Excited-State Processes in 8-Hydroxyquinoline: Photoinduced Tautomerization and Solvation Effects

Elisabeth Bardez,* Isabelle Devol, Bernadette Larrey, and Bernard Valeur

Laboratoire de Chimie Générale, Conservatoire National des Arts et Métiers, 292 rue Saint-Martin, 75003 Paris, France, and Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires (CNRS URA 1906), Ecole Normale Supérieure de Cachan, 61 Avenue du Président Wilson, 94235 Cachan Cedex, France

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8-Hydroxyquinoline (8-HQ), referred as to oxine in analytical chemistry, is a fluorogenic ligand. Its lack of fluorescence in water and alkanes, and its low quantum yield in many other organic solvents, are rationalized in the present study in terms of photoinduced formation of a nonfluorescent tautomeric form 8-HQ(T*). In water, intermolecular proton transfers with surrounding water molecules are expected, but intrinsic intramolecular proton transfer between the −OH and ⩾N functions cannot be ruled out because the presence of a weak internal H bond can be inferred from the ground-state properties of 8-HQ such as pK_a values or solubility. In organic solvents, vapor pressure osmometry measurements in conjunction with infrared spectra allow us to show that (i) in alkane solvents, a very stable dimer is formed in the ground state ($K_{dim} = 7 \times 10^7$ at 25 °C); biprotonic concerted proton transfers are then expected to occur within the dimer upon excitation, as was previously reported for 7-azaindole; (ii) in chlorinated solvents (CH_2Cl_2, $CHCl_3$), hydration by residual water molecules likely leads to a nonnegligible fraction of hydrated open structures where excited-state proton transfer is impaired; a weak fluorescence can then be observed ($\Phi_F \approx 4 \times 10^{-3}$).

1. Introduction

Photoinduced proton-transfer reactions are of fundamental importance in photochemical and photobiological processes. Numerous studies have been devoted to monofunctional compounds able to exhibit excited-state intermolecular proton transfers[1−4] and the impact of solvation on these processes has been pointed out.

The behavior of amphoterous bifunctional molecules whose functions become very acidic and very basic, respectively, upon excitation is not necessarily relevant to the behavior of monofunctional compounds. Bifunctional compounds are likely to undergo photoinduced tautomerization and, in this respect, three types of compounds can be distinguished. First are the compounds whose donor acidic and acceptor basic groups are in close proximity and hydrogen-bonded to each other. Upon excitation, an excited-state proton transfer (ESPT) occurs intramolecularly between the two functions leading to a phototautomer. During this intrinsic ESPT, a single proton is transferred. Back to the ground state, reverse tautomerization occurs and leads to the initial form. The earliest compound where this phenomenon was reported is methyl salicylate in the pioneering work of Weller.[5] The compounds undergoing intrinsic ESPT form a wide class and, even nowadays, are by far the most studied, for example, 3-hydroxyflavone or 2-(2-hydroxyphenyl)benzothiazole and derivatives.[6,7]

The second category is made up of compounds whose functions are in such positions that photoinduced tautomerization results from a concerted double-proton transfer from one function to the other in hydrogen-bonded complexes. This may occur in doubly hydrogen-bonded dimers as for example in the case of 7-azaindole.[8−10] Proton transfer may also be relayed by a bridge of solvent molecules in a cyclically hydrogen-bonded solvent/solute complex as it occurs for instance with 7-hydroxyquinoline (7-HQ) in alcoholic solutions or in apolar solvents in the presence of low fractions of alcohol.[11−14] In both cases, the prerequisite of hydrogen bonds linking the acidic and basic groups, via solvent molecules or not, can be fulfilled only in the absence of water because water is considered to favor polyhydration of the prototropic groups, thereby inhibiting the solvent arrangement necessary for this concerted mechanism.

The third kind of compounds that can undergo phototautomerization possesses on the contrary very distant functions from each other. The excited-state proton transfers likely to occur are then unconcerted intermolecular transfers between each of the two functions and the surrounding solvent molecules. Because of the amphiprotonic character of the water molecule, aqueous or water containing media are therefore suitable. Nevertheless, few recent studies are devoted to such compounds.[15−17] In a previous paper dealing with 6-hydroxyquinoline (6-HQ) in aqueous media, proton transfers between each of the −OH and ⩾N functions and the surrounding water molecules were shown by us to consist in a one-way reaction whatever the acidity, basicity, or ionic strength of the medium.[16] The reason is a coupling of the ESPT with an intramolecular electron transfer from one ring to the other which removes the resulting charge from the initial prototropic site at a faster rate than any back ESPT reaction.[16] Moreover, the structure of the resulting phototautomer was proved to be ketonic (quinonoid), and not zwitterionic as claimed by others.[17,18] We suggested that these results could be transposable to hydroxyquinolines possessing each of their two functional groups on neighboring rings, especially 8-hydroxyquinoline (8-HQ).[16]

The fluorescence behavior of 8-HQ in aqueous media is in fact quite similar to that of 6-HQ (see below).[16] However, the proximity of the two functions is similar to that observed in 7-azaindole and allows one to expect concerted ESPT mechanisms in contrast to 6-HQ. Besides, in the ground state, the reactivities of both functions are already exhibited in a cooperative way especially when 8-HQ form complexes with metal ions; 8-HQ is an outstanding complexing agent, a bidentate ligand,

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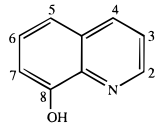
considered as the second chelating agent in importance after EDTA.[19]



In analytical chemistry, 8-HQ is referred to as *oxine*. Many derivatives can be used, with improvement of either the water solubility of the ligand and chelates (5-sulfonic-8-hydroxyquinoline), or the selectivity vs some metal ions (5,7-dihalogeno-8-hydroxyquinoline or 2- and/or 7-methyl-8-hydroxyquinoline, for instance).[20] 8-HQ itself and its uncharged chelates are very poorly water soluble, which leads to use them in extraction, mainly liquid−liquid extraction.[21,22] In this respect, the 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline is the major complexing reagent (82%) of the industrial extractant Kelex 100.[23,24]

Besides its chelating properties, 8-HQ is a fluorogenic ligand; i.e., it shows a very low quantum yield in aqueous and organic solutions, and fluorescence arises from cation binding with most metal ions. It is then used for fluorimetric determination of metals.[25] However, this fluorogenic character is not yet fully understood. In particular, the very low fluorescence emission in most media has never been really explained.

