Dual Fluorescence of the Quinolinium Cation

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Abstract: pH and Hammett acidity dependences of the blue fluorescences of the quinolinium ion and some related species indicate that the thermally relaxed ^1L_b and ^1L_a states of the quinolinium ion are degenerate and that fluorescence occurs from both states. The quinolinium cation is a weaker acid in one of these states than in the ground state and a stronger acid in the other excited state. Spectral shifts upon protonation suggest that the ^1L_a state is the more basic of the two low-lying excited singlet states. Prototropic equilibrium in the more basic excited state is not complete while in the more acidic excited state equilibrium appears to be attained.

The dramatic increase in the quantum yield of the ultraviolet fluorescence of quinoline with increasing solvent polarity and hydrogen bond donor capacity has been recognized, for some time, as the result of depopulation of a low-lying n–π^* excited singlet state by interaction of the lone pair on the nitrogen atom with the solvent.[1-3] The low-lying n–π^* singlet state of quinoline has, however, been observed only in the vapor phase.[1] The absorption spectrum of quinoline, in solution, shows only π–π^* transitions similar in form and position to those of naphthalene.[1,4] In dilute acidic solutions in aqueous and ethanolic media, the π–π^* absorption band of quinoline corresponding to the ^1L_a band of naphthalene disappears, while the band corresponding to the ^1L_b band of naphthalene intensifies to very near the sum of the molar absorptivities of the ^1L_a and ^1L_b bands of the neutral species. These changes are obviously brought about by the protonation of quinoline, the ground state pK_a of which is 4.94.[5] It appears that in the quinolinium ion the ^1L_a state has red shifted and is degenerate, or nearly so, with the ^1L_b state.[4]

In dilute acid solutions, the fluorescence spectrum of quinoline red shifts some 5100 cm^{-1} and increases sharply in intensity. The blue fluorescence of the quinolinium ion was reported to reach half-maximum intensity at a pH of about 7,[1] suggesting that quinoline is a stronger base in the lowest excited singlet state. In this laboratory, it has recently been found that the blue quinolinium fluorescence reaches maximum intensity at pH 4 and remains essentially constant with decreasing pH until a Hammett acidity of 0 in dilute sulfuric acid is reached. With further increase in sulfuric acid concentration, a sharp rise in the intensity of the quinolinium ion fluorescence, with no change in absorption spectra, corrected excitation spectra, or emission wavelength, was observed. The rise in the quinolinium ion quantum yield of fluorescence culminated at about H_0 −4. The variation of the relative quantum yield of the quinolinium fluorescence with pH and Hammett acidity is shown in Figure 1. At acidities greater than H_0 −4, the fluorescence intensity remained nearly constant. In the pH region 4–0 some fluorescence from the neutral species was still detectable on the short-wavelength side of the quinolinium ion fluorescence. However, in more concentrated acid solutions all traces of the neutral species fluorescence disappeared.

These results suggested that an acidity-dependent excited-state process was occurring in the quinolinium ion. In order to characterize this process, the following study of the acidity dependences of the fluorescences of some quinoline derivatives and related molecules was undertaken.

Experimental Section

Quinoline was purchased fromt he J. T. Baker Chemical Co., Inc., Phillipsburg, N. J. 2-Methylquinoline, 4-methylquinoline, 6-methylquinoline, 8-methylquinoline, and 6-methoxyquinoline were obtained from Pfaltz and Bauer, Inc., Flushing, N. Y. Isoquinoline was purchased from Eastman Organic Chemicals, Rochester, N. Y. All of these compounds were purified by low-pressure distillation and then, for duplicate experiments, by precipitating the perchlorate salts from ethanolic perchloric acid solutions. A purified sample of 8-methoxyquinoline was obtained, as a gift, from Dr. Herman Gershon of the Boyce Thompson Institute for Plant Research, Inc., Yonkers, N. Y. Acridine was purchased from Eastman Organic Chemicals, Rochester, N. Y., and recrystallized three times from ethanol. Perchloric and sulfuric acids were purchased as the reagent grade chemicals from Mallinckrodt Chemical Works, Inc., St. Louis, Mo. Fluorimetric titrations and absorption spectra were taken on solutions *ca.* 1×10^{-4} *M* in the quinoline derivatives.

Absorption spectra were taken on a Beckman DB-GT spectrophotometer. Corrected fluorescence spectra were taken on a Perkin-Elmer MPF-2A fluorescence spectrophotometer, equipped with a rhodamine-B quantum counter and whose monochromators were calibrated against the xenon line emission spectrum.

