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7-Hydroxyquinoline-8-carbaldehydes. 2. Prototropic Equilibria

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S *Supporting Information*

ABSTRACT: Prototropic equilibria were studied for a series of 7-hydroxyquinoline-8-carbaldehydes (**7-HQCs**) by ^{1}H NMR spectroscopy, photostationary and time-resolved UV–vis spectroscopic methods, and quantum chemical computations. These molecules represent trifunctional proton-donating/accepting systems that in aqueous solutions may assume four main neutral and ionic structures: 7-quinolinol (**OH**), 7(1*H*)-quinolinone (**NH**), deprotonated anion (**A**), and protonated cation (**C**). Electronic absorption and fluorescence of **7-HQCs** are rationalized in terms of the ground and excited-state long-range tautomerization (part 1) as well as protonation and deprotonation processes. The photophysical properties of neutral and ionic forms of **7-HQCs** are compared with those of 7-hydroxyquinolines (**7-HQs**), synthetic precursors of the former. The experimental results are corroborated by ab initio computations.
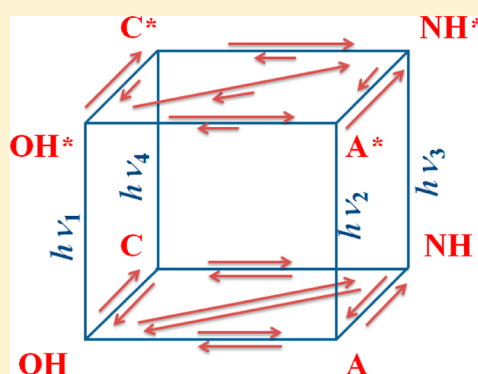
1. INTRODUCTION

Studies of 7-hydroxyquinoline (**7-HQ**) started more than 60 years ago. **7-HQ** is one of the most comprehensively examined compounds revealing solvent-assisted excited-state long-range proton transfer. Absorption spectra of **7-HQ**, presented for the first time in 1946,[1] showed bathochromic shifts in both acidic and basic solutions. The results of IR and UV–vis spectroscopic and photophysical investigations were rationalized in terms of the ground-state tautomerization.[2−5] In 1968 Mason explained[6] prototropic equilibria in the ground-state S_0 and in the lowest excited singlet-state S_1 between four neutral and ionic species of **7-HQ** appearing in water solutions: 7-quinolinol, abbreviated as the **OH** tautomeric form, a deprotonated anion (**A**), a protonated cation (**C**), and a zwitterion (**Z**) (Scheme 1). The resonance hybrid of the zwitterionic form is the **NH** tautomer (7(1*H*)-quinolinone).

It was found[6] that the spectral positions of the lowest absorption bands and fluorescence spectra of the neutral and ionic forms are located at wavelengths decreasing in the order **Z** ↔ **NH** > **A** > **C** > **OH**. On the basis of these experimental results and using the Förster cycle,[7,8] the pK_a values describing the prototropic equilibria between the neutral and ionic forms in both S_0 and S_1 states were determined.[6,9] It was observed that upon excitation to the S_1 state the phenolic group of **7-HQ** becomes more acidic, and the quinoline nitrogen atom becomes more basic than in the ground state. This finding suggests a shift of the **OH**, **C**, and **A** forms toward the **NH** form upon excitation. In the case when two groups with opposite pK_a tendencies in excited states exist in a molecule, a photon may

Scheme 1. Prototropic Equilibria and Formulas of Neutral and Ionic Forms of 7-HQ (OH, 7-Quinolinol; A, Deprotonated Anion; C, Protonated Cation; NH, 7(1*H*)-Quinolinone, Its Resonance Hybrid Being Z, Zwitterion)
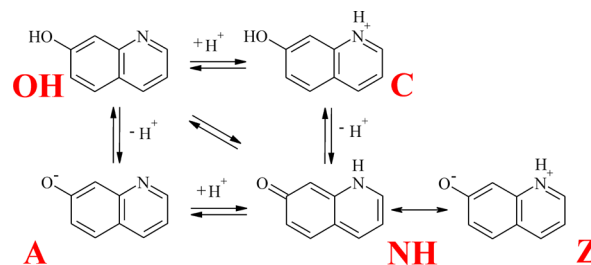
initiate protonation and deprotonation to yield a zwitterion **Z**. Because of that, the fluorescence of **C** and **A** is only observed in strong acids (pH < 1) or bases (pH > 13), respectively. In aqueous solutions in the range of pH from 2 to 13, only emission of the neutral forms of **7-HQ** (the dominant band corresponds to the **NH** form) is observed, although the absorption spectra show the existence of the ionic forms in the ground state. The ground-state fractions of the various forms of **7-HQ** in aqueous solution at pH = 7 estimated from the relative Gibbs free energies are: 67% (**OH**), 29% (**NH**), 3%

(cation), and 1% (anion).[10] Similar results were recently reported[11] for two **7-HQ** derivatives: 7-hydroxy-4-methylquinoline (**H4MQ**) and 7-hydroxy-2,4-dimethylquinoline (**HDMQ**).

The distance between proton-donating and proton-accepting centers of **7-HQ** is too long to allow formation of an intramolecular hydrogen bond, and therefore excited-state intramolecular proton transfer (ESIPT) cannot occur. The only way phototautomerization can appear is via multiple proton transfer in alcohol or water complexes. Investigations of the formation of complexes of **7-HQ** with protic partners (methanol and water mostly) provided interesting results. Transient absorption studies[12] of **7-HQ** in mixed n-hexane–methanol solvents reveal two ground-state complexes of 1:1 and 1:2 stoichiometry. In pure n-hexane there is only one fluorescence band at 350−400 nm, which is a mirror image of the absorption and thus can be attributed to the **OH** form. Addition of methanol to the solution leads to the appearance of a second band centered at 530 nm. Its intensity increases with the increase of methanol concentration. The long-wave fluorescence was attributed to the tautomer formed via a triple proton transfer in the 1:2 cyclic complex of **7-HQ** with methanol molecules.[13] Time-resolved measurements determining reaction rates have been conducted since 1982.[10,12−18] The solvent-assisted ESPT of **7-HQ** in neutral aqueous solution,[10] as well as in 1:1 complexes with glycerol and ethylene glycol,[19] was described as a stepwise process, as a process incorporating rotational diffusion dynamics of the protic solvent within 1:1 complexes with acetic acid,[20] as a two-step process in neat alcohols,[13] and as a multiple proton transfer in cyclic 1:2 and 1:3 complexes with water and methanol[21,22] and with other alcohols (ethanol, 2-propanol).[23]