The purpose of the present study is therefore to clarify the behavior of 8-HQ in neat solvents, with the aim to understand why it is weakly or practically nonfluorescent in aqueous *and* organic solvents. First, several ground-state properties of 8-HQ in aqueous medium will be collected in order to take into consideration the possibility of hydrogen bonding between the −OH group and the N atom in a five-membered ring, even in water. The consequences on the excited-state behavior will be drawn. Then, attention will be directed to solvation in organic solvents, especially in chlorinated solvents (e.g. dichloromethane and chloroform) and alkanes. It is worthwhile to mention that chlorinated solvents, and especially chloroform, are widely used in extraction processes of metals from aqueous phases by means of oxine 8-HQ and many of its derivatives.[22] With regard to alkanes, they can be used as oil phases when inverted microemulsions are employed in extraction[26] or in fluorogenic determination of metals.[27] In each case, molecular modeling calculations will be used in support of the proposed interpretations.

2. Materials and Methods

8-Hydroxyquinoline was purchased from Aldrich and twice recrystallized from hexane-ethyl acetate, dried in a vacuum and kept in a desiccator over $CaCl_2$. Elementary analysis results (C % 74.38; H % 4.84; N % 9.60; O % 10.95) show that 8-HQ is anhydrous and does not contain any crystallization water molecule. 8-Methoxyquinoline was purchased from Lambda probes and used as received. All organic solvents for spectroscopic measurements were of spectrograde quality and were used without further purification. In particular, dichloromethane and chloroform are certified to contain less than 0.02 wt % water, i.e., 1.47×10^{-2} and 1.66×10^{-2} mol·dm^{-3}, respectively. This was checked by a Karl-Fischer titration on a spectrograde CH_2Cl_2 sample whose water content was found to be $(1.06 \pm 0.04) \times 10^{-2}$ mol·dm^{-3}. Chloroform for vapor pressure lowering measurements was from Merck and of high purity, containing water contents lower than 0.1 wt % (8.3×10^{-2} mol·dm^{-3}).

Vapor pressure lowering measurements were performed on a KNAUER vapor pressure osmometer, using benzile and 8-methoxyquinoline as standard compounds for measurements in chloroform (at 35 °C), and benzile and anthracene as standard compounds in heptane (at 40 °C). Chloroform as a chlorinated solvent was preferred to dichloromethane according to the recommendations of the osmometer manufacturer.

TABLE 1: Ground-State pK_a Values of Hydroxyquinolines (20 °C)[31]

	pK_a (⩾NH$^+$/⩾N)	pK_a (−OH/−O$^-$)
5-HQ	5.20	8.54
6-HQ	5.17	8.88
7-HQ	5.48	8.85
8-HQ	5.13	9.89

The infrared absorption spectra were recorded on a single beam UNICAM Mattson 1000 FTIR spectrometer. The near IR spectra were recorded on a double beam CARY 5 "E-Line" spectrometer.

Light-scattering measurements were conducted on a SPEX Fluorolog 2 spectrofluorimeter employing a synchronous-scan protocol and right-angle geometry.[28]

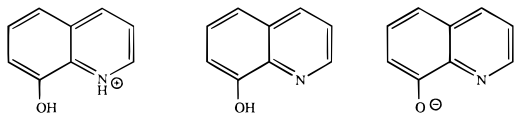
The UV−vis absorption spectra were recorded on a KONTRON Uvikon-940 spectrophotometer. Corrected fluorescence spectra were obtained with a SLM 8000 C spectrofluorometer. Fluorescence quantum yields were measured using PPO in undegassed cyclohexane as the standard ($\Phi_F = 0.90$).

Time-resolved fluorescence experiments were carried out with our multifrequency (0.1−200 MHz) phase-modulation fluorometer described elsewhere.[29] The samples were excited at 325 nm with an Omnichrome He−Cd laser. The data were analyzed by a nonlinear least-squares method using Globals software (Globals Unlimited, University of Illinois at Urbana−Champaign, Laboratory for Fluorescence Dynamics).

The Hyperchem software (Hypercube Inc.) was used for molecular modeling calculations.

3. Properties of 8-HQ in Aqueous Solutions

Ground-State pK_a Values and Prototropic Forms of 8-HQ. The ground-state pK_a values of 8-HQ in aqueous solutions at 20 °C are 5.13 (⩾NH$^+$/⩾N) and 9.89 (−OH/−O$^-$) (Table 1).[30,31] Both functions, ⩾N and −OH, appear then as either a weak base or a weak acid, respectively. At pH values lower than pH = 3, 8-HQ is exclusively in the protonated quinolinium form 8-HQ(C), whereas it is in the deprotonated quinolinate form 8-HQ(A) at pH values larger than 12. In neutral water, the predominant form is the neutral enolic 8-HQ(N) form.

