto the pyridine-type nitrogen atom.[15−17] The driving force for this reaction is provided by large pK_a changes in the lowest excited electronic singlet state. For instance, it has been shown for 1*H*-pyrrolo[3,2-*h*]quinoline (**PQ**) that, upon excitation, the pyridine nitrogen becomes much more basic ($\Delta pK_a = +9.6$); the acidity of the NH group is also strongly enhanced ($\Delta pK_a = -6$).[16] As long as the activation energy remains high, these thermodynamic factors are not sufficient to ensure that the proton transfer will take place during the lifetime of S_1. The process is facilitated in alcohols by the formation of complexes in which one solvent molecule simultaneously acts as a hydrogen bond donor and acceptor. The structure of such 1:1 cyclic, doubly hydrogen-bonded species is shown for **7AI** in Chart 1.

At first glance, the dual character of luminescence in **7AI** and in the compounds depicted in Chart 2 suggests a similar mechanism of the excited-state photoreaction in these molecules. However, closer examination of spectroscopy and photophysics reveals meaningful differences. For alcohol solutions of **7AI** and **1AC**, lowering of temperature leads to disappearance of F_2, the low-energy fluorescence band. The F_2/F_1 intensity ratio is dependent

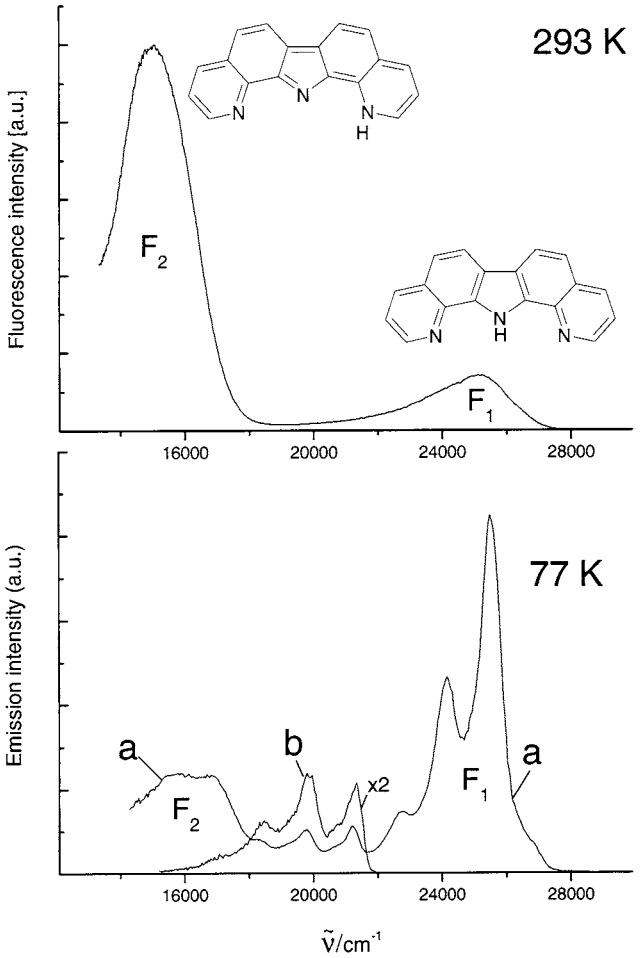


FIGURE 1. Top: room-temperature emission of **DPC** in propanol-1, revealing the fluorescence of the initially excited form (F_1) and of the tautomeric species (F_2). Bottom: total emission at 77 K (a), phosphorescence spectrum (b).

on alcohol viscosity.[18] On the contrary, in **PQ** and **DPC** the F_2 emission is still observed in rigid glasses at temperatures as low as 77 K (Figure 1). Phosphorescence is also detected, located between the F_1 and F_2 fluorescence bands. The excitation spectra taken at 77 K show that two different ground-state species are responsible for this unusual luminescence pattern: the "normal" F_1 emission and phosphorescence have the same precursor, whereas the tautomeric emission occurs from another type of complex.[15] Thus, only "correctly" solvated molecules are able to tautomerize at low temperatures. Since no F_2 fluorescence is observed in **7AI** at 77 K, it is logical to conclude that the cyclic 1:1 structure of the solvate can only be achieved in this molecule upon electronic excitation, whereas in **PQ** or **DPC** such forms already exist in the ground state.