The mechanism of the ESPT process in aqueous solutions seems to be more complex than in alcohols. There is no doubt that in this excited-state process the alcohol molecules act as a proton-relay system. In the complex they deliver a proton to the N atom of the solute and receive in return a proton from its hydroxyl group, which leads to a tautomeric solute and unchanged alcohol molecules.[13] In aqueous solutions, however, the excited-state tautomerization is reported to proceed in a stepwise fashion via forming ionic intermediate species. Lee and Jang found[10] that after excitation of the **OH** species in aqueous solution, the emission decays of the cation and anion are in a good agreement with the rise of the **NH** form. The **OH** fluorescence decay at 430 nm is described by three components: 30 ps (92%), 230 ps (7%), and 2.6 ns (1%). The kinetic profile of the **NH** fluorescence at 520 nm shows two rise components of 30 ps (90%) and 200 ps (10%) and a 2.6 ns decay. The observed 30 ps decay and rise times at neutral pH were ascribed to the **OH** deprotonation of the cation whereas 200 ps decay and rise times were attributed to the protonation of the anion on the quinoline nitrogen atom (Scheme 2). It was suggested that the excited-state **OH** species undergoes, within 10 ps, protonation on the nitrogen atom to form an excited cation intermediate or deprotonation from the OH group to form an excited anion intermediate. The lowest excited singlet state of the photochemically produced **NH** form is depopulated in 2.6 ns. Using time-resolved transient absorption spectroscopy, ground-state relaxation of the prototropic equilibrium perturbation was estimated to take about 20 μs.

Laser induced fluorescence (LIF) excitation and dispersed emission (DF) spectroscopy experiments under supersonic jet

Scheme 2. Schematic Interpretation of the Mechanism of the Proton-Transfer Cycle in Neutral Aqueous 7-HQ Solution (As Inferred from Ref 10)[a]
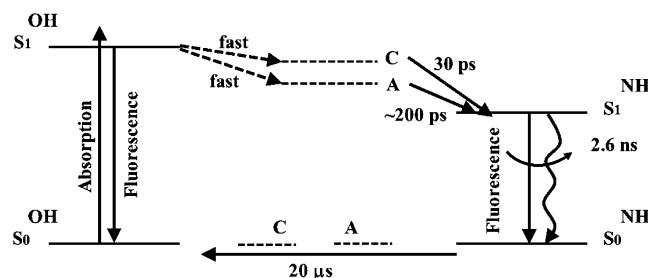
[a]**OH** and **NH** denote the neutral tautomeric forms; **C** and **A** are protonated cation and deprotonated anion, respectively.

isolation conditions[24] revealed 1:1 and 1:3 water-chain clusters of **7-HQ** with an unusually large spectral shift for the latter. However, no significant excited-state proton transfer was found. Supersonic jet investigations combined with mass-selected resonant two-photon ionization (R2PI MS) technique indicate the existence of water-chain complexes of various structures and stoichiometry: **7-HQ**·$(H_2O)_n$ with n = 1−4 water molecules.[25]

Potential energy profiles of the multiproton transfer in the ground state of hydrogen-bonded complexes between **7-HQ** and water[21] or methanol[22] were computed using various ab initio methods. The calculations predict a formation of clusters **7-HQ**·$(H_2O)_n$ with n = 1−3. The global minimum corresponds to the 1:1 complex with the water molecule attached to the oxygen atom. From among 1:2 and 1:3 complexes, the preferential ones are those of cyclic structures. The MP2/6-31G potential energy barriers for the endothermic **OH → NH** tautomerization were found to be 12.6 and 8.5 kcal mol^{-1} for 1:2 and 1:3 clusters, respectively, whereas the barrier heights of the reverse reaction were only 2.3 kcal mol^{-1} or zero, correspondingly.[21] This suggests that the **NH** form is kinetically unstable.

The derivatives of **7-HQ** that can undergo ESIPT (such as 7-hydroxy-(8-oxazin-2-one)quinoline,[26,27] 3-hydroxy-2,4,6-heptatriene−butadienimine,[28] and 7-hydroxyquinoline-8-carbaldehydes[27,29]) have been proposed as optically driven reversible molecular switches. Computational[26−29] and experimental[29] studies have led to the proposition to use the carbaldehyde group as a rotating proton "crane". Sobolewski and co-workers[26−29] developed an idea of an optically driven reversible molecular switch based on the twisting mechanism, postulated by Varma,[30,31] of the (one-way) phototautomerization process in 7-hydroxy-8-(N-morpholinomethyl)quinoline (see also part 1[32]).

The aim of this work is to study the solvent-dependent ground and excited-state tautomerization (exemplified by intra- and intermolecular hydrogen atom transfer, see part 1[32]) and acid−base equilibria in especially synthesized series of 7-hydroxyquinoline-8-carbaldehydes (**7-HQCs**) [7-hydroxyquinoline-8-carbaldehyde (**HQC**), 7-hydroxy-2-methylquinoline-8-carbaldehyde (**H2MQC**), 7-hydroxy-4-methylquinoline-8-carbaldehyde (**H4MQC**), 7-hydroxy-2,4-dimethylquinoline-8-carbaldehyde (**HDMQC**), 7-hydroxy-2-methoxy-4-methylquinoline-8-carbaldehyde (**HMMQC**), 7-hydroxy-2-phenylquinoline-8-carbaldehyde (**HPQC**), 7-hydroxy-2-(2′-methylphenyl)-quinoline-8-carbaldehyde (**HMPQC**)] as well as respective 7-

hydroxyquinoline (**7-HQ**) derivatives [7-hydroxy-2-methylquinoline (**H2MQ**), 7-hydroxy-4-methylquinoline (**H4MQ**), 7-hydroxy-2,4-dimethylquinoline (**HDMQ**), 7-hydroxy-2-methoxy-4-methylquinoline (**HMMQ**), 7-hydroxy-2-phenylquinoline (**HPQ**), 7-hydroxy-2-(2′-methylphenyl)quinoline (**HMPQ**)] (Scheme 4 in part 1[32]). The effects of polarity, hydrogen-bonding ability, and acidity and basicity of the environment on the ground- and excited-state prototropic equilibria, as well as on the spectroscopic and photophysical properties of the solute (e.g., quantitative characterization of the electronic structure, radiative transitions, and the resulting structural changes), are examined and discussed.

