Temperature-Induced Reversal of Proton Tautomerism: Role of Hydrogen Bonding and Aggregation in 7-Hydroxyquinolines

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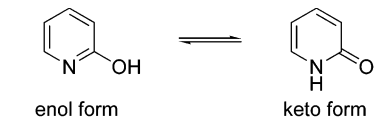
UV−vis absorption spectra of 7-hydroxyquinolines in saturated hydrocarbon solvents were measured at various temperatures between 293 and 77 K. The tautomeric equilibrium was found to reverse when the temperature was lowered. At 293 K, the enol form was exclusively present. As the temperature was lowered, the enol form decreased substantially, and the keto form became predominant. A close examination of the spectral changes suggests that the reversal of the tautomeric equilibrium at lower temperatures proceeds in two steps: aggregation of the enol forms by intermolecular hydrogen bonding and further aggregation of the hydrogen-bonded aggregates.

Introduction

Proton tautomerism is a general phenomenon in organic molecules and plays a vital role in many fields of chemistry and biochemistry. This phenomenon has attracted considerable attention as a potential means for controlling the properties of organic materials,[1] because it causes a substantial change in the properties of materials and can be controlled thermally[2−5] and photochemically.[3,4,6,7] Proton tautomerism is also of fundamental importance in biological processes.[8] Watson and Crick pointed out that the DNA architecture stems from the predominance of specific tautomeric forms of nucleic acid bases and that a change in the tautomeric equilibrium can promote mismatches in the DNA, leading to spontaneous mutations in the genome.[9] Elucidation of factors that control proton tautomerism is therefore highly important.

Tautomeric equilibrium depends on the molecular environment. A tautomeric equilibrium in the gas phase is biased toward the tautomer that is energetically favorable as a free molecule. In different environments, however, the equilibrium can be biased toward other tautomers. For example, the equilibrium between 2-hydroxypyridine and its tautomer 2-pyridone[10−13] (eq 1) is biased toward the enol form in the gas phase[11] but toward the keto form in polar solvents[12] and in the solid state.[13]

A tautomeric equilibrium also depends on the temperature and usually follows the Boltzmann distribution law. As the temperature is lowered, the amount of the tautomer with a larger population at room temperature increases, and concomitantly, that of the tautomer with a smaller population at room temperature decreases.



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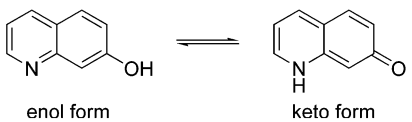
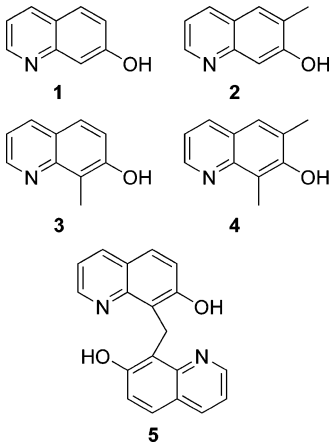


(2)

In this article, we report on the remarkable temperature dependence of the tautomeric equilibrium in 7-hydroxyquinoline (**1**, abbreviated 7HQ) and its derivatives (eq 2): a reversal of the tautomeric equilibrium takes place with variation of temperature.

The proton tautomerism of 7HQ has been extensively studied for the past four decades.[14] The enol form is much more stable than the keto form as a free molecule in the electronic ground state. In contrast, in the excited state, the keto form is more stable than the enol form. As a result, photoinduced proton transfer readily occurs to cause the tautomerization from the enol to the keto form. A characteristic feature of this proton transfer is that it cannot proceed intramolecularly because of the large distance between the proton-accepting N atom and the proton-donating OH group of the molecule. It has been proposed that the proton transfer proceeds intermolecularly with the assistance of solvent molecules such as water and methanol. Although the mechanism of the proton tautomerization has been well documented, the temperature dependence of the tautomerization has not received much attention. In this study, we measured UV−vis absorption spectra of **1** and its derivatives **2**−**5** in saturated hydrocarbon solvents at various temperatures from 293 to 77 K and discovered that the tautomeric equilibrium between the enol and keto forms was reversed when the temperature was lowered.