This idea has been corroborated by the results of measurements of F_1 decay and F_2 rise profiles. In **7AI**, the F_1 fluorescence decays in a few hundred picoseconds, the exact value depending on the alcohol.[19] The monoexponential decay time is the same as the rise time of F_2. In **PQ**, **DPC**, and 7,8,9,10-tetrahydro-11*H*-pyrido[2,3-*a*]carbazole (**TPC**), the F_1 decay is not monoexponential.[20] It consists of a short component (a few ps) and a long

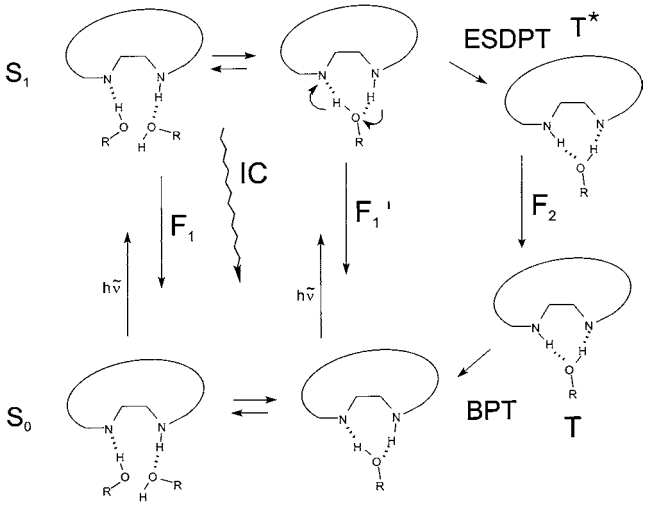


FIGURE 2. Scheme showing equilibria between various types of complexes and excited-state deactivation channels. BPT denotes back proton transfer, other acronyms are explained in the text.

component (tens of picoseconds in less viscous alcohols, more than a hundred in more viscous ones). Only the short component, not much dependent on the nature of the alcohol, is observed in the rise of F_2 and is therefore assigned to a cyclic 1:1 complex, a ground-state-preformed species.

The general picture thus corresponds to a dynamic equilibrium between cyclic and noncyclic solvates, with the former having a very small barrier for ESDPT (Figure 2). In the latter, the photoreaction is not possible without solvent rearrangement around the excited chromophore. This solvent relaxation process is connected with a rapid nonradiative internal conversion to the ground state, described in the next section.

It is to be expected that phototautomerization in correctly solvated species may involve tunneling. Indeed, an isotope effect, more pronounced at lower temperatures, has been observed.[20]

The huge differences in the rate of excited state formation of the tautomeric species reflect different photoreaction mechanisms. In **7AI** or **1AC**, solvent rearrangement around the excited chromophore is required prior to ESDPT, whereas in molecules with **PQ** topology, properly solvated structures are present already before the excitation.

The origin of different propensities to form cyclic 1:1 species is due to slightly different topologies of **7AI** and **PQ**-type molecules. In the former, the HB acceptor and donor groups are separated by two bonds, as compared to three in the latter, which results in a much more linear character of the two hydrogen bonds in the cyclic 1:1 complex. Interestingly, in the dimers the situation is reversed: **7AI** and **1AC** can form much more linear hydrogen bonds than the derivatives of **PQ**. The tendency to undergo ESDPT in dimers should thus be opposed to that found in the alcohol solvates. Indeed, the tautomeric fluorescence has been observed in solid **1AC** at a temperature as low as 1.5 K.[10] Crystalline **1AC** consists of planar, doubly hydrogen bonded cyclic dimers, whereas

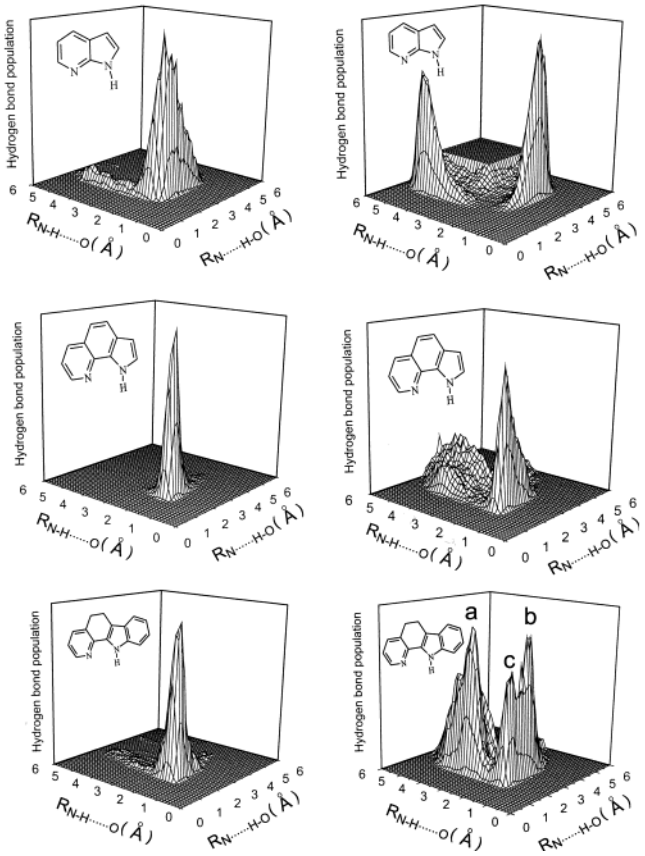


FIGURE 3. Results of MD simulations for **7AI**, **PQ**, and **PyIn-2** in *n*-hexane containing 1 molecule of methanol (left) and in bulk methanol (right).