2. METHODS

2.1. Experimental Section. *Syntheses.* The synthesis, purification, and identification of the compounds were described in part 1.[32]

Solvents. Acetonitrile (ACN) was of spectroscopic or fluorescence grade (Aldrich or Merck), water was used after four distillations over $KMnO_4$ in a quartz apparatus. Perchloric acid, $HClO_4$ (60% aqueous solution, for analysis, Merck, p.a.), and sodium hydroxide, NaOH (Merck, p.a.), were used to obtain protonated cations and deprotonated anions, respectively. All solvents were checked for the presence of fluorescing impurities. ^{1}H NMR studies of the neutral and ionic forms of the representatives of **7-HQCs** (**H4MQC**, **HPQC**) and respective **7-HQs** (**H4MQ**, **HPQ**) were performed in deuterated solvents (99.8% D, ARMAR Chemicals and Cambridge Isotope Laboratories, Inc.), acetonitrile (CD_3CN) and acetonitrile with a drop of sulfuric acid (98% D_2SO_4 in D_2O).

Instrumentation and Procedures. Electronic absorption spectra were obtained on Shimadzu UV 2401 and Shimadzu UV 3100 spectrophotometers. Stationary fluorescence and fluorescence excitation spectra were measured on an Edinburgh FS 900 CDT fluorometer and with the Jasny multifunctional spectrofluorometric system.[33] The spectra were corrected using the spectral sensitivity curves of the instruments. Fluorescence spectra were recorded as a function of wavelength (λ) and subsequently multiplied by a factor of λ^2 to convert counts per wavelength into counts per wavenumber.

NMR spectra were recorded on a Bruker Avance II 300 spectrometer operating at 300.17 MHz for ^{1}H with a BVT-3200 variable-temperature unit.

2.2. Computations. The ground-state equilibrium geometries of all the molecular systems considered in this work, either in their neutral (part 1[32]) or ionic (protonated or deprotonated) state, have been determined with the MP2 method. Excitation energies and response properties have been calculated with the CC2 method,[34,35] which is a simplified and computationally efficient version of the coupled-cluster method with singles and doubles (CCSD). The equilibrium geometries of the lowest excited singlet states have been determined at the CC2 level, making use of the CC2 analytic gradients.[36,37] Dunning's correlation-consistent split-valence double-ζ basis set with polarization functions on all atoms (cc-pVDZ)[38] was employed in these calculations. All MP2 and CC2 calculations were carried out with the TURBOMOLE program package,[39] making use of the resolution-of-the-identity (RI) approximation for the evaluation of the electron-repulsion integrals.[40]

3. RESULTS AND DISCUSSION

3.1. Theoretical Predictions. All the protonated cations and deprotonated anions were studied theoretically with the aid of electronic-structure methods in their ground and lowest electronically excited singlet states $^1(\pi,\pi^*)$ and $^1(n,\pi^*)$. The stable forms for these electronic states were optimized and their spectroscopic properties were analyzed with respect to the absorption and fluorescence spectra. The ab initio computed transition energies of the respective tautomeric and rotameric forms of the studied compounds are collected in Tables S3– S12 (Supporting Information).

3.2. Experimental Investigations. The comparative investigations of the photophysical properties of the ionic forms of the studied **7-HQCs** and **7-HQs** were performed in acidic (by adding an aqueous solution of perchloric acid, $HClO_4$) and basic (by adding an aqueous solution of sodium hydroxide, NaOH) solutions in acetonitrile and water. The investigations were carried out for a wide range of acid (from 10^{-3} to 9.1 mol dm^{-3}) and base (between 3×10^{-3} to 8.6 mol dm^{-3}) concentrations to track the evolution of the electronic absorption and emission spectra and to observe the spectra of the protonated cations (**C**) and deprotonated anions (**A**).

Prototropic Equilibria of 7-HQs. It has been shown (part 1[32]) that all the **7-HQs** under study, similarly to 7-**HQ**,[1,12−18,23] in nonpolar (*n*-hexane) polar aprotic (ethyl acetate and acetonitrile) media and in alcohols (methanol, 1-propanol) exist in the ground state as the **OH** form (7-quinolinol) and upon excitation show a single fluorescence band in nonpolar and polar aprotic media (which is assigned to the **OH** tautomer) and a dual luminescence phenomenon in alcohols (the long-wave band corresponds to the 7(1*H*)-quinolinone (**NH**) form). The corresponding spectroscopic and photophysical data are collected in Table S1 (Supporting Information).