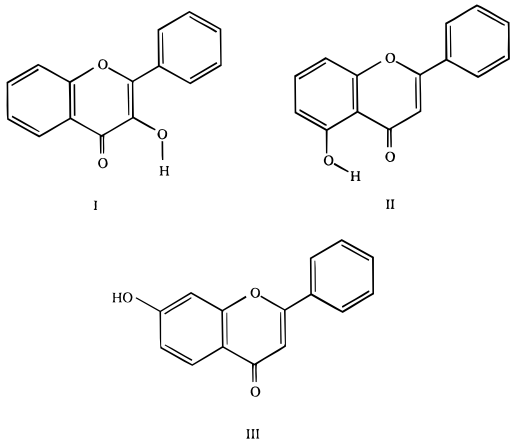


8-HQ(C) 8-HQ(N) 8-HQ(A)

It is generally observed for bifunctional compounds that the coexistence of a tautomeric form in equilibrium with the neutral form in the ground state results in an additional band on the absorption spectrum at wavelengths longer than those of the N, C, and A bands. According to Mason in the case of hydroxyquinolines,[32] the tautomer band peaks at $\lambda_{max} \geq 400$ nm, as observed for example with 7-hydroxyquinoline. For 8-HQ in water, such a band is hardly noticeable. At pH $\approx$ 7 the lowest energy band is in fact located at 305 nm and is ascribed to the neutral enolic N form which then appears more stable than the tautomer in the ground state.

Comparison between the pK_a values of 8-HQ with those of 5-, 6-, and 7-HQ (Table 1) shows that the pK_a (⩾NH$^+$/⩾N) value is nearly the same for the four compounds, whereas for

8-HQ, the pK_a ($-$OH/$-O^-$) value is larger than those of the other hydroxyquinolines, the difference being at least one unit.[31] The mobility of the hydrogen atom is then reduced in 8-HQ in comparison with the three other hydroxyquinolines. A similar observation is made when comparing the acidities of the hydroxyl groups of 7-hydroxyflavone (III) (pK_a = 7.39) and 3-hydroxyflavone (I) (pK_a = 9.6).[33] The moderate increase in the pK_a values is ascribed to the existence of a H bond between the hydroxyl and the carbonyl groups of 3-hydroxyflavone, but this bond is rather weak because it takes place in a five-membered ring. The same explanation can be put forward for 8-hydroxyquinoline in which a weak H bond between the $-$OH group and the pyridinic nitrogen atom must then be taken into account, even in water. It is noteworthy that hydrogen bonding occurring in six-membered rings is stronger as exemplified by larger increases in the pK_a values than above: for example, the pK_a of 5-hydroxyflavone (II) is 11.56, and the pK_a of the well-known intramolecularly H-bonded 2-hydroxybenzoic acid (salicylic acid) is 13.4 whereas it is 9.9 and 9.3 for the 3- and 4-hydroxy derivatives.[34]



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Solubility. The solubility of the neutral form 8-HQ(N) in neutral water is low. A solubility value of 4.7×10^{-3} mol·dm^{-3} is reported at 25 °C in water at pH = 7,[35] whereas the ionized forms 8-HQ(C) and 8-HQ(A) are of course much more soluble. Moreover, we have observed in this work that solubilization in neutral water at room temperature is unexpectedly slow. For instance, dissolution of 8-HQ at a concentration of 9×10^{-7} mol·dm^{-3} cannot be completed within 5 to 6 h, under magnetic stirring. On the contrary, 5-, 6-, and 7-HQ can be solubilized in neutral water under stirring without observing long delays for solubilization, and their solubility appears to be at least 2 or 3 times larger than that of 8-HQ. Comparison can be made again with the hydroxybenzoic acids. At 20 °C, salicylic acid is 3.9 and 2.3 times less soluble than 3- and 4-hydroxybenzoic acids, respectively, because of the intramolecular hydrogen bond.[34] The behavior of 8-HQ can then be, once again, accounted for by intramolecular H-bonding.

Molecular Modeling Calculations. After energy minimization performed in vacuum by using the semiempirical method AM1, a 8-HQ molecule was put in a "periodic box" of water whose size was chosen to be $12 \times 10 \times 12$ Å (so that it contains 37 water molecules). The molecular mechanics method MM+ was then used to optimize the geometry. The distance between the hydrogen atom of the hydroxyl group and the heterocyclic nitrogen atom was found to be 2.43 Å which is consistent with the existence of a hydrogen bond linking these atoms. It is worth making a comparison with the optimized geometry of glycine under exactly the same molecular modeling conditions because the number of bonds separating the hydrogen and nitrogen atoms involved in an intramolecular hydrogen bond, (i.e., the hydrogen atom of the carboxylic group and the nitrogen atom of the amino group) is the same as in 8-HQ; the existence of a hydrogen bond in glycine was demonstrated by Tortonda et al.[36] In spite of some differences between our data and those of these authors owing to the different methods of calculations, Figure 1 clearly shows the strong analogy between 8-HQ and glycine in terms of spatial arrangement of atoms (five-membered ring). These considerations further support the existence of an intramolecular hydrogen bond in 8-HQ.

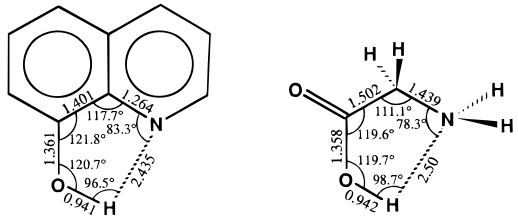


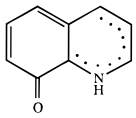
Figure 1. Energy-minimized geometries of 8-HQ (left) and glycine (right) in the presence of water molecules.