in solid **DPC**, the two molecular planes are tilted with respect to each other. No ESDPT has been detected in the latter, even at room temperature.[21]

Simulations of the structure of ground-state alcohol and water complexes have been performed using molecular dynamics (MD).[22] Three molecules have been selected: (1) **7AI**, for which the experiments suggest the lack of cyclic 1:1 species in bulk alcohols; (2) **PQ**, for which the majority of complexes is of cyclic type; (3) **PyIn-2**, in which the cyclic species seem to be present in smaller amounts than the noncylic ones. The results are shown in Figure 3. HB distance distribution is used, representing the probability of a simultaneous occurrence of a pair of NH···O and N···HO distances. The values of these distances provide a criterion for distinguishing between cyclic and noncyclic solvates. The complex is considered cyclic when both distances are simultaneously smaller than a certain value (2.2 and 2.5 Å have been used;[22] the population maxima occur at around 1.8−2.0 Å). The computations that simulate adding minute traces of alcohol to nonpolar solutions predict a similar structure, a cyclic 1:1 species in all cases, even though the **7AI** solvate is definitely less "rigid". The situation changes dramatically for the simulation of bulk alcohol solutions: no cyclic 1:1 solvates whatsoever are obtained for **7AI**, whereas for **PQ** this form remains dominant. For **PyIn-2**, both cyclic and noncylic species are predicted to exist (cf. forms a, b, and c in Figure 3), the noncyclic ones in larger amounts. These

conclusions are in perfect agreement with the experimental data and with previous Monte Carlo and MD calculations for **7AI**, **1AC**, and **DPC**.[23]

In summary, both experimental and theoretical results show that the rate and thus, the efficiency of ESDPT in solvates of bifunctional HB donor/acceptor molecules depend on the specific structure of the hydrogen bonds to the solvent. Cyclic 1:1 species are predestined for a rapid phototautomerization, which cannot be stopped even in a rigid, low-temperature environment. On the contrary, for noncyclic solvates solvent rearrangement is required; as a consequence, the reaction becomes slower; moreover, it can be stopped by increasing solvent viscosity.

Fluorescence Quenching by Specific HB Solvation

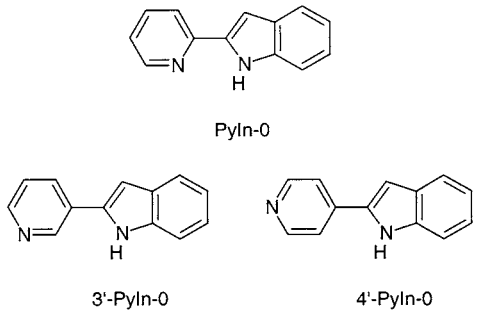
Even though ESDPT in **PQ** and related molecules only occurs in cyclic 1:1 complexes, formation of the other types of solvates also has a dramatic impact on the excited state properties. In comparison to the behavior in aprotic solvents, the fluorescence of HB complexes is weaker and shorter-lived. The excited state lifetime strongly depends on the alcohol viscosity and, thus, on temperature. At sufficiently low temperatures, where the environment is rigid, the radiative properties of the chromophore are recovered.

By using transient absorption spectroscopy, it was demonstrated that the quenching of fluorescence is due to enhanced rate of the $S_0 \leftarrow S_1$ internal conversion.[24,25] In alcohols, the process becomes much faster than $T_1 \leftarrow S_1$ intersystem crossing, the latter being a dominant S_1 nonradiative depopulation channel in aprotic media. As a result, no triplet population is observed in liquid, nonviscous alcohols.

It was found that the rapid internal conversion is only observed in bifunctional molecules. The process is absent when the chromophore lacks one of the HB centers, e.g., in 2-phenylindole, or in 2-(2′pyridyl)indoles for which the NH hydrogen is replaced by a methyl group. This finding implies that both centers are involved in the quenching and that the mechanism of the process is different from those postulated previously to account for the quenching observed in singly hydrogen-bonded chromophores.[26] A plausible explanation is similar to a recently proposed "unsuccessful chemical reaction mechanism".[27] According to this model, which was put forward for the case of an excited-state single hydrogen transfer process, the "downhill" movement of the proton in the excited state leads to a configuration corresponding to a large destabilization of the ground-state energy. S_0-S_1 conical intersection may thus occur, which rapidly brings the excited molecule back into the ground state.