Room-temperature electronic absorption and fluorescence spectra of **H4MQ**, **HMMQ**, and **HPQ** (as representatives of all the **7-HQs** under study) in neutral, acidic, and basic aqueous solutions are presented in Figure 1. The corresponding data in water solutions of the studied **7-HQs** are collected in Table 1 (the data obtained in acetonitrile solutions are presented in Table S2, Supporting Information). The absorption spectra of **7-HQs** in water at pH = 7 show a long-wave absorption band at about 400 nm (~25000 cm^{-1}), which was not observed in aprotic solvents and in alcohols (Figure 9 in part 1[32]). This finding is a manifestation of the appearance of the **NH** tautomeric form.[6,11] The intensity of the long-wave band is relatively high for methylated derivatives of 7-**HQ**, significantly lower for **HPQ** and **HMPQ**, and the lowest for **HMMQ**. The ground-state protonation and deprotonation was monitored by observing changes in absorption. The formation of the cations was achieved by adding about 10^{-3}–10^{-1} mol dm^{-3} of $HClO_4$ to the acetonitrile or water solutions, as was evidenced by the disappearance of the long-wave band and the formation of a new band at ca. 340−350 nm (~28600−29400 cm^{-1}) for 7-**HQ** and its methylated derivatives, 334 nm (~29900 cm^{-1}) for **HMMQ**, and 365 nm (~27400 cm^{-1}) for **HPQ**. The absorption spectra of the protonated cations do not show any changes up to the concentration of $HClO_4$ as large as 9.1 mol dm^{-3}. Similarly, the ground-state deprotonation was achieved by adding about 3×10^{-1} mol dm^{-3} of NaOH to the aqueous solutions; the absorption spectra show a new band that is shifted to the red by about 1000 cm^{-1} with respect to that of
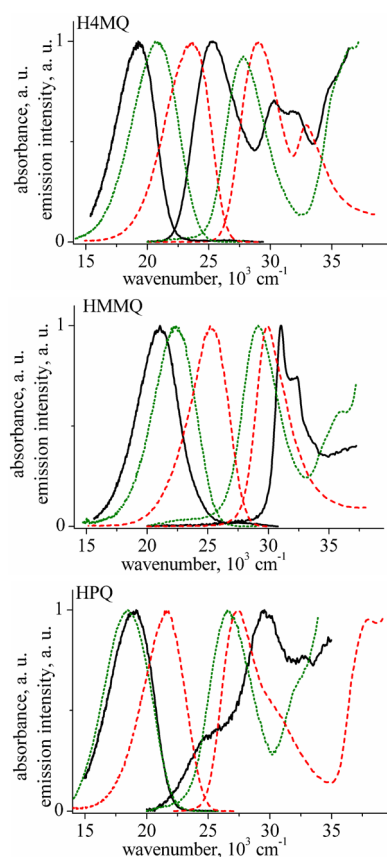
Figure 1. Comparison of the room-temperature normalized absorption spectra and corrected and normalized fluorescence spectra of **H4MQ** (top panel), **HMMQ** (medium panel), and **HPQ** (bottom panel) in water at pH = 7 (full lines, black) with those recorded in strongly acidic (in 60% $HClO_4$ solution, dashed lines, red) and basic (by adding about 8.6 mol dm^{-3} NaOH, dotted lines, green) aqueous solutions. Concentrations of the compounds are in the range from 10^{-5} to 10^{-4} mol dm^{-3}. The fluorescence spectra were recorded upon excitation to the maximum of the lowest-energy absorption band of the respective species (Table 1).

the corresponding cation. The fluorescence of the ionic forms is observed (with some exceptions, Table 1) in very strongly acidic (60% $HClO_4$) and basic (c(NaOH) = 8.6 mol dm^{-3}) solutions. The fluorescence spectra in aqueous solutions in a wide range of pH from 1 to 13 correspond to the **Z ↔ NH** forms of **7-HQs**. The driving force for the excited-state transformation of the **C** and **A** forms into the **NH** form (via ESIPT process) is an increase of acidity of the hydroxyl group and an increase of basicity of the quinoline nitrogen atom (Table 2). Assuming that the entropy changes are the same in the ground and the excited-state reactions, the change of pK_a upon electronic excitation can be obtained from the Förster cycle,[7,8] employing eq 1:

$$\Delta pK_a = pK_a^* - pK_a^G \approx -0.00207(\tilde{\nu}_{00}^{BH+} - \tilde{\nu}_{00}^B) \qquad (1)$$

where pK_a^* and pK_a^G denote the values in the excited and ground state, respectively, and $\tilde{\nu}_{00}^{BH+}$ and $\tilde{\nu}_{00}^B$ (cm^{-1}) are the electronic transition energies in an acid and base forms, correspondingly. These energies can be estimated from the absorption and fluorescence maxima $\tilde{\nu}_{00} = 0.5(\tilde{\nu}_{abs} + \tilde{\nu}_{flu})$ determined at room temperature.[8]

Prototropic Equilibria of 7-HQCs. The ground- and excited-state prototropic reactions of the **OH** and **NH** tautomeric forms of the studied **7-HQCs** reveal some peculiarities with respect to those of the corresponding **7-HQs** due to the presence of the carbaldehyde group. The spectral positions of the absorption and fluorescence maxima of the neutral **OH** and **NH ↔ Z** forms of **7-HQCs** and protonated cations (**C**) and deprotonated anions (**A**) are collected in Table 3. The room-temperature absorption and fluorescence spectra of **H4MQC**, **HMMQC**, and **HPQC** (as the representatives of **7-HQCs**) in neutral and acidic acetonitrile solutions as well as in neutral, acidic, and basic aqueous solutions are presented in Figures 2−4, respectively. The ground-state protonation and deprotonation was monitored by observing changes in absorption.

H4MQC in water at pH = 7 shows (Figure 2) an increase of the intensity of the long-wave absorption band with respect to the second absorption band (the bands are centered at about 26300 and 30000 cm^{-1}, respectively) in comparison with acetonitrile and alcohol solutions (Figures 2 and 4 in part 1[32]).

Table 1. Spectral Positions of the Room-Temperature Absorption (abs) and Fluorescence (em) Maxima (cm^{-1})^b of 7-HQs in Neutral Aqueous Solutions and under Acidic and Basic Conditions^a

| | +HClO$_4$ | | | | pH ≅ 7 | | +NaOH | |
| | $c \cong 9.1$ mol/dm^3 | | pH ≅ 1 | | | | $c \cong 8.6$ mol/dm^3 | |
	abs (C)	em (C)	abs (C)	em (NH)	abs	em	abs (A)	em (A)
7-HQ^c			28900		30500(**OH**)	≈18800(**NH**)	27600	≈20500
						≈25000(**OH**)		
H2MQ^d					25400(**NH**)	≈19700(**NH**)		
					30300(**OH**)			
H4MQ	29100	23500	29100	19300	25300(**NH**)	19300(**NH**)	27900	20900
					30200(**OH**)			
HDMQ^d					25700(**NH**)	≈19800(**NH**)		
					30300(**OH**)			
HMMQ	29900	25300	29900	21100	31100(**OH**)	21100(**NH**)	29100	22300
HPQ	27400	21600	27400	19300	24800(**NH**)	19000(**NH**)	26600	18500(**NH**)
					29600(**OH**)			
HMPQ					24200(**NH**)			
					30400(**OH**)			

^{a}OH, NH, C, and A denote the assignment of the bands to the tautomeric forms of neutral molecules, protonated cations, and deprotonated anions, respectively. ^{b}Scatter of results: ±150 cm^{-1}. ^{c}References 9 and 11. ^{d}Our results are similar to those published in ref 11.