Fluorescence. It was mentioned in the Introduction that 8-HQ is nearly nonfluorescent in water. In fact, the fluorescence intensity is very weak in the acidity range $H_0 = -6$ to pH = 13 (H_0 is the Hammett acidity function). The quantum yield Φ_F is reported to be lower than 2×10^{-4}.[37] Fluorescence emission appears in very concentrated acidic ($H_0 < -6$)[38] or basic (pH >13)[39] solutions. Then, Φ_F increases when the concentration of acid or base increases. For instance, the fluorescence of the excited 8-quinolinate 8-HQ(A*) is increased 100-fold in NaOH solutions when going from pH $\approx$ 13 to $H_- \approx$ 17.5 (H_- is the Hammett acidity function for strongly basic media).[39] In concentrated acidic media, the increase of fluorescence is observed when H_0 decreases from -6 to -10. Such acidities can be obtained only with concentrated sulfuric acid. However, sulfonation occurs and leads to a sulfo derivative whose fluorescence properties are different from those of the parent hydroxyquinoline.[38,40,41] That may be the reason why the only two published values of the quantum yield of 8-HQ(C*) in sulfuric acid available are quite different: 0.31 in 98% H_2SO_4,[37] or 0.565 in 97% H_2SO_4.[42]

The interpretation of the observed phenomena and especially of the fluorescence quenching in the major part of the acidity and pH range must take the nature of the excited form into account. Two cases are to be considered: the excited form is either the cationic 8-HQ(C) or the anionic 8-HQ(A) form, or on the contrary, it is the neutral form 8-HQ(N) (the pH ranges for the predominance of each form can be inferred from the above pK_a values).

When the excited forms are C or A, the analysis and conclusions proposed by us for 6-HQ[16] are transposable to 8-HQ. Thus, the fluorescent 8-HQ(C*) form is proved to be an outstanding photoacid: excited-state deprotonation of the $-$OH group occurs even in concentrated acidic media as soon as dilution releases from hydration shells water molecules able to accept the ejected proton, the ionic strength of the medium being very high. In the same way, the fluorescent 8-HQ(A*) form is an outstanding photobase, and protonation of the $\geqslant$N group occurs even in concentrated basic media as soon as water molecules exist that are able to give a proton, again because of the high ionic strength of the medium. These reactions are intermolecular monoprotonic transfers between either 8-HQ(C*) or 8-HQ(A*) and water. They were shown to be one-way reactions because they are coupled with a simultaneous charge transfer from the prototropic site to the adjacent ring. They take place on the nanosecond scale and compete with

direct deexcitation of C* and A*. In each case, the photoproduct is 8-HQ(T*), whose structure is a ketotautomer of the neutral enolic form, and in which deexcitation takes place preponderantly via a nonradiative way, as for 6-HQ(T*). When dilution provides enough free water, the ESPT reactions become the preponderant phenomena: fluorescence is then quenched.



8-HQ(T*)

When the excited form is the neutral 8-HQ(N) form, it undergoes both deprotonation of −OH group and protonation of ⩾N atom, coupled to the intramolecular charge transfer from one ring to the other. The question now is: are the ESPT reactions mostly intermolecular ones with the surrounding water molecules in polysolvated structures, or can they partially consist of intrinsic intramolecular proton transfers between −OH and ⩾N hydrogen-bonded functions? This latter mechanism is usually discarded as soon as solvents (or impurities) with H-bonding abilities can interact with the functional groups via external H bonds. Nevertheless, the experimental considerations on pK_a and solubility, together with the calculation results, do not allow to discard the assumption of an intrinsic proton transfer process within the molecule. In fact, only dynamic characterization of the process would allow one to answer, because intrinsic ESPT occurs generally on the picosecond or subpicosecond time scale while intermolecular proton transfers are slower.[6] Unfortunately, time-resolved measurements turned out to be impossible because the fluorescence quantum yield is too low ($\Phi_F < 2 \times 10^{-4}$), and due to lack of kinetic data we can only say that the assumption of two competing, unconcerted intermolecular ESPT on the one hand, and intrinsic intramolecular ESPT according to Scheme 1 on the other hand, is not deprived of physical meaning.

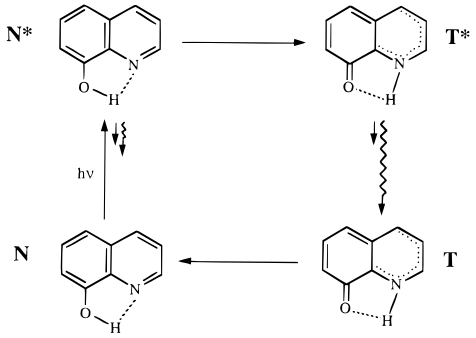
4. Properties of 8-HQ in Organic Solvents

The structure of 8-HQ dissolved in organic solvents should be clearly established for the understanding of the excited-state processes leading to the poor fluorescence emission in these solvents. Before describing our own results and interpretations, it is worth relating what was the situation when we started studying 8-HQ. As far as we are aware, the related papers were published between 1957 and 1961,[43−46] and when referring to them, it can be noted that intramolecular hydrogen bonding in 8-HQ dissolved in organic solvents was commonly accepted. Two major arguments were put forward for this:

(i) In the solid state, the intramolecular hydrogen bond is unquestionable: the infrared absorption spectrum shows a broadband due to −OH stretching vibrations in the range 3100−3200 cm^{-1} which is characteristic of the hydrogen bonding between the −OH groups and the ⩾N atoms. Moreover, the low melting point of 8-HQ (72−74 °C) compared to those, for instance, of 2-HQ (198−199 °C), 5-HQ (223−226 °C), 6-HQ (193 °C), or 7-HQ (235−238 °C), means that hydrogen bonds in solid 8-HQ are mainly intramolecular. Such internal hydrogen bonds are expected to be partially retained upon dissolution at least in solvents with low hydrogen-bonding power.