The corrected Hammett acidity scales of Jorgenson and Hartter,[6] for sulfuric acid solutions, and of Yates and Wai,[7] for perchloric acid solutions, were employed in these studies.

Results

The absorption and fluorescence features of the neutral and protonated species derived from quinoline, the 2-methyl, 4-methyl, 6-methyl, 8-methyl, 6-methoxy, and 8-methoxy derivatives of quinoline, isoquinoline, and acridine are presented in Table I. The fluorescence spectra were unstructured and the frequencies of these were taken at the band maxima as were the frequencies of the ^1L_a bands of the absorption spectra of the neutral species. The ^1L_b bands of the absorption spectra of the neutral species were highly structured except for those of 6-methoxyquinoline and 8-methoxyquinoline.

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Table I. Absorption and Fluorescence Maxima of the Cations and Neutral Species Derived from Quinoline and Its 2-Methyl, 4-Methyl, 6-Methyl, 8-Methyl, 6-Methoxy, and 8-Methoxy Derivatives, Isoquinoline, and Acridine

B	Absorption spectra: $\bar{\nu}_{BH^+}$, $cm^{-1} \times 10^{-4}$		Absorption spectra: $\bar{\nu}_B$, $cm^{-1} \times 10^{-4}$		Fluorescence spectra: $\bar{\nu}_{BH^+}$, $cm^{-1} \times 10^{-4}$	Fluorescence spectra: $\bar{\nu}_B$, $cm^{-1} \times 10^{-4}$
	^1L_b	^1L_a	^1L_b	^1L_a		
Quinoline	3.19	3.19	3.20	3.61	2.44	3.01
2-Methylquinoline	3.15	3.15	3.17	3.68	2.49	2.95
4-Methylquinoline	3.20	3.20	3.20	3.63	2.53	2.95
6-Methylquinoline	3.19	3.19	3.14	3.61	2.40	2.94
8-Methylquinoline	3.18	3.08	3.18	3.45	2.33	2.69
6-Methoxyquinoline	2.96	3.19	3.06	3.68	2.27	2.70
8-Methoxyquinoline	3.13	2.79	3.30	3.30	2.03	2.38
Isoquinoline	2.98	3.77	3.12	3.73	2.69	2.96
Acridine	2.80	2.47	2.80	2.76	2.08	2.35

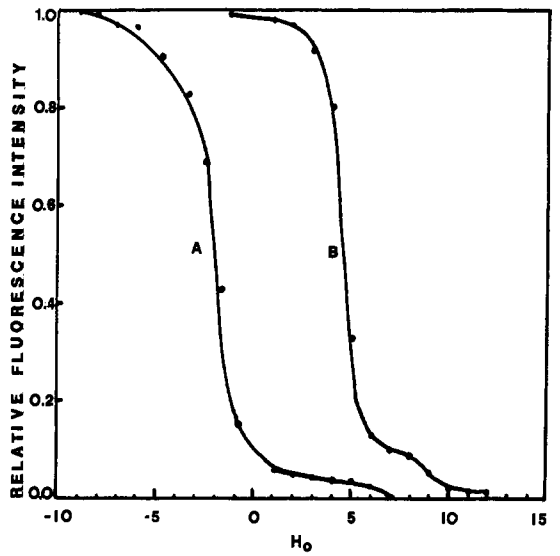

Figure 1. pH and Hammett acidity dependences of the quinolinium and 8-methylquinolinium cation relative fluorescence intensities. The concentrations of the cations are 1.00×10^{-4} *M*. Curve A is the acidity dependence of the quinolinium ion fluorescence. Curve B is the acidity dependence of the 8-methylquinolinium ion fluorescence.

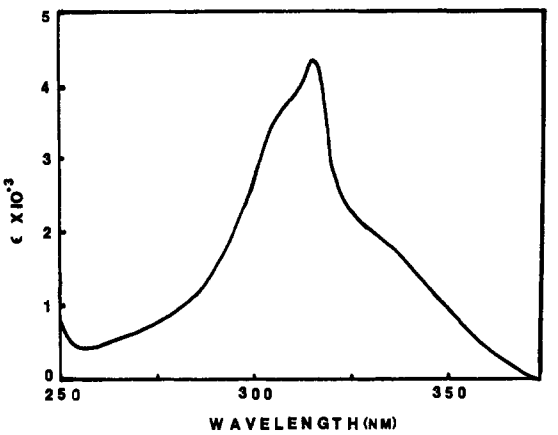

Figure 2. Absorption spectrum of the 8-methylquinolinium ion.