Table 2. Changes of pK_a ($\Delta pK_a = pK_a^* - pK_a^G$) upon $S_1 \leftarrow S_0$ Excitation (Estimated from Eq 1 with the Use of the Förster Cycle and the Data Collected in Table 1) of the Equilibria between Various Neutral (NH ↔ Z and OH) Tautomeric Forms and Protonated Cations (C) and Deprotonated Anions (A) of the Representatives of 7-HQs (Explanation in Text)[a]

solvent	equilibrium	7-HQ[e]	H4MQ	HDMQ[f]	HMMQ	HPQ	HMPQ
ACN[b]	C ⇌ OH + H^{+}	7.4	6.6	5.6	6.2	7.7	7.6
H₂O[c]	C ⇌ Z + H^{+}	≈−7 to −8[6]	−8.3			−5.4	
H₂O[d]	Z ⇌ A + H^{+}	≈5.4[6,11]	4.3				

[a]Concentrations of the compounds were in the range $10^{-5}-10^{-4}$ mol dm^{-3}. [b]Protonation was achieved by adding about 0.9 mol dm^{-3} of HClO$_4$. [c]The pK_a changes are estimated for the 0−0 electronic transitions estimated from the absorption and fluorescence maxima in water at pH = 7 and in strongly acidic aqueous solutions obtained by adding 9.1 mol dm^{-3} of HClO$_4$. [d]The changes of pK_a are estimated for the 0−0 electronic transitions in water at pH = 7 and in strongly basic aqueous solutions obtained by adding 8.6 mol dm^{-3} of NaOH. [e]The values of pK_a^G for the quinoline nitrogen and 7-hydroxy group are 5.6 and 9.8.[11] [f]The values of pK_a^G for the quinoline nitrogen and 7-hydroxy group are 6.5 and 10.1.[11]

Table 3. Spectral Positions[b] of Absorption (abs) and Fluorescence (em) Maxima (cm^{-1}) of 7-HQCs in Neutral Acetonitrile and Aqueous Solutions and under Strongly Acidic and Basic Conditions[a]

	H₂O								ACN			
	+HClO₄		+HClO₄		pH = 7		+NaOH				+HClO₄	
	9.1 mol dm⁻³		3 mol dm⁻³				8.6 mol dm⁻³				3 mol dm⁻³	
	C·········?		C·········NH		NH		A[c]·········?[c]				C	
	abs	em	abs	em	abs	em	abs	em	abs	em	abs	em
HQC									25000 (NH) 29000 (OH)	20200 (NH)	28900	22900
H2MQC			29000	22500	26600	21800	26600	19200 (P)	25000 (NH) 29100 (OH)	20800 (NH)	28700	24200
H4MQC	28900	23550 (C)	28800	21600	26300	21600	26300	20500 (P)	25000 (NH) 28800 (OH)	20500 (NH) ≈24500(OH)	29000	23300
HDMQC			28800	22800	25800	22300	26400	19700 (P)	25000 (NH) 28800 (OH)	21100 (NH)	28400	24000
HPQC	26300	17500 (??)	26400	19800	24900	19600	25700	18700 (P) 21400 (A)[d]	23700 (NH) 28300 (OH)	19300 (NH) ~24000(OH)	26500	18800[e] 23500
HMPQC									24500 (NH) 28600 (OH)	19500 (NH)	26900	22700
HMMQC	28500	18900 (NH)	28570	18300	≈25900[d]	19600	26600	21900 (A)	28900 (OH)	19700 (NH)	28570	18800[e]

[a]OH, NH, C, and A denote the assignment of the bands to the tautomeric forms of neutral molecules, protonated cations, and deprotonated anions, respectively. [b]Scatter of results: ±150 cm^{-1}. [c]See text for the assignment; P denotes the assignment of the emission band to a product of (photo?)reaction. [d]Shoulder. [e]Assigned to the NH form.

This finding indicates the increase of the ground-state fraction of the **NH** tautomer with respect to that of the **OH** tautomer. The spectral position and shape of the single fluorescence band centered at 21600 cm^{-1} do not depend on excitation. Without any doubt, this emission, which is very similar to that observed in polar aprotic media and alcohols (Figures 4 and 9 in part 1[32]), corresponds to the **NH** tautomer (as evidenced by direct excitation of this form). The absorption spectra recorded in acidic acetonitrile or water solutions (achieved by adding about $10^{-3}-10^{-1}$ mol dm^{-3} of HClO$_4$), located at about 28800−29000 cm^{-1} (Table 3), are assigned to the protonated cation (**C**). The cations in acidic acetonitrile solutions emit fluorescence centered at 23300 cm^{-1} (the emission does not depend on the concentration of perchloric acid in the range from 0.1 to 4.5 mol dm^{-3}). On the other hand, the emission spectrum of **H4MQC** in water in a wide range of pH from 0 to 7 (and even for the concentration of HClO$_4$ as large as 3 mol dm^{-3}), recorded upon excitation to the maximum of the lowest-energy absorption band of the cation at 28800 cm^{-1}, shows a large Stokes shift of about 7200 cm^{-1}. This emission originates from the **Z ↔ NH** form. Thus, similarly to the case of **7-HQs**, the electronic excitation leads to the deprotonation of the cations to yield a zwitterion. The fluorescence of the cations centered at 23550 cm^{-1} is observed in very strong acidic

aqueous solutions (e.g., in 60% HClO$_4$). An interesting result is provided by the very similar shapes and spectral positions of the absorption and fluorescence spectra of the cations of **H4MQC** and **H4MQ**. The NMR spectra of **H4MQC** in strongly acidic solutions do not show any sign of the creation of **H4MQ**. These findings suggest that (i) the protonation center in both cations is the quinoline ring nitrogen atom and (ii) the π-electronic decoupling of the carbaldehyde group and a quinoline ring is achieved in the cation of **H4MQC** most probably due to the intramolecular twist to a mutually perpendicular conformation. Similar effects are observed for **HQC**, **H2MQC**, and **HDMQC**.