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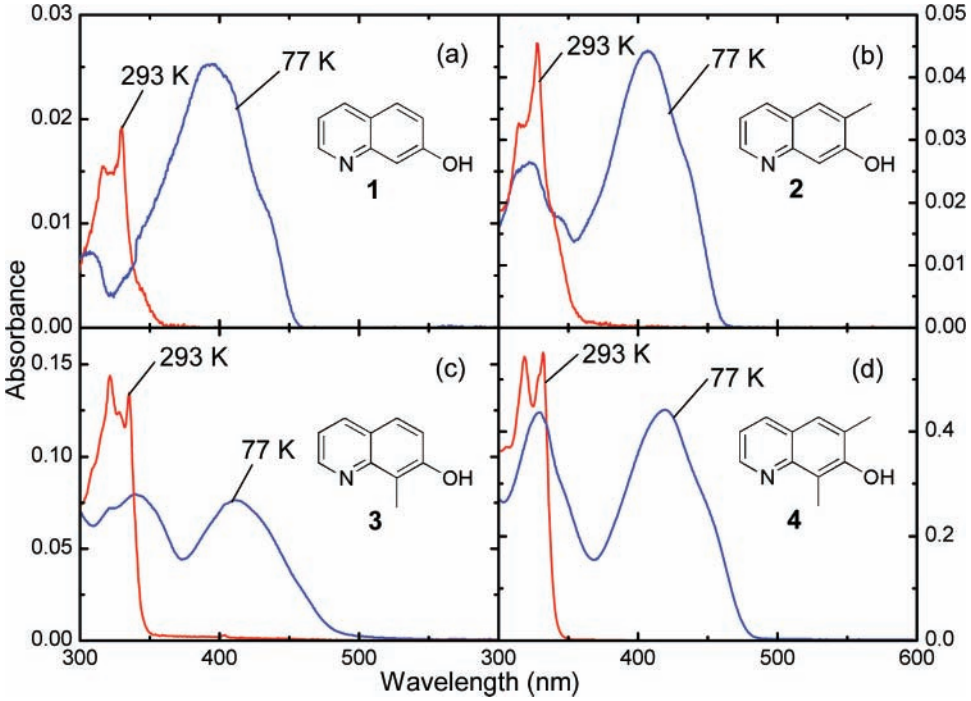


Figure 1. UV−vis absorption spectra of (a) 7-hydroxyquinoline (**1**), (b) 6-methyl-7-hydroxyquinoline (**2**), (c) 8-methyl-7-hydroxyquinoline (**3**), and (d) 6,8-dimethyl-7-hydroxyquinoline (**4**) in an isopentane/methylcyclohexane mixture (4:1) at 293 and 77 K (path length = 1.0 cm) and at the following concentrations: **1**, 5×10^{-6} M; **2**, 1×10^{-5} M; **3**, 5.0×10^{-5} M; **4**, 1.3×10^{-4} M.

Experimental Section

Materials. Compound **1** was purchased from Acros and recrystallized from acetonitrile. Compounds **2**[15] and **5**[16] were synthesized by the procedures described in the literature. Compound **2** was recrystallized from acetonitrile and subsequently sublimed under reduced pressure. Compound **5** was recrystallized from acetonitrile. Compounds **3** and **4** were synthesized using the Skraup reaction. Detailed procedures are given in the Supporting Information.

Measurements. UV−vis absorption spectra were measured on a Jasco Ubest V-560 spectrometer equipped with a liquid-nitrogen-bath cryostat (Oxford DN1704 or Optistat DN). The temperature of the cryostat was held constant to within ±0.1 K during each spectral measurement. The optical path length was 1.0 cm. Spectroscopic-grade isopentane from Merck (UVASOL) and spectroscopic-grade methylcyclohexane from Aldrich were used as received. All spectra were measured in an isopentane/methylcyclohexane mixture (volume ratio = 4:1). Compounds **1**−**3** were sparingly soluble in hydrocarbon solvents and easily precipitated at low temperature. To prevent precipitation at low temperature, the solutions of the compounds were flash-cooled from 293 to 77 K. When the temperature was slowly changed to or from low temperature, good-quality spectra could not be obtained because of the precipitation. An apparent increase in absorbance due to the contraction of the solvent at low temperature was corrected using the method described in the literature.[17]

Calculations. All calculations were performed at the B3LYP/6-31+G** level using the Gaussian 03 program.[18] Vibrational frequencies were calculated for the dimers of 7-hydroxyquinoline (**1**) to verify that the optimized structures were at energy minima. Geometry optimizations and frequency calculations for the dimers were carried out using the counterpoise correction[19] for basis set superposition error (BSSE).