(ii) In solutions of organic solvents, the −OH stretching vibration frequency $\bar{\nu}_{OH}$ is reported to progressively decrease from 3418 to 3400 cm^{-1} when going from hexane to dioxane via carbon tetrachloride, chloroform, benzene, toluene, and

SCHEME 1



diethyl ether. Furthermore, $\bar{\nu}_{OH}$ is independent of the concentration of 8-HQ below 0.1 mol·dm^{-3}.[44,45] Vibration frequencies lower than those of a free −OH group (typically in the 3600 cm^{-1} region) are a criterion for the presence of either inter- or intramolecular hydrogen bonding, but the absence of dependence on the concentration led the authors to think that the observed phenomena resulted in fact from intramolecular hydrogen bonding (favoring then the cis structure of 8-HQ rather than the trans isomer). Moreover, the small shift (18 cm^{-1}) when going from hexane to dioxane was compared to the shift of the phenol −OH stretching band in the same solvents, i.e., 307 cm^{-1}. Phenol self-associates to give dimers, trimers, and polymers and also exhibits intermolecular bonding with the solvent when possible. The 307 cm^{-1} shift indicates the increasing contribution of intermolecular binding with the solvent when the strength of the solvents to act as proton acceptors in hydrogen bonding increases. On the contrary, the small variation, 18 cm^{-1} for 8-HQ, rules out a change from intramolecular to intermolecular hydrogen bonding in spite of dissolution in solvents possessing increasing hydrogen-bonding power. 8-HQ was then considered to be intramolecularly hydrogen bonded whatever the solvents.

However, several experimental observations in the present study will be shown to refine the above interpretation of −OH···N⩽ internal hydrogen bonding of 8-HQ whatever the organic solvents. That is why the behavior of 8-HQ solubilized in chlorinated or alkane solvents will be carefully examined because the mechanism of the excited-state processes depends on the solvation modes.

Solubility of 8-HQ in Dichloromethane and in Alkane Solvents. It is surprising at first sight that, in dichloromethane as well as in heptane and cyclohexane, 8-HQ is much more soluble than 5-, 6-, and 7-HQ (by a factor of at least 10^3 at room temperature). But, on the other hand, the rates of solubilization at room temperature do not vary in a similar way in these two kinds of solvents: in dichloromethane, the rate of solubilization decreases when both 8-HQ and solvent are dried (water content lower than 0.015 wt %); in alkanes, it decreases when 8-HQ has not been dried prior to dissolution.

Considering the large solubility of 8-HQ in the solvents used in this study, once more salicylic acid can be used as a reference compound as concerns its solubility in an organic solvent. Thus, it is reported that salicylic acid is nearly 100 times more soluble than 3-hydroxybenzoic acid, and 300 times more soluble than 4-hydroxybenzoic acid in benzene at 20 °C.[35] Consequently, the solubility due to intramolecular hydrogen bond in salicylic acid increases by a factor which is not at all in the same range as the factor 10^4 observed when comparing 8-HQ with its isomers. Therefore, the question arises as to whether in the case of 8-HQ, intramolecular hydrogen bonding or other phenomena, for example self-association of 8-HQ molecules, may be responsible for such enhancements of solubility as

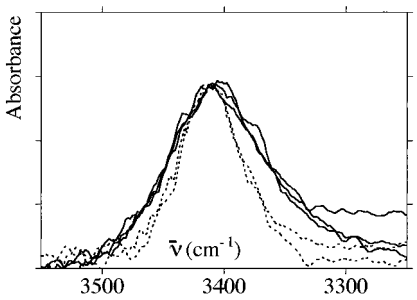


Figure 2. Normalized infrared absorption spectra of 8-HQ (−OH stretching vibration range): (—) in CH_2Cl_2, $CHCl_3$, and CH_3CN; (- - -) in benzene and toluene.

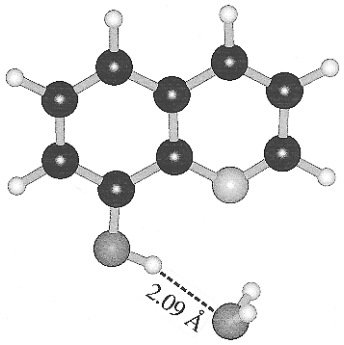


Figure 3. 3-D energy-minimized structure of a 8-HQ·H_2O complex obtained by the semiempirical method AM1.

compared with the other hydroxyquinolines. Moreover, the observations on the rates of solubilization show that the presence of dissolved water plays a different role according to the solvents. It is now worth considering separately the two kinds of solvents.

Behavior of 8-HQ in Chlorinated Solvents. *Infrared Absorption Spectra.* The near-IR and IR spectra of 8-HQ were recorded in dichloromethane, chloroform, and carbon tetrachloride. The observed −OH stretching band is located at 6622 cm^{-1} (1510 nm) and 3410−3412 cm^{-1}, respectively. This band is quite similar in shape in both solvents CH_2Cl_2 and $CHCl_3$, and somewhat narrower in CCl_4. Its shape and frequency were checked to be independent of the 8-HQ concentration in the $2 \times 10^{-2} - 0.2$ mol·dm^{-3} range. Figure 2 shows the IR −OH vibration band of 8-HQ in CH_2Cl_2 and $CHCl_3$. On the contrary, 5-, 6-, and 7-HQ spectra exhibit in CCl_4 the free −OH stretching band at 3600 cm^{-1}.[43] This difference confirms the previous interpretation of the abovementioned hydrogen bonding. Moreover, we have also recorded the spectra in acetonitrile on the one hand, in benzene and toluene on the other hand (Figure 2). In CH_3CN we have found that the −OH band is exactly similar in shape and position to the one observed in CH_2Cl_2 and $CHCl_3$, with a half-width of 95 cm^{-1}. In benzene or toluene, the maxima remain in the range 3409−3410 cm^{-1}, but the −OH band is a bit narrower than in CH_2Cl_2, $CHCl_3$, or CH_3CN, with a half-width of ≈63 cm^{-1}, respectively. The slight differences on the maxima wavelengths reported previously (see above)[45] seem in fact to be deprived of physical meaning. It is striking that no environmental effects due the nature of the solvents appear on the −OH stretching frequencies and that the influence on the band shape is of minor importance. In order to better characterize the solvation state of 8-HQ in chlorinated solvents, we have turned to molecular mass determination of dissolved 8-HQ.