The assignment of the electronic absorption and emission spectra recorded in basic aqueous solutions of methylated **HQC** derivatives is not obvious. The shape and relative intensity of the three lowest absorption bands of **H4MQC** in water are changed with the increase of pH from 7 to 13. The intensity of the second absorption band located at 30000 cm^{-1} decreases, and the band disappears at pH = 13.5. The positions of the bands centered at 26300 and 34300 cm^{-1} do not depend on a further increase of concentration of NaOH up to 8.6 mol dm^{-3}; the lowest absorption band is shifted to the red by about 1600 cm^{-1} with respect to that of **H4MQ**. The decrease of the intensity of the absorption band at 30000 cm^{-1} is accompanied
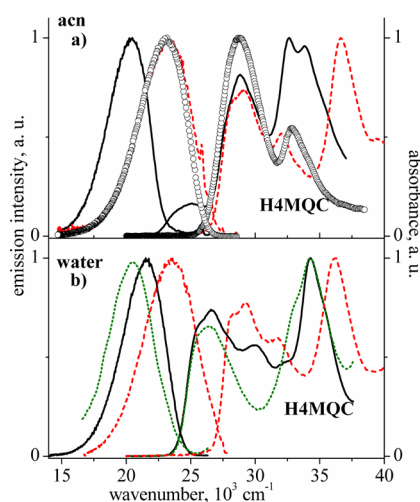
Figure 2. Comparison of the room-temperature normalized absorption spectra and corrected and normalized fluorescence spectra of **H4MQC** in neutral (full lines, black) acetonitrile (a) and water at pH = 7 (b) with those recorded in strongly acidic (by adding $HClO_4$, dashed lines, red) and basic (by adding about 8.6 mol dm^{-3} NaOH, dotted lines, green) acetonitrile and aqueous solutions. Open circles (gray) correspond to the absorption and emission of **H4MQ** upon adding an amount of about 10^{-1} mol dm^{-3} of $HClO_4$ to ACN. The concentrations of $HClO_4$ added to ACN and water are ~4.5 and ~9.1 mol dm^{-3}, respectively. Concentrations of the compound are in the range from 10^{-5} to 10^{-4} mol dm^{-3}. The fluorescence spectra were recorded upon excitation to the maximum of the lowest-energy absorption band of the respective species (see text and Table 3).
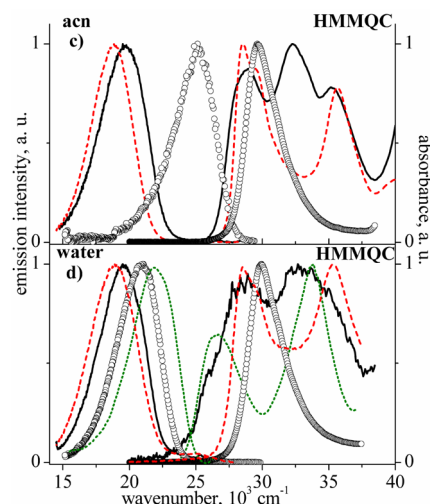

Figure 3. Comparison of the room-temperature normalized absorption spectra and corrected and normalized fluorescence spectra of **HMMQC** in neutral (full lines, black) acetonitrile (c) and water at pH = 7 (d) with those recorded in strongly acidic (by adding $HClO_4$, dashed lines, red) and basic (by adding about 8.6 mol dm^{-3} NaOH, dotted lines, green) acetonitrile and aqueous solutions. Open circles (gray) correspond to the absorption and emission of **HMMQ** upon adding an amount of about 10^{-2} mol dm^{-3} of $HClO_4$ to ACN. The concentrations of $HClO_4$ added to ACN and water are ~3.0 and ~9.1 mol/dm^3, respectively. Concentrations of the compounds are in the range from 10^{-5} to 10^{-4} mol dm^{-3}. The fluorescence spectra were recorded upon excitation to the maximum of the lowest-energy absorption band of the respective species (see text and Table 3).

by an efficient quenching of the **NH** fluorescence (Figure S1, Supporting Information). At pH = 13.5 a new emission band appears. Further increase of the concentration of NaOH causes the changes in the shape and the increase of intensity of this fluorescence. Similar effects are observed for **H2MQC** and **HDMQC** in basic aqueous and acetonitrile solutions. Most probably, the emission spectra in strongly basic aqueous solutions correspond to products of a photoreaction (or a ground-state reaction) connected with the carbaldehyde group. The absorption spectra seem to be related to the anions (**A**) of the compounds (see below).

The absorption spectrum of **HMMQC** in neutral aqueous solution at pH = 7 presented in Figure 3 is noisy due to very low solubility of this compound in water. In spite of that, the appearance of the long-wave shoulder at about 25900 cm^{-1} clearly indicates the ground-state formation of the **NH** form. The direct excitation of the **NH** tautomer at 25000 cm^{-1} leads to the single fluorescence band centered at 19600 cm^{-1} (Table 3). This finding proves that this emission band, similarly to that in other solvents (Figure 4 in part 1[32]), corresponds to the **NH** tautomer. The spectral positions of the absorption spectra of **HMMQC** in acidic (by adding about 10^{-3}–10^{-1} mol dm^{-3} of $HClO_4$) solutions are similar to those of methyl derivatives of **HQC** (Table 3). Thus, the spectra are attributed to the protonated cations. The emission, however, recorded upon excitation to the maximum of the lowest-energy absorption band of the cation at ~28600 cm^{-1}, in both strongly acidic acetonitrile and water solutions shows a huge Stokes shift of about 9600–10300 cm^{-1} (Table 3). There is no doubt that the fluorescence corresponds to the **NH ↔ Z** form (even in such strong acidic medium as 60% $HClO_4$ solution in water). Noticeably, the absorption and emission spectra of **HMMQC**

in acidic media, contrary to the similar absorption and emission spectra of the cations of **H4MQC** and **H4MQ**, differ from those of **HMMQ**. The location of the lowest absorption band of **HMMQC** in basic aqueous solutions at 26600 cm^{-1} is similar to that of the methyl derivatives of **HQC**. On the other hand, the emission spectrum of **HMMQC**, centered at 21900 cm^{-1}, is shifted to the blue by about 1400–2700 cm^{-1} with respect to the latter compounds. The spectral position of this low-intensity emission, recorded upon excitation to the maximum of the lowest-energy absorption band of the anion, does not depend on the concentration of NaOH and is similar to that of the emission spectrum of the anion of **HMMQ**. Most probably, the absorption and emission spectra of **HMMQC** in basic aqueous solutions at pH varying from 11.5 to 14 correspond to the deprotonated anion (**A**).