Results and Discussion

UV−vis absorption spectra of **1**−**5** in a mixture of isopentane and methylcyclohexane (volume ratio = 4:1) were measured at different temperatures. The absorption spectra of **1** are shown in Figure 1a. At 293 K, **1** exhibits only an absorption band with sharp peaks (λ_{max} = 330 nm) that is assigned to the enol form. At 77 K, the intensity of this band substantially decreases, and the sharp peaks of this band disappear. Concomitantly, a broad absorption band appears at much longer wavelength (λ_{max} = 397 nm). The new band is assigned to the keto form on the basis that it is comparable in wavelength to that of the keto form in water (λ_{max} = 402 nm).[20] The spectral change was reversible.

The spectral change shows that the favored tautomer switches from the enol form to the keto form when the temperature is decreased; that is, a reversal of the tautomeric equilibrium occurs at low temperature.

Other 7HQs, namely, 6-methyl-7-hydroxyquinoline (**2**), 8-methyl-7-hydroxyquinoline (**3**), and 6,8-dimethyl-7-hydroxyquinoline (**4**), exhibited a similar spectral change when the temperature was decreased (Figure 1b−d). At 293 K, only the absorption bands of the enol form were present, but at 77 K, those of the keto form were predominant. Thus, the temperature-induced reversal of the tautomeric equilibrium from the enol to the keto form takes place in the 7HQs in the isopentane/methylcyclohexane mixture.

In accordance with the spectral changes, a solution of **4** changes from colorless at room temperature to yellow at 77 K.[21] Because of this thermochromism, the appearance of the keto form is easily perceived. The keto form appeared at 77 K in various saturated hydrocarbon solvents such as pentane, isopentane, hexane, 2-methylpentane, 3-methylpentane, heptane, octane, and methylcyclohexane, but not in toluene, methanol, or 2-methyltetrahydrofuran. These results indicate that the

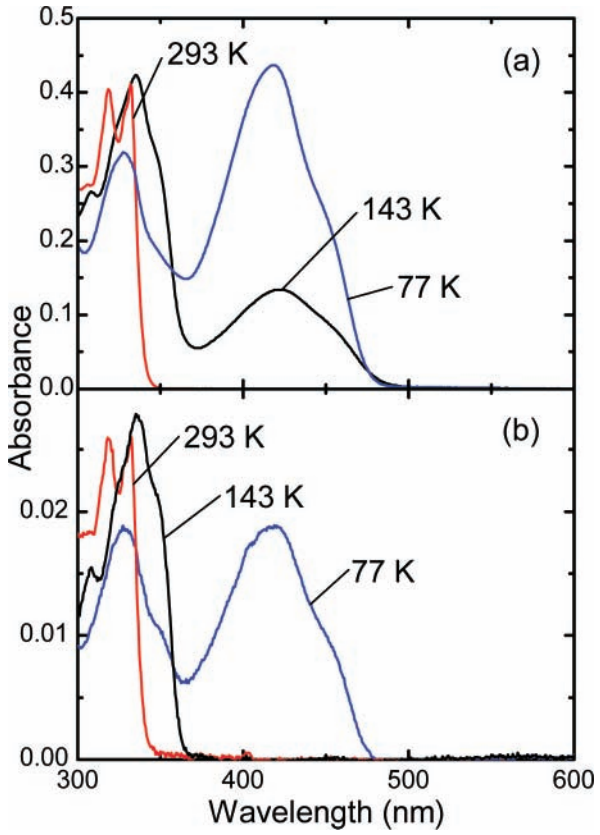


Figure 2. UV−vis absorption spectra of 6,8-dimethyl-7-hydroxyquinoline (**4**) at different concentrations: (a) 1.1×10^{-4} and (b) 1.1×10^{-5} M.

temperature-induced reversal of the tautomeric equilibrium of 7HQs is a general phenomenon in saturated hydrocarbon solvents.