A structure that seems most probable for the elucidation of the nature of the rapid IC process is a 1:2 complex, with one alcohol molecule hydrogen-bonded to the NH group and the other attached to the pyridine nitrogen (see Figure 2). If these two alcohol molecules additionally form a hydrogen bond among themselves, a cyclic bridged structure results, which, in principle, can take part in phototautomerization. However, the process now requires a correlated shift of three protons, a highly improbable event, given that the cyclic 1:2 complex is much less rigid than its 1:1 counterpart. Therefore, the dissipation of the excited state energy along the proton transfer path seems highly probable. Somewhat similar models have been proposed to explain the proton transfer along solvent bridges in 7-hydroxyquinoline[28] and the energy dissipation in **7AI**.[29,30] What remains to be explored is the role of different electron density distribution and minor geometry differences along a series of structurally similar molecules.

Chart 3. 2-(2′-Pyridyl)indole (PyIn-0), 2-(3′-Pyridyl)indole (3′-PyIn-0), and 2-(4′-Pyridyl)indole (4′-PyIn-0)



The hypothesis of the crucial role of 1:2 complexes in the nonradiative S_1 decay is confirmed by the comparison of properties of isomeric pyridylindoles (Chart 3). In 2-(3′-pyridyl)indole (**3′-PyIn-0**), it was shown that the preferential stoichiometry of alcohol solvates is 1:2, as expected from the fact that the two hydrogen bonding centers are too far apart to form a cyclic 1:1 complex.[31] The fluorescence of this molecule is strongly quenched in alcohols, but no trace of the tautomeric emission can be found. In turn, 2-(4′-pyridyl)indole (**4′-PyIn-0**) emits exceptionally strong fluorescence in both aprotic and alcohol solvents; no quenching whatsoever is detected in the latter. The electronic absorption spectra show that both **3′-PyIn-0** and **4′-PyIn-0** form complexes with alcohols. Thus, the proximity of two alcohol molecules bound to the same chromophore in **3′-PyIn-0**, and thus able to form a 1:2 cyclic complex, enables the quenching. In principle, larger complexes with more than two alcohol molecules bridging the two centers are possible in **4′-PyIn-0**. The lack of the nonaradiative process in this molecule provides an argument against the presence of such forms.

One can conclude that the "successful" and "aborted" excited state proton transfer processes are complementary to each other. Which of them is dominant depends on the relative fractions of differently hydrogen-bonded ground-state solvates. These, in turn, seem to be very sensitive to minor structural details, as witnessed by the results obtained for molecules with the same topological motif of HB donor/acceptor location (Chart 2). For **PQ**, **DPC** or **TPC** the cyclic 1:1 species are dominant. In 3,3′-dimethylene-2-(2′-pyridyl)indole (**PyIn-2**) they are outnumbered by other type of solvates, similarly to 11*H*-pyrido[2,3-*a*]carbazole (**PC**), where only a very small

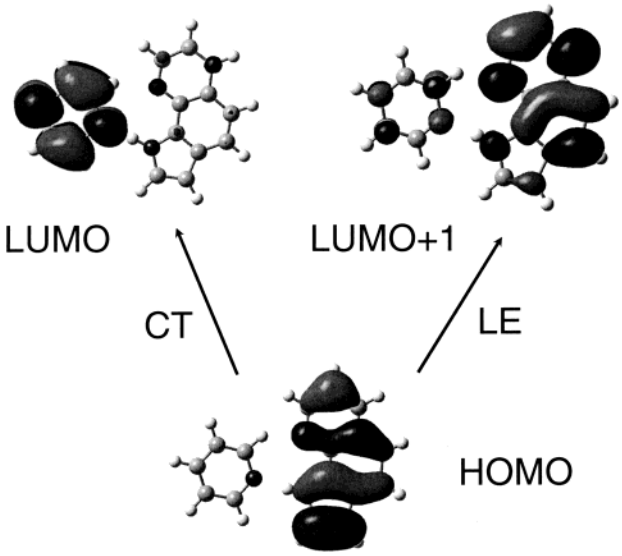


FIGURE 4. Molecular orbitals involved in low-lying LE and CT states of **PQ**:pyridine 1:1 complex. The structure was optimized using B3LYP/6-31G**.[33]

amount of such form is present, as evidenced by extremely weak tautomeric fluorescence. No tautomeric fluorescence could be detected at all in unbridged 2-(2′-pyridyl)indole (**PyIn-0**).