Room-temperature electronic absorption and fluorescence spectra of **HPQC** in various neutral, acidic, and basic media are shown in Figure 4. In neutral aqueous solutions at pH = 7 the dominant absorption band is centered at 24900 cm^{-1} (Table 3) and corresponds to the **NH** form. The single fluorescence band in water at 19600 cm^{-1} does not depend on excitation and originates from this tautomer (as evidenced by direct excitation of the **NH** form). Although the absorption spectra of the cations and anions in aqueous solutions at pH $\cong$ 1–3 and at pH $\cong$ 12–14, respectively, are similar to those in acidic and basic (not shown) acetonitrile solutions, different fluorescence spectra are observed in these media. Two luminescence bands (centered at 18800 and about 23500 cm^{-1}) are observed in acidic acetonitrile solutions upon excitation to the maximum of the lowest-energy absorption band of the cation at 26500 cm^{-1}. Noticeably, the former emission band is located in the same spectral region as the **NH** fluorescence bands of **HPQC** in
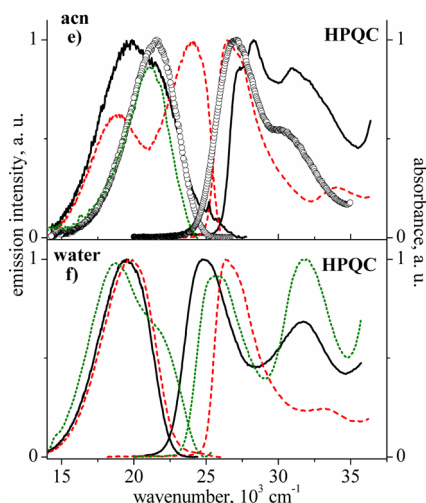
Figure 4. Comparison of the room-temperature normalized absorption spectra and corrected and normalized fluorescence spectra of **HPQC** in neutral (full lines, black) acetonitrile (e) and water at pH = 7 (f) with those recorded in strongly acidic (by adding $HClO_4$, dashed lines, red) and basic (by adding NaOH, dotted lines, green) acetonitrile and aqueous solutions. Open circles (gray) correspond to the absorption and emission of **HPQ** upon adding an amount of about 10^{-2} mol dm^{-3} of $HClO_4$ to ACN. The concentrations of $HClO_4$ added to ACN and water are ~4.5 and ~3 mol dm^{-3}, respectively. The concentrations of NaOH added to ACN and water are ~0.03 and 8.6 mol dm^{-3}, respectively. Concentrations of the compounds are in the range from 10^{-5} to 10^{-4} mol dm^{-3}. The fluorescence spectra were recorded upon excitation to the maximum of the lowest-energy absorption band of the respective species (see text and Table 3).

neutral acetonitrile and of **HMMQC** in aqueous solutions (Figure 3), and the latter, in the emission region of the protonated cations (**C**) of **HQC** and its methylated derivatives (Figure 2, Table 3). The intensity ratio of both bands strongly depends on the amount of 60% perchloric acid aqueous solution added to acetonitrile, at low concentration of $HClO_4$ the short-wave band is about 3 times more intense than the long-wave band (Figure S2, Supporting Information). On the other hand, **HPQC** in acidic aqueous solutions for a wide range of perchloric acid (from 10^{-3} to 3 mol dm^{-3}) shows, upon excitation to the maximum of the lowest-energy absorption band of the cation at ~26400 cm^{-1}, a single fluorescence band centered at about 19600−19800 cm^{-1}. Thus, similarly to **H4MQC** and **HMMQC**, this emission (which shows a large Stokes shift) is attributed to the **NH ↔ Z** tautomer. Unexpectedly, the spectral position of this emission shifts to 17500 cm^{-1} in 60% $HClO_4$ aqueous solution (Table 3). The spectral location of the second emission band at 23500 cm^{-1} in acidic acetonitrile solutions suggests its origin from the protonated cations (**C**).

The absorption spectra of **HPQC** in basic aqueous and acetonitrile (not presented) solutions show two bands located at 25700 and 31800 cm^{-1} and are similar to those of the methyl derivatives of **HQC** and **HMMQC**. The spectra are attributed to the deprotonated anions (**A**). A very-low-intensity emission centered at about 21100 cm^{-1} is observed in basic acetonitrile solutions containing NaOH ($c \approx 0.03$ mol dm^{-3}). The luminescence spectrum of **HPQC** in basic aqueous solutions depends on the concentration of NaOH. The single fluorescence band of the **NH** form is strongly quenched with the increase of the pH value up to about 12. At pH ≅ 14 new

broad emission appears with the maximum centered at about 21400 cm^{-1}. A further increase of the concentration of NaOH up to 8.6 mol dm^{-3}, similarly to **H4MQC** (Figure 2) and other methyl derivatives of **HQC** (Table 3), results in the appearance and growth of a new emission band located at about 18700 cm^{-1}. Most probably, the former emission, which is similar in basic acetonitrile and aqueous solutions, corresponds to the deprotonated anion (**A**) of **HPQC** and the latter to the product of a photoreaction (or a ground-state reaction) connected with the carbaldehyde group.

The assignments of the absorption and emission spectra to the **OH** and **NH** forms of **H4MQC**, **HMMQC**, and **HPQC**, as well as to their protonated cations (**C**) and deprotonated anions (**A**) allow us to determine the changes of pK_a values in the fluorescent state with use of the Förster cycle.[7,8] The estimated ΔpK_a values (eq 1) for various acid−base equilibria are collected in Table 4. The representatives of **7-HQCs**,

Table 4. Changes of pK_a (ΔpK_a = pK_a^* − pK_a^G) upon $S_1 \leftarrow S_0$ Excitation (Estimated from Eq 1) with the use of the Förster Cycle and the Data Collected in Table 3) of the Equilibria between Various Neutral (NH ↔ Z and OH) Tautomeric Forms and Protonated Cations (C) and Deprotonated Anions (A) of the Representatives of 7-HQCs (Explanation in Text)[a]

| solvent	equilibrium	ratio[b]	H4MQC	HPQC	HMMQC
ACN[c]	C ⇌ OH + H$^+$	[OH]/[C] = K_a/[H$^+$]	1.0	≥2.9[f]	
ACN[c]	C ⇌ Z + H$^+$	[NH ↔ Z]/[C] = K_a/[H$^+$]	−7.0	−7.2	
H$_2$O[d]	C ⇌ Z + H$^+$	[NH ↔ Z]/[C] = K_a/[H$^+$]	−4.7		
H$_2$O[e]	Z ⇌ A + H$^+$	[NH ↔ Z]/[A] = [H$^+$]/K_a		~2.0	~3.1