The occurrence of the temperature-induced reversal of the tautomeric equilibrium suggests that aggregation is involved in this phenomenon. Evidence for the aggregation is the concentration dependence of the spectral change (Figure 2).[22] In both high- and low-concentration solutions (1.1×10^{-4} M, Figure 2a; 1.1×10^{-5} M, Figure 2b), only the absorption band of the enol form is observed at 293 K. As the temperature is lowered, the absorption band of the keto form ($\lambda_{max} \approx 420$ nm) appears at 143 K in the high-concentration solution but not in the low-concentration solution. At 77 K, both solutions exhibit the absorption band of the keto form. Thus, the keto form appears at higher temperatures in the higher-concentration solution. These results show that aggregation takes place at low temperature and that the keto form becomes more stable than the enol form in the aggregates.

The spectral change at lower temperature also suggests that the temperature-induced reversal of the tautomerism proceeds in two steps as shown below.

First, as the temperature is lowered from 293 K, a new absorption band appears at 350 nm as a shoulder and gradually increases in intensity until 180 K (Figure 3a). The newly appearing broad band, which is red-shifted with respect to the sharp band of the monomer of the enol form, is ascribed to the hydrogen-bonded aggregate of the enol form. The formation of intermolecular hydrogen bonds has been reported to cause similar red-shifted spectral changes.[14h,23]

Second, when the temperature is lowered further, the absorption bands of the enol form, present in the UV region, decrease in intensity, and concomitantly, the absorption band of the keto form appears in the visible region and gradually increases in intensity (Figure 3b). At 90 K, the small absorption maximum of the enol form at 308 nm disappears, and the absorption maximum of the keto form at 420 nm becomes prominent. The spectrum does not change from 90 to 77 K, indicating that the equilibrium shift is completed and, thus, the NH form is exclusively present at 90 K and below.

The above results demonstrate that, below room temperature, aggregation of the enol forms takes place through intermolecular hydrogen bonding and that, at lower temperatures, further aggregation of the hydrogen-bonded aggregates occurs, resulting in the reversal of the tautomeric equilibrium.

This interpretation is supported by the spectral changes of **5** (Figure 4), which can be regarded as a model compound of the cyclic hydrogen-bonded dimer of **1** (Figure 5). At 293 K, **5** exhibits only the absorption band of the enol form ($\lambda_{max} =$ 342 nm). The longer-wavelength edge of the absorption band in **5** (ca. 400 nm) is much longer than that in **1**−**4** (ca. 350 nm) at 293 K (Figure 1), indicating that intramolecular hydrogen bonds are formed in **5** even at 293 K. In contrast to that of **4**, the spectrum of **5** remains unchanged and exhibits no red shift from 293 to 170 K, because **5** cannot form additional hydrogen bonds. When the temperature is decreased further, the absorption band of the keto form appears and increases in intensity.

The temperature dependence of **4** and **5** indicates that the stabilization of the keto form through hydrogen bonding[24] is not sufficient for the reversal of the tautomeric equilibrium. If the reversal of the tautomeric equilibrium were caused only by intermolecular hydrogen bonding, the keto form of **4** should appear simultaneously with the formation of the hydrogen-bonded aggregates of the enol form and **5** should exist as the keto form at room temperature. However, this is not the case. Thus, the keto form is stabilized by intermolecular hydrogen bonding, but the stabilization by hydrogen bonding is not large enough to make the keto form more stable than the enol form in a hydrogen-bonded aggregate.