Fluorescence Quenching by Electron Transfer

Not only hydroxylic solvents are efficient in the fluorescence quenching of **PQ** and related molecules. Upon adding pyridine to a nonpolar solution, emission intensity decreases.[32,33] At the same time, the absorption spectra reveal isosbestic points, indicative of complex formation. These complexes, of 1:1 stoichiometry, are formed due to hydrogen bonding between the NH group and the pyridine nitrogen. Ground-state complex formation also occurs for other HB acceptors, such as dimethyl sulfoxide, or amines, e.g., morpholine and piperidine. However, no quenching is observed in these cases. Morpholine and piperidine are much stronger bases than pyridine, but the latter is easier to reduce. This suggests that the quenching may be due to electron transfer. Indeed, using quinoline, a better electron acceptor, instead of pyridine, results in stronger quenching.

The TD-DFT calculations of excited electronic states of isolated **PQ** and of its complexes with pyridine predict that in the complex, a low-lying transition of CT character is present, close in energy to the locally excited (LE) S_1 state (Figure 4). The charge is transferred from the **PQ** moiety onto the pyridine ring. The much larger dipole moment of the CT state with regard to that of the LE state may lead to stabilization of the former with respect to the latter in polar solvents.

The mechanism of fluorescence quenching is shown in Figure 5. Formation of the HB complex is a prerequisite for the subsequent charge transfer. In contrast to the case of quenching by alcohols, which is only efficient in bifunctional molecules, the deactivation now occurs also in molecules with just one HB center, the NH group. Thus,

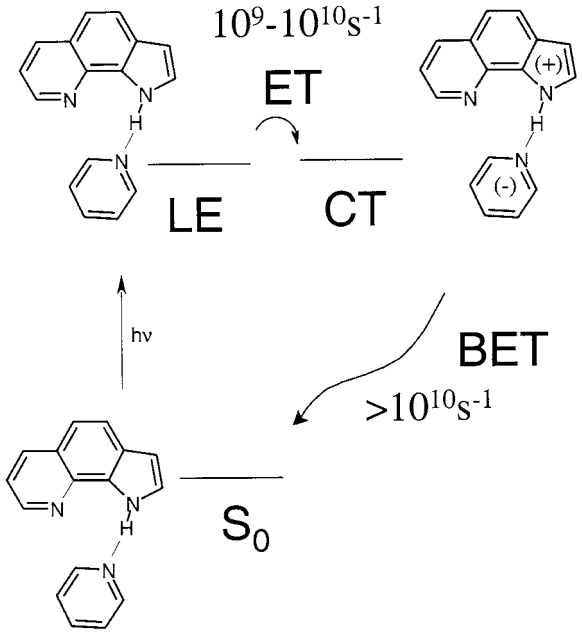


FIGURE 5. The mechanism of fluorescence quenching by electron transfer (ET) in the **PQ**:pyridine complex. LE and CT indicate locally excited and charge transfer states, respectively. Back electron transfer is denoted as BET.

the emission is quenched in such molecules as 2-phenylindole and its derivatives, but not in the *N*-methyl substituted pyridylindoles. Lack of intensity decrease in the latter excludes a possibility of quenching via non-hydrogen-bonded exciplexes, whose existence could have been expected for indole derivatives.

Systematic studies of twenty-odd different molecules have shown that the rate of the quenching, and thus of the ^{1}LE → ^{1}CT state conversion, becomes faster for molecules with the larger equilibrium constant for ground-state complexation, and thus with the stronger hydrogen bonds.[33] The search for transient absorption originating in the ^{1}CT state was unsuccessful, which suggests that the charge transfer state is deactivated faster than it is formed. For the same reason, no indication of proton transfer from the NH group toward the negatively charged pyridine moiety was found.

Solvent-Induced Rotamerization

The processes described above demonstrated the influence of hydrogen bonding upon the excited-state behavior. For a class of molecules in which the HB donor and acceptor groups are located in separate parts, linked by a single bond, use of alcohol solvents also leads to interesting consequences for the ground-state structure.[31] In **PyIn-0**, the pyridine nitrogen and the indole NH group may be located either on the same, or on the opposite sides of the molecule. These two positions correspond to syn and anti forms, respectively. The calculations predict that in the isolated molecule the syn form should be more stable by about 5 kcal/mol. Indeed, in aprotic solvents, both nonpolar and polar, only the syn form is detected. However, in alcohol solvents, syn → anti rotamerization