Vapor Pressure Osmometry. The sensitivity of this technique is well-known for the determination of the average molecular weight of small macromolecules or micellar systems. Consequently, this technique was used here in order to provide some information about a possible self-association of 8-HQ leading to the outstanding solubility reported above by comparison with the other hydroxyquinolines. The measurements were performed on solutions of 8-HQ in chloroform at a concentration ranging from 1.03×10^{-2} to 5.14×10^{-2} mol·dm^{-3}. A molecular weight of 163.2 ± 6.0 g·mol^{-1} was found using benzil as a reference compound, and 169.1 ± 6.3 g·mol^{-1} using 8-methoxyquinoline. These values are not consistent with any aggregated form of 8-HQ (molecular weight 145.16 g·mol^{-1}). Nevertheless, they are consistent with a 8-HQ monohydrate, 8-HQ·H_2O whose molecular weight is 163.16 g·mol^{-1} and whose stability would be sufficient to make it observable by this technique. Measurements in other chlorinated solvents were not done, but remembering the exact similarity of the IR spectra in $CHCl_3$ and CH_2Cl_2, the results obtained in $CHCl_3$ can be transposable to CH_2Cl_2. Moreover, owing to the role of water in the solubilization rate, it seems reasonable to consider that 8-HQ is solvated in the chlorinated solvents under hydrated structures, at least 8-HQ·H_2O. In particular, when the 8-HQ concentration is lower than those used in vapor pressure osmometry experiments, for example in fluorescence measurements where typical concentrations used in the present study are $\approx 5 \times 10^{-5}$ mol·dm^{-3} in spectrograde CH_2Cl_2 (residual water $\approx 10^{-2}$ mol·dm^{-3}, see Experimental Section), the residual water content of the solvent may induce polyhydrate structures.

Molecular modeling calculations were then performed in order to see whether it is possible to propose the structure 8-HQ·H_2O inferred from osmometry, and how one H_2O molecule could be located.

Molecular Modeling Calculations. Geometry optimization of a single 8-HQ molecule was first performed by using the semiempirical methods AM1 and PM3. Then, an optimized 8-HQ molecule was allowed to interact with a water molecule; the same semiempirical method was again used for geometry optimization. AM1 finds a single hydrogen-bonded structure involving the hydrogen atom of the −OH group (Figure 3), whereas PM3 predicts a double hydrogen-bonded species in which a water molecule forms a bridge between the −OH group and the heterocyclic nitrogen atom. The same kind of discrepancy between the results obtained by AM1 and PM3 was reported by Kim and Bernstein[47] in the case of 7-azaindole interacting with a water molecule. In its studies on the same system, Gordon[48] found that the results obtained by PM3 were in better agreement with its ab initio calculations.

Therefore, it is difficult to draw a reliable conclusion from these calculations on the interaction between 8-HQ and one water molecule.

Fluorescence. It is surprising to observe some fluorescence emission of the 8-HQ form in CH_2Cl_2 ($\lambda_{max} = 391$ nm) compared to the very poor fluorescence in water, and as will be seen below, in alkanes (with quantum yields lower than 2×10^{-4} at room temperature).[37] The quantum yield of 8-HQ in spectrograde CH_2Cl_2 was measured and found to be equal to $(3.8 \pm 0.2) \times 10^{-3}$ at 25 °C. This value is of the same order of magnitude as the quantum yields in acetonitrile or dimethylformamide, for example.[37]

In order to attribute with certainty the fluorescence of 8-HQ to the N* form (as expected from the emission wavelength), comparison with the fluorescence emission of 8-methoxyquinoline (8-MeOQ) in CH_2Cl_2 was made because this compound cannot undergo any excited-state prototropic reaction in neutral medium and is then supposed to mimic the 8-HQ(N) form. Figure 4 shows that the emission spectra of 8-HQ and 8-MeOQ are quite similar in shape. The blue shift of ≈10 nm observed when going from 8-HQ to 8-MeOQ is comparable to the shift

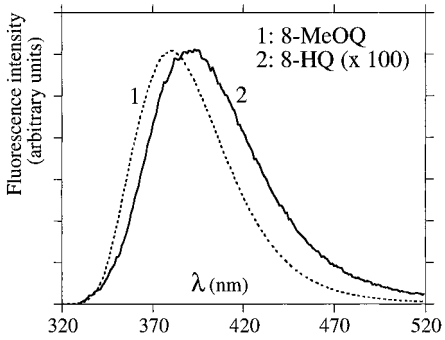


Figure 4. Fluorescence spectra of 8-methoxyquinoline and 8-hydroxyquinoline in dichloromethane ($\approx 5 \times 10^{-5}$M). Concentrations are chosen such as the optical densities are the same at the excitation wavelength: 305 nm. The spectra are intensity normalized at the maximum emission wavelength.

in their absorption spectra: $\lambda_{max} = 309$ and 302 nm for 8-HQ and 8-MeOQ, respectively, in CH_2Cl_2 (spectra not shown). These shifts can reasonably be accounted for by the substitution of the −OH group in 8-HQ by the $-OCH_3$ group in 8-MeOQ. Hence the emission of 8-HQ in CH_2Cl_2 can be ascribed to the only neutral form 8-HQ(N*).