There are some examples in which a minor tautomer as a free molecule becomes the major tautomer as a result of intermolecular hydrogen bonding.[5a,25] For example, the keto form of a salicylideneaniline, which is negligible in solution, becomes predominant in crystals because of intermolecular hydrogen bonding.[5a] It is therefore expected that the keto form in 7HQs also becomes predominant by intermolecular hydrogen bonding. This reversal of the tautomerism, however, does not occur because of the large energy difference between the keto and enol forms as free molecules. According to DFT calculations (B3LYP/6-31+G**), the keto form of **1** is less stable than the enol form by 11.8 kcal mol^{-1} as a monomer, whereas the keto form in the cyclic hydrogen-bonded dimer is less stable than the enol form by 10.8 kcal mol^{-1} (Figure 5). The energy difference of 10.8 kcal mol^{-1} in the dimer means that the keto form is less stable than the enol form by 5.4 kcal mol^{-1} per molecule and that intermolecular hydrogen bonding stabilizes the keto form by only 6.4 kcal mol^{-1}. Intermolecular hydrogen bonding is, therefore, not sufficient for the reversal of the tautomeric equilibrium in **1**.

Nevertheless, the tautomeric equilibrium is reversed in a saturated hydrocarbon solvent at low temperatures. It is therefore suggested that, in addition to intermolecular hydrogen bonding, another intermolecular interaction that stabilizes the keto form is involved in the reversal of the tautomeric equilibrium.

Electrostatic interactions can play a major role in the stabilization of the keto form for the following reasons: The

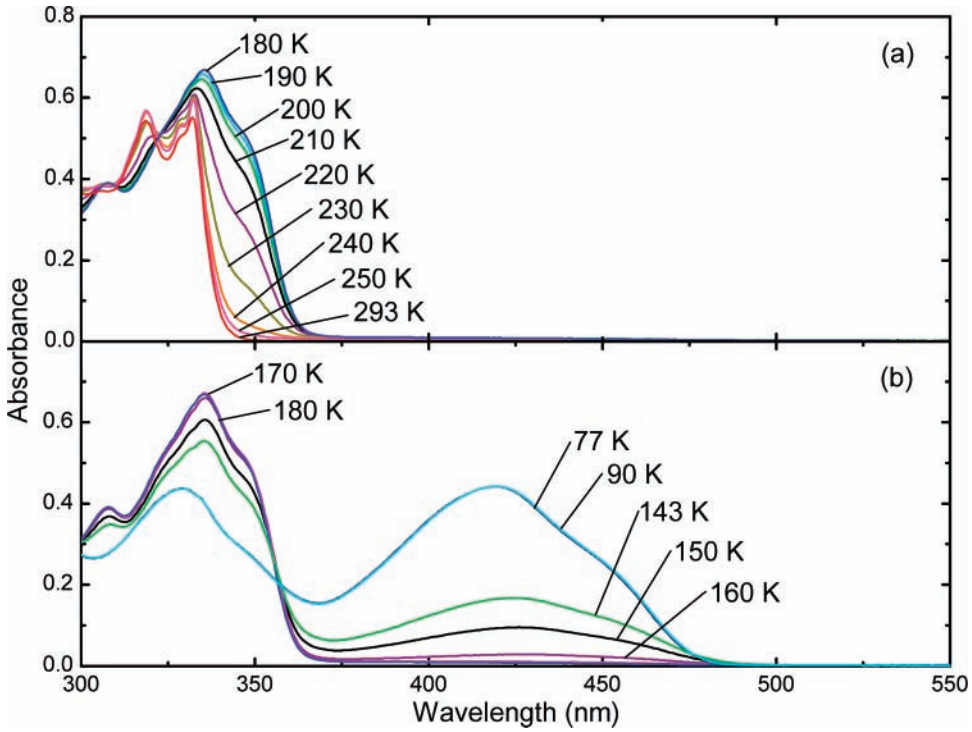


Figure 3. UV−vis absorption spectra of 6,8-dimethyl-7-hydroxyquinoline (**4**, 1.3 × 10^{-4} M) at (a) 250−180 and (b) 180−90 K.