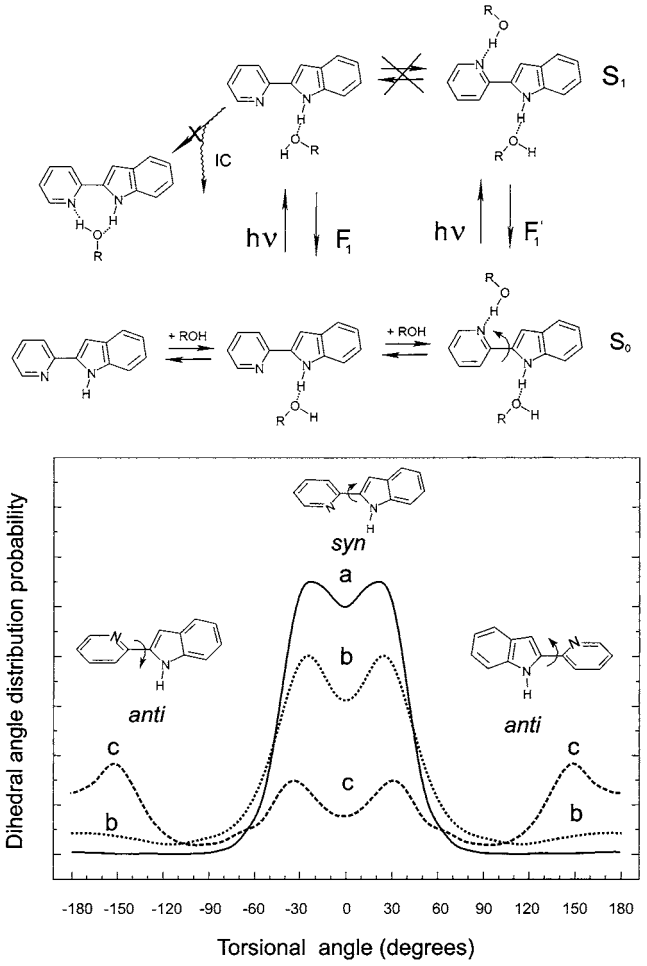


FIGURE 6. Top: scheme of ground and excited-state equilibria between syn and anti rotamers of **PyIn-0**. Bottom: results of MD simulations for three different solvents: *n*-hexane (a), chloroform (b), and methanol (c).

occurs, and the anti form is present in a 4-fold excess over the syn structure. This has significant implications for the photophysics, since neither the ESDPT or enhanced internal conversion can occur in the anti form. Therefore, the two rotamers can easily be spectrally distinguished, not only due to slightly different positions of the emission maxima but, most of all, because of very different fluorescence quantum yields and lifetimes.

The driving force for rotamerization is provided by two different factors: (i) specific hydrogen bonding interactions, which seem thermodynamically more favorable in the anti form, where the donor and acceptor groups are bound by separate alcohol molecules; (ii) a substantial dielectric constant of alcohols, stabilizing the anti structure, which has a larger dipole moment than the syn form.

Molecular dynamics simulations have been performed for **PyIn-0** in three solvents: hexane, CCl_4, and methanol.[31] The results, presented in Figure 6, confirm the experimental picture: in alcohol, the majority of molecules are in the anti form, whereas the opposite is true for the other two solvents.

The phenomenon of solvent-induced rotamerization seems quite general, as is revealed by our current studies of an isomer of **PyIn-0**, 2-(2′-pyrrolyl)quinoline, 2-(2′-pyrrolyl)-1,8-diazanaphthalene, and by the simplest molecule of the series, 2-(2′-pyridyl)pyrrole.

Summary and Conclusions

The above examples show that a careful design of hydrogen bonding topology in chromophores with multiple bonding sites may lead to structures showing completely different photophysical characteristics in different environments. In protic solvents, excited-state tautomerization can be controlled by changing the positions of the donor and acceptor relative to each other. For instance, moving the pyridine nitrogen just one bond away from the NH group, as in **3′-PyIn-0**, eliminates the possibility of ESDPT, but maintains the propensity for efficient internal conversion in hydroxylic solvents. A further shift by one bond, from **3′-PyIn-0** to **4′-PyIn-0**, results in the recovery of strong emission.

The possibility of applyng the bifunctional molecules as probes is obvious. In a recent work, we used fluorescence characteristics to probe the hydrophilic versus hydrophobic character of surfaces of graphite, paper, and wool.[21]

Finally, careful analysis of structures capable of, or unable to tautomerize, sheds light on the proton transfer mechanism and the reaction coordinate. In appropriately hydrogen-bonded solvates, the tautomerization coordinate corresponds to the actual motion of protons, whereas for other type of complexes, the process is slowed, or even limited by solvent rearrangement. To better understand the role of and interplay between various reaction coordinates, our current studies involve well-defined solvates, studied under conditions of isolation and low temperature.