Nevertheless, the lack of any fluorescence band of the 8-HQ-(T*) form must not be interpreted by the absence of photoinduced tautomerization but rather by the fact that deexcitation of 8-HQ(T*) is nearly nonradiative as in water. The extent of phototautomerization N* → T* is in fact to be correlated with the decrease in the N* fluorescence quantum yield because of its conversion to T*. 8-MeOQ, which cannot undergo phototautomerization, fluoresces indeed much more efficiently than 8-HQ(N*). We have determined its quantum yield in CH_2Cl_2 (0.38 ± 0.02) which is 100 times larger than the quantum yield of 8-HQ in the same solvent (see above). This is exhibited in Figure 4 by the normalization factor of 100 between the spectra of 8-MeOQ and 8-HQ. It is then concluded that 8-HQ undergoes phototautomerization in CH_2Cl_2. However, when the fluorescence quantum yields in CH_2Cl_2 and in water are compared along this line, phototautomerization can be thought to be really less efficient in CH_2Cl_2 than in aqueous solution.

As concerns 8-HQ(N*) fluorescence decay, measurements performed using multifrequency phase-modulation fluorometry show that it is composed of a main component of about 15 ns and a much shorter one (with a fractional intensity of a few percents) which cannot be determined accurately owing to the very low level of light. Remembering that coupled electron transfer and proton transfer in excited-state tautomerization[16] result in a one-way reaction whatever the solvent, those two decays can be understood as arising from two kinds of solvated molecules that are both excited: (i) polyhydrate open structures where water is attached to the hydroxyl group of 8-HQ but not bridging the two functions; such structures are expected to compete with the intramolecular H bonding (which is essential for intrinsic ESPT), precluding then excited-state proton transfer; they may exhibit consequently a noticeable fluorescence (let us note that a similar interpretation has already be put forward in the case of 3-hydroxyflavone);[49] (ii) intramolecularly H-bonded molecules leading, within a short time scale, to excited-state nonfluorescent tautomers.

Behavior of 8-HQ in Alkane Solvents. *Infrared Absorption Spectra.* The spectra of 8-HQ in solutions of *n*-heptane or cyclohexane are basically the same: narrow −OH stretching bands are observed at 6605 cm^{-1} (1514 nm), and 3419−3421 cm^{-1} (Figure 5). The half-width of the latter band is ≈ 25 cm^{-1} and its location is in agreement with measurements of Bellamy and Hallam in *n*-hexane.[45] In addition to the different frequency

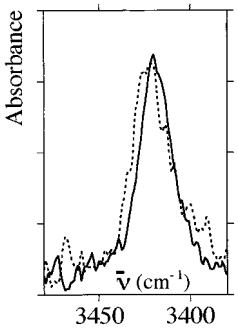


Figure 5. Normalized infrared absorption spectra of 8-HQ (−OH stretching vibration range): (—) in cyclohexane; (- - -) in *n*-heptane.

range, the narrowness of the bands distinguishes them from the previous spectra recorded in chlorinated solvents, acetonitrile, benzene, or toluene (see above). It may signify that the 8-HQ molecules fit in a well-defined and rigid structure where hydrogen bonds involving the −OH groups are responsible for self-association and indicates anyway quite a different behavior in alkanes than in the other organic solvents. Other examples of self-association through hydrogen bonding can be found in the literature (e.g. concerning aminoacridines[50] or azaindole[51]).

UV−Visible Absorption Spectra. Absorption spectra of 8-HQ in *n*-heptane and cyclohexane were recorded at various concentrations ranging from 9×10^{-7} to 2×10^{-3} mol·dm^{-3}. It turned out that the spectral changes were very small and the Beer−Lambert law was obeyed.

Resonance Light Scattering. This technique is suitable for the characterization of aggregates of chromophores that are strongly interacting via electronic coupling.[28] For instance, Pasternack and co-workers successfully applied this method to porphyrin arrays.[52,53] Unfortunately, in the present study, no significant signal was observed which may be due to the small size of the aggregates or to insufficient electronic coupling.

Vapor Pressure Osmometry. The measurements were performed on solutions of 8-HQ in *n*-heptane at concentrations ranging from 4.7×10^{-3} to 9.4×10^{-3} mol·dm^{-3}. A molecular weight of 282.5 ± 10.0 g·mol^{-1} was found using benzil as a reference compound, and 283.5 ± 10.0 g·mol^{-1} using anthracene. These values are close (within 2.5%) to twice the molecular weight of 8-HQ (145.16 g·mol^{-1}); we can thus conclude the presence of *dimers* in *n*-heptane solutions. Measurements in other alkanes, in particular cyclohexane, were not performed, but according to the strong analogies of the properties of 8-HQ in this solvent and in *n*-heptane, dimers certainly exist in cyclohexane as well.

Stability Constant of the Dimers. The stability constant K_{dim} of the dimer is not measurable by using the UV absorption spectra because of the lack of changes in these spectra in the considered concentration range (see above). The stability constant was then indirectly measured upon studying association of 8-HQ to the AOT (sodium bis(2-ethylhexyl) sulfosuccinate) surfactant molecule in *n*-heptane.[27] The experimental results obtained by fixed wavelength absorbance or stationary fluorescence intensity measurements were fitted by a model in which dimerization and association of 8-HQ monomer to the surfactant compete. The obtained value is $K_{dim} = (7.0 \pm 1.5) \times 10^7$ at 25 °C. This value shows that in a 8-HQ solution in *n*-heptane whose concentration is 10^{-6} mol·dm^{-3}, 92% of 8-HQ is under the dimer form. In view of this calculation, one can understand why no UV-absorption spectral change could be detected: the concentration range where the measurement could be performed was larger than 9×10^{-7} mol·dm^{-3}.