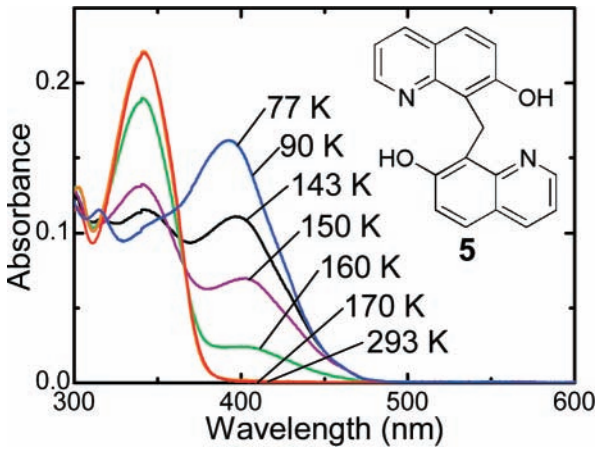


Figure 4. UV−vis absorption spectra of 8,8′-methylene-di-7-hydroxyquinoline (**5**, 2.0 × 10^{-5} M) at various temperatures.

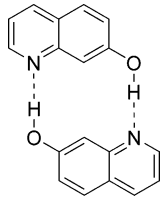
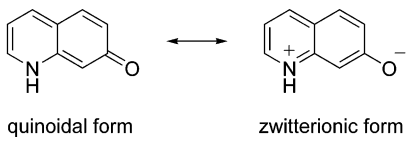


Figure 5. Cyclic hydrogen-bonded dimer of **1**. .

keto form is more polar than the enol form because of its zwitterionic character (eq 3). According to DFT calculations (B3LYP/6-31+G**), the dipole moments of the enol and keto forms of **1** are 1.15 and 8.21 D, respectively. Therefore, the stabilization due to electrostatic interactions should be larger in the keto form than in the enol form. If the molecular environment becomes highly polar as the temperature is decreased, the keto form can be stabilized and become predominant. Such a highly polar molecular environment can be realized if the hydrogen-bonded aggregates further aggregate in hydrocarbon solvents. In these higher-order aggregates, a molecule is surrounded by polar molecules, by which the keto form becomes more stable than the enol form.



(3)

The reason for the reversal of the tautomeric equilibrium at low temperatures can be explained as follows: Aggregates are enthalpically favorable but entropically unfavorable compared to monomers. Thus, the enthalpy change, ΔH, and the entropy change, ΔS, for aggregation are both negative. The Gibbs energy change, ΔG ($= \Delta H - T\Delta S$), can therefore be positive at room temperature because of a large contribution of the entropy term $-T\Delta S$. In contrast, at low temperature, ΔG can be negative because of a smaller contribution of the entropy term, and the equilibrium moves toward the aggregates, in which the keto form is more stable than the enol form. Therefore, the keto form predominates at low temperatures, whereas the enol form predominates at room temperature. It is thus concluded that the reversal of the tautomeric equilibrium is caused by the formation of aggregates and the stabilization of the keto form therein.

Concluding Remarks

We have demonstrated herein that the energetically unfavorable tautomer of 7HQs is greatly stabilized to reverse the tautomeric equilibrium in saturated hydrocarbon solvents at low temperature. This study suggests that the temperature-induced reversal of the tautomeric equilibrium requires aggregation of the enol forms by intermolecular hydrogen bonding and subsequent higher-order aggregation.

A similar phenomenon has been observed in closely related compounds such as 2-hydroxyphenazines and 2-hydroxypyridines.[26] We previously reported that a class of compounds with a much different molecular skeleton, salicylideneanilines, also exhibits a similar phenomenon.[5d] The temperature-induced

reversal of tautomeric equilibrium would, therefore, generally take place in a variety of compounds that exhibit proton tautomerism.

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Supporting Information Available: Detailed procedures for the syntheses of compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Solubility of **1** and **2** in saturated hydrocarbon solvents is too sparse to let the color of the solution perceptible.

(22) The absorbance of the absorption band in the higher-concentration solution (1.1×10^{-4} M, Figure 2a) is more than 10 times the absorbance of the corresponding band in the lower-concentration solution (1.1×10^{-5} M, Figure 2b) at 293 K. The hyperchromic effect suggests that aggregation takes place in the higher-concentration solution at room temperature. For a discussion of the hyperchromic effect, see: Tinoco, I. *J. Am. Chem. Soc.* **1960**, *82*, 4685−4790.

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