Most of the results presented in this review could not have been obtained without intense collaboration with the synthetic group of R. P. Thummel (University of Houston). The author wishes to thank J. Herbich and A. Kyrychenko for their crucial contributions to both spectral and theoretical studies. The efforts of J. Dobkowski, P. Borowicz, M. Kijak, W. Rettig, M. Gil, Y. Stepanenko, A. Zielińska, V. Galievsky are highly appreciated. Femto- and picosecond studies have been carried out in cooperation with the group of M. Glasbeek at the University of Amsterdam. Inspiration for studying bifunctional chromophores was provided by aesthetetically appealing papers of Michael Kasha. The work was sponsored, in part, by Grant 7T09A 02420 from the Polish State Committee for Scientific Research.

References

(1) Arnaut, L. G.; Formosinho, S. J. Excited-state proton-transfer reactions. I. Fundamentals and intermolecular reactions. *J. Photochem. Photobiol. A: Chem.* **1993**, *75*, 1−20.
(2) Formosinho, S. J.; Arnaut, L. G. Excited-state proton-transfer reactions. II. Intramolecular reactions. *J. Photochem. Photobiol. A: Chem.* **1993**, *75*, 21−48.
(3) Ormson, S. M.; Brown, R. G. Excited-state intramolecular proton transfer. Part 1: ESIPT to nitrogen. *Prog. React. Kinet.* **1994**, *19*, 45−91.