[a]Concentrations of the compounds were in the range 10^{-5}−10^{-4} mol dm^{-3}. [b]The ratio of the concentrations of the neutral and ionic forms. [c]Protonation was achieved by adding about 0.1−3 mol dm^{-3} of $HClO_4$. [d]The pK_a changes are estimated for the 0−0 electronic transitions estimated from the absorption and fluorescence maxima in water at pH = 7 and in strongly acidic aqueous solutions obtained by adding 9 mol dm^{-3} of $HClO_4$. [e]The changes of pK_a are estimated for the 0−0 electronic transitions in water at pH = 7 and in strongly basic aqueous solutions obtained by adding 8.6 mol dm^{-3} of NaOH. [f]The value is estimated under the assumption that the maximum of the emission of the protonated cation is centered at 23500 cm^{-1} (Table 3).

similarly to **7-HQs**, show the increase of basicity of the quinoline nitrogen atom and the increase of acidity of the hydroxyl group upon excitation to the fluorescent state. The ratios of the concentrations of the neutral and ionic forms [**C**]/[**OH**], [**NH**]/[**C**], and [**NH**]/[**A**] increase in the excited state. This indicates the increase of the fraction of **NH ↔ Z** tautomer in the excited state with respect to that in the ground state, which is indeed observed.

4. CONCLUSIONS

The results of comparative investigations of the UV−vis spectroscopic properties of the neutral and ionic forms in the series of 7-hydroxyquinoline-8-carbaldehydes (**7-HQCs**) and 7-hydroxyquinolines (**7-HQs**), allow us to characterize quantitatively the prototropic equilibria in the ground state and the changes induced by electronic excitation.

Scheme 3. Equilibria between Neutral and Ionic Forms of 7-HQs in the Ground State (Top) and the Lowest Excited State (Bottom) in the Range of pH from 0 to 13 (Explanation in Text)
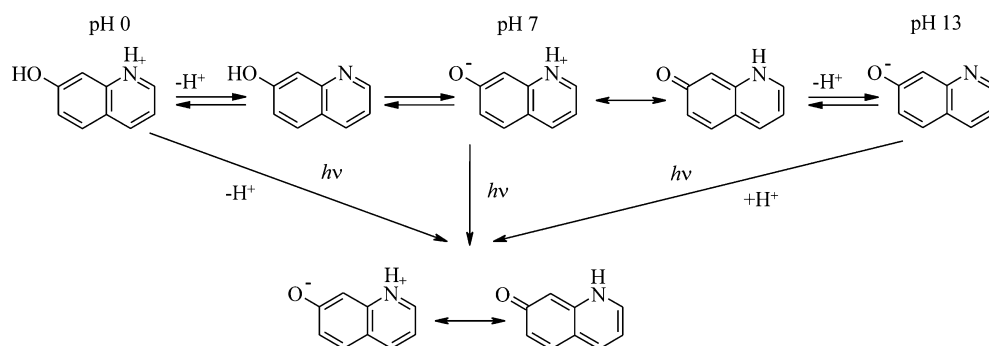
7-Hydroxyquinolines (**7-HQs**), similarly to **7-HQ**[1] exist in the ground state as the **OH** (7-quinolinol) form in nonpolar and polar aprotic solvents, and in alcohols. In aqueous solutions at pH = 7, however, the appearance of the low-energy electronic absorption band located about 25000 cm^{-1} proves the existence of the **NH** form for all the **7-HQs**. The intensity of the long-wave band is relatively high for methylated derivatives of **7-HQ**, significantly lower for **HPQ** and **HMPQ**, **HMMQ** reveals only a trace of this band (Figure 1). The compounds show a single short-wave fluorescence band in aprotic solvents and two emission bands in alcohols (Figure 9 in part 1[32]). The long-wave band corresponds to the 7(1*H*)-quinolinone (**NH**) tautomer (its resonance hybrid is the zwitterionic species **Z**) created by the excited-state triple proton transfer in the hydrogen-bonded complexes of 1:2 stoichiometry. In water the long-wave fluorescence is dominant (Figure 1). The investigations of **7-HQs** in acidic and basic acetonitrile and water solutions allow us to assign the absorption and emission spectra to the protonated cations (**C**) and deprotonated anions (**A**). Noticeably, the fluorescence of the **C** and **A** ionic forms of **7-HQs** is observed only in very strong acids (60% HClO$_4$) or bases (c_{NaOH} = 8.6 mol dm^{-3}); in the range of pH between 1 and 13 only the emission of the **NH** form is observed. The driving force for the excited-state transformation of the **C** and **A** forms into the **Z** ↔ **NH** form via the ESIPT process (Scheme 3) is the increase of acidity of the hydroxyl group and the increase of basicity of the quinoline nitrogen atom (Table 2).

Similar effects are observed for **7-HQCs**. In neutral aqueous solutions, the intensity of the long-wave absorption band of all the studied **7-HQCs** increases with respect to the second absorption band, in comparison with polar aprotic (e.g., acetonitrile, Figures 2–4) and alcohol solutions (Figures 4 and 6 in part 1[32]). This finding indicates an increase of the ground-state fraction of the **NH** tautomer with respect to that of the **OH** form with an increase of solvent polarity and proton-donating ability of the solvent. This result is corroborated by ab initio and DFT computations (Tables 3, 6, and S14 in part 1[32]). The mechanism of tautomerization in water and alcohol solutions can involve formation of various hydrates or hemiacetals, respectively, which are in dynamic equilibria with the **OH** and **NH** tautomers (Scheme 5 in part 1[32]). The assignment of the absorption and emission spectra to the neutral (**OH** and **NH**) and ionic (**C** and **A**) forms of **H4MQC**, **HMMQC**, and **HPQC** allows us to estimate the ΔpK$_a$ changes (Table 4) with use of the Förster cycle.[7,8] The electronic excitation leads to a simultaneous increase of acidity (i.e., a decrease in the excited-state pK$_a$) of the proton donor and

basicity (i.e., an increase in the excited-state pK$_a$) of the proton acceptor, and to the excited-state deprotonation of the cations and protonation of the anions to yield the **Z** ↔ **NH** form.

■ ASSOCIATED CONTENT

ⓢ **Supporting Information**

Titration curves, fluorescence spectra, and tables of solvent effect data, absorption and fluorescence spectral positions, ionic structures, vertical excitation energies and oscillation strengths, and adiabatic energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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