It is interesting to compare the stabilities of the 8-HQ and 7-azaindole dimers, the latter being the reference aggregates in

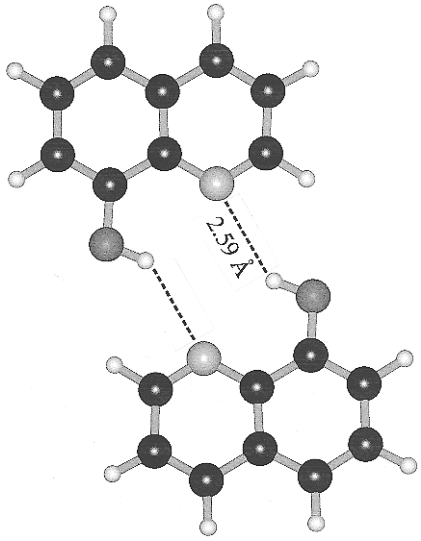


Figure 6. 3-D energy-minimized structure of a 8-HQ dimer obtained by the semiempirical method AM1.

which concerted excited-state biprotonic transfers occur. The stability constant determined by Ingham and El-Bayoumi for 7-azaindole dimers is 1.8×10^3 in 3-methylpentane at 25 °C.[51] This value shows that the 8-HQ dimers are 4×10^4 times more stable than the 7-azaindole dimers in alkane solvents. The outstanding stability of the 8-HQ dimers deserves consequently to be emphasized. It may be linked to the observation of narrow IR bands consistent with narrow energy distribution of the −OH stretching vibration within well-defined structures as the dimers. This prompted us to perform molecular modeling calculations.

Molecular Modeling Calculations. Geometry optimization of a single 8-HQ molecule was first performed by using the semiempirical methods AM1 or PM3. Then, two optimized 8-HQ molecules were allowed to interact, AM1 (or PM3) being used again for geometry optimization. Energy minimization by both methods leads to a dimer involving two intermolecular hydrogen bonds −OH···N⩽. It should be noted that AM1 predicts longer hydrogen bonds (2.6 Å) than PM3 (1.8 Å); the fact that nonbonded interactions are less repulsive in PM3 than in AM1 may account for this difference. Moreover, the dimer predicted by AM1 is planar in contrast to that obtained by PM3. The 3-D energy-minimized structure found by AM1 is shown in Figure 6. The calculations were performed in vacuum, and a better description would be obtained by simulation of the apolar solvent molecules, but the relevant tools are not presently available in our software package. The conformation of the dimer could then be somewhat different, but there is no doubt on the existence of an energy minimum corresponding to dimers.

Fluorescence. The fluorescence quantum yield of 8-HQ in alkane solvents is very low ($<2 \times 10^{-4}$ at room temperature), and in particular much lower than that of 5-HQ in isopentane (0.30) or that of 8-methoxyquinoline in isopentane (0.05).[37] It is moreover noteworthy that decreasing the temperature to 77 K does not improve the fluorescence emission, the quantum yield remaining lower than 2×10^{-4}.[37] The weak fluorescence emission was tentatively explained in the following way: the intramolecular hydrogen bond between the −OH and ⩾N groups, which is stronger in the excited state, would favor the deexcitation $S_1^* \rightarrow S_0^*$ via internal conversion.[37]

The presence of dimers in alkanes, as demonstrated above, together with our findings on the mechanism of coupled proton and electron transfers, lead us to give a different explanation for the very low fluorescence quantum yield of 8-HQ in these solvents: light excitation induces a double concerted proton transfer within the dimer, coupled to an intramolecular electron transfer within each 8-HQ moiety. The efficiency of the process is very high at room temperature and at 77 K as well. The proton transfers in the excited state seems then to be barrier-free or to involve a barrier ineffective at 77 K. The excited-state phenomena within 8-HQ dimers may match the concerted biprotonic proton transfers within 7-azaindole dimers[8−10,51,54−56] occurring at a rate larger than 2×10^{11} s^{-1} in hydrocarbon solvents at room temperature.[10,57] Moreover, dimers are almost solely present at the usual concentration where the measurements are carried out (10^{-5}−10^{-4} mol·dm^{-3}). The probability of finding and consequently exciting a monomer is so low that the phenomena occurring in the monomers are not detectable.

5. Conclusion

The poor fluorescence emission of 8-HQ has been shown to result in all cases from a photoinduced tautomerization reaction followed by deexcitation of the tautomer which occurs mainly via a nonradiative route. Various solvated structures have been proposed according to the solvent in which the ESPT reaction can occur in different ways.

(i) In water, it is likely that the tautomerization mainly results from intermolecular proton transfers between each of the two functions (−OH and ⩾N) and surrounding water molecules. However, it has been shown that the properties of 8-HQ are consistent with the existence of a weak intramolecular hydrogen bond in a five-membered ring. An intrinsic intramolecular proton transfer between the two functions is thus likely to occur as well.

(ii) In alkane solvents, 8-HQ molecules self-associate to form highly stable dimers which can undergo concerted biprotonic transfer in the excited state as in 7-azaindole. The efficiency and the extent of this process is related to the stability of the dimers consistently with a very low quantum yield which is not improved by lowering the temperature down to 77 K.

(iii) In dichloromethane and chloroform, a monohydrated form has been detected at high concentrations by vapor pressure osmometry. The existence of polyhydrates at lower concentrations in 8-HQ cannot be discarded. In some of these structures, hydration of the −OH group may occur without a bridge between the two functions. Consequently, the photoinduced tautomerization is less efficient than in pure water and fluorescence emission is detectable ($\Phi_F \approx 4 \times 10^{-3}$).

The results as a whole show that 8-HQ is a prototype compound where all possible modes of ESPT can be observed. The conceptual interest of this molecule is then remarkable. Unfortunately, the lack of fluorescence of the tautomer precludes time-resolved fluorescence experiments, but ultrafast transient absorption spectroscopy may provide in the future further insight into the excited-state processes. Time-resolved infrared or Raman spectroscopy is also to be considered. On the other hand, analytical applications take advantage of the lack of fluorescence since complexation with some metal ions induces a fluorescence enhancement (fluorogenic effect); in fact, the structure of a complex with a cation resembles the cationic form of 8-HQ and is thus fluorescent.

The present study is the first one aiming to rationalize and understand the excited-state behavior of the 8-HQ ligand, mainly in organic solvents where it is generally used.

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