(4) Le Gourrierec, D.; Ormson, S. M.; Brown, R. G. Excited-state intramolecular proton transfer. Part 2: ESIPT to oxygen. *Prog. React. Kinet.* **1994**, *19*, 211−275.
(5) Waluk, J. Conformational aspects of intra- and intermolecular excited-state proton transfer. In *Conformational Analysis of Molecules in Excited States*; Waluk, J., Ed.; Methods in Stereochemical Analysis Series; Wiley-VCH: New York, 2000; Chapter 2, pp 57−111.
(6) Taylor, C. A.; El-Bayoumi, M. A.; Kasha, M. Excited-state two-proton tautomerism in hydrogen-bonded N-heterocyclic base pairs. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *63*, 253−260.
(7) Avouris, P.; Yang, L. L.; El-Bayoumi, M. A. Excited-state interactions of 7-azaindole with alcohol and water. *Photochem. Photobiol.* **1976**, *24*, 211−216.
(8) Chang, C.; Shabestary, N.; El-Bayoumi, M. A. Excited-state double proton transfer in 1-azacarbazole hydrogen-bonded dimers. *Chem. Phys. Lett.* **1980**, *75*, 107−109.
(9) Waluk, J.; Komorowski, S. J.; Herbich, J. Excited-state double proton transfer in 1-azacarbazole-alcohol complexes. *J. Phys. Chem.* **1986**, *90*, 3868−3871.
(10) Waluk, J.; Herbich, J.; Oelkrug, D.; Uhl, S. Excited-state double proton transfer in the solid state: The dimers of 1-azacarbazole. *J. Phys. Chem.* **1986**, *90*, 3866−3868.
(11) Folmer, D. E.; Wisniewski, E. S.; Castleman, A. W. Excited state double proton transfer in the 7-azaindole dimer revisited. *Chem. Phys. Lett.* **2000**, *318*, 637−643.
(12) Catalán, J.; del Valle, J. C.; Kasha, M. Conformity of the 7-azaindole dimer cationic potential with photoionization/Coulomb-explosion MS observations and the concerted biprotonic transfer mechanism. *Chem. Phys. Lett.* **2000**, *318*, 629−636.
(13) Douhal, A.; Kim, S. K.; Zewail, A. Femtosecond molecular dynamics of tautomerization in model base pairs. *Nature* **1995**, *378*.
(14) Goodman, M. Mutations caught in the act. *Nature* **1995**, *378*, 237−238.
(15) Herbich, J.; Dobkowski, J.; Thummel, R. P.; Hegde, V.; Waluk, J. Intermolecular excited state double proton transfer in dipyridocarbazole:alcohol complexes. *J. Phys. Chem. A* **1997**, *101*, 5839−5845.
(16) Kyrychenko, A.; Herbich, J.; Izydorzak, M.; Gil, M.; Dobkowski, J.; Wu, F. Y.; Thummel, R. P.; Waluk, J. Photoinduced double proton transfer: Inter- and intramolecular cases. *Isr. J. Chem.* **1999**, *39*, 309−318.
(17) Kyrychenko, A.; Herbich, J.; Izydorzak, M.; Wu, F.; Thummel, R. P.; Waluk, J. Role of ground state structure in photoinduced tautomerization in bifunctional proton donor−acceptor molecules: 1*H*-pyrrolo[3,2-*h*]quinoline and related compounds. *J. Am. Chem. Soc.* **1999**, *121*, 11179−11188.
(18) Herbich, J.; Sepioł, J.; Waluk, J. Determination of the energy barrier origin of the excited state double proton transfer in 7-azaindole:alcohol complexes. *J. Mol. Struct.* **1984**, *114*, 329−332.
(19) Konijnenberg, J.; Huizer, A. H.; Varma, C. Solute−solvent interaction in the photoinduced tautomerization of 7-azaindole in various alcohols and in mixtures of cyclohexane and ethanol. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1163−1175.
(20) Marks, D.; Zhang, H.; Borowicz, P.; Waluk, J.; Glasbeek, M. (Sub)-picosecond fluorescence upconversion studies of intermolecular proton transfer of dipyrido[2,3-*a*:3′,2′-*i*]carbazole and related compounds. *J. Phys. Chem. A* **2000**, *104*, 7167−7175.
(21) Herbich, J.; Kijak, M.; Luboradzki, R.; Gil, M.; Zielińska, A.; Hu, Y. Z.; Thummel, R. P.; Waluk, J. In search for phototautomerization in solid dipyrido [2,3-*a*:3′, 2′-*i*] carbazole. *J. Photochem. Photobiol. A: Chem.* **2002**, *154*, 61−68.
(22) Kyrychenko, A.; Stepanenko, Y.; Waluk, J. Molecular dynamics and DFT studies of intermolecular hydrogen bonds between bifunctional heteroazaaromatic molecules and hydroxylic solvents. *J. Phys. Chem. A* **2000**, *104*, 9542−9555.
(23) Mente, S.; Maroncelli, M. Solvation and the excited-state tautomerization of 7-azaindole and 1-azacarbazole: Computer simulations in water and alcohol solvents. *J. Phys. Chem. A* **1998**, *102*, 3860−3876.
(24) Herbich, J.; Hung, C. Y.; Thummel, R. P.; Waluk, J. Solvent-controlled excited-state behavior: 2-(2′- Pyridyl)indoles in alcohols. *J. Am. Chem. Soc.* **1996**, *118*, 3508−3518.
(25) Dobkowski, J.; Herbich, J.; Galievsky, V.; Thummel, R. P.; Wu, F. Y.; Waluk, J. Diversity of excited-state deactivation paths in heteroazaaromatics with multiple intermolecular hydrogen bonds. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 469−475.
(26) See, e.g., O'Connor, D. B.; Scott, G. W.; Coulter, D. R.; Yavrouian A. Temperature dependence of electronic energy transfer and quenching in copolymer films of styrene and 2-(2′-hydroxy-5′-vinylphenyl)-2H-benzotriazole. *J. Phys. Chem.* **1991**, *95*, 10252−10261, and references therein.
(27) Sinicropi, A.; Nau, W. M.; Olivucci, M. Excited-state quenching via "unsuccessful" chemical reactions. *Photochem. Photobiol. Sci.* **2002**, *1*, 537−546.
(28) Bardez, E. Excited-state proton transfer in bifunctional compounds. *Isr. J. Chem.* **1999**, *39*, 319−332.
(29) Smedarchina, Z.; Siebrand, W.; Fernández-Ramos, A. A direct-dynamics study of proton transfer through water bridges in guanine and 7-azaindole. *J. Chem. Phys.* **2000**, *112*, 566−573.
(30) Fernández-Ramos, A.; Smedarchina, Z.; Siebrand, W.; Zgierski, M. Dynamics of the water-catalyzed phototautomerization of 7-azaindole. *J. Chem. Phys.* **2001**, *114*, 7518−7526.
(31) Kyrychenko, A.; Herbich, J.; Wu, F.; Thummel, R. P.; Waluk, J. Solvent-induced syn-anti rotamerization of 2-(2′-pyridyl)indole and the structure of its alcohol complexes. *J. Am. Chem. Soc.* **2000**, *122*, 2818−2827.
(32) Herbich, J.; Waluk, J.; Thummel, R. P.; Hung, C. Y. Mechanisms of fluorescence quenching by hydrogen-bonding in various aza aromatics. *J. Photochem. Photobiol. A: Chem.* **1994**, *80*, 157−160.
(33) Herbich, J.; Kijak, M.; Zielińska, A.; Thummel, R. P.; Waluk, J. Fluorescence quenching by pyridine and derivatives induced by intermolecular hydrogen bonding to pyrrole-containing heteroaromatics. *J. Phys. Chem. A* **2002**, *106*, 2158−2163.

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