6-Methoxyquinoline showed blurred vibrational structure in its ^1L_b band while the ^1L_a and ^1L_b bands of 8-methoxyquinoline were nearly degenerate. Except for 8-methoxyquinoline all ^1L_b absorption frequencies were taken at the long wavelength vibrational feature, which was assumed to be the 0–0 vibronic band. The maximum of the overlapping ^1L_a and ^1L_b bands of 8-methoxyquinoline was taken to represent the positions of both of the latter bands. In the absorption spectra of the cation species the structured ^1L_b bands were well separated from the unstructured ^1L_a bands in 6-methoxyquinoline, 8-methoxyquinoline, isoquinoline, and acridine. In these compounds the maximum of the ^1L_a absorption and the 0–0 band of the ^1L_b absorption are reported in Table I. The absorption spectrum of the 8-methylquinolinium ion (Figure 2) shows the ^1L_a band emerging as an unstructured shoulder on the long wavelength side of the structured ^1L_b band. A similar situation is observed for neutral acridine. The ^1L_b band is listed in Table I as the frequency of the 0–0 band, while the ^1L_a band position is listed as the frequency at the point of insertion into the ^1L_b band. In quinoline and its 2-, 4-, and 6-methyl derivatives, the ^1L_a and ^1L_b bands of the cations are degenerate and the positions of both bands are taken at the maxima of the composite bands.

In the mid-pH range all compounds studied demonstrated variations of fluorescence intensity with pH. All of the compounds studied also showed variations of absorption spectra with pH, although the absorptiometric titrations generally occurred in slightly different pH regions than the fluorimetric titrations. In moderately concentrated perchloric acid or sulfuric acid, quinoline and its 2-, 4-, and 6-methyl derivatives demonstrated variations of fluorescence intensity with Hammett acidity. The shapes and positions of the plots of fluorescence intensity *vs.* Hammett acidity were essentially identical, whether perchloric acid or sulfuric acid solutions were employed, and the data points of the fluorimetric titrations fit well the Henderson–Hasselbach equation. No variations of absorption spectra were observed, for any compound studied, as a function of Hammett acidity. Nor were variations of fluorescence intensities of the 8-methylquinolinium ion, 6-methoxyquinolinium ion, 8-methoxyquinolinium ion, isoquinolinium ion, or acridinium ion observed, as a function of Hammett acidity. However, in the mid-pH range, while the fluorescences of all protonated species, except those of the acridinium and 8-methylquinolinium ions, were completely quenched, the 8-methylquinolinium ion fluorescence leveled off at about pH 7 and was not completely quenched until pH 12 was reached, although a second region of sharp variation of fluorescence intensity centered at pH 9.7 and not accompanied by change in the absorption spectrum (of the neutral species) with pH was observed (Figure 1). Similar behavior was observed for the acridinium ion. The pK_a values of quinoline,[5] 2-methylquinoline, 4-methylquinoline, 6-methylquinoline, 8-me-

thylquinoline,[4] 6-methoxyquinoline, 8-methoxyquinoline,[8] isoquinoline,[9] and acridine[5] along with the pH and Hammett acidity values at the midpoints of the fluorimetric titration curves of the cations in mid-pH range and in concentrated acid solutions, respectively, are listed in Table II.

Table II. Ground State pK_a Values, pH Values at Half-Maximum Fluorescence Intensity ($pH_{1/2}$), and Hammett Acidity Values at Half-Maximum Fluorescence Intensity ($H_0^{1/2}$) in the Fluorimetric Titrations of Quinolinium Ion, Its 2-Methyl, 4-Methyl, 6-Methyl, 6-Methoxy, and 8-Methoxy Derivatives, the Isoquinolinium Ion, and the Acridinium Ion

BH^+	pK_a	$pH_{1/2}$	$H_0^{1/2}$
Quinolinium	4.94	5.8	−1.6
2-Methylquinolinium	5.43	5.9	−1.1
4-Methylquinolinium	5.34	5.8	−1.4
6-Methylquinolinium	4.89	5.1	−0.8
8-Methylquinolinium	4.65	4.6 (9.7)	
6-Methoxyquinolinium	5.18	5.2	
8-Methoxyquinolinium	5.14	5.1	
Isoquinolinium	5.40	6.1	
Acridinium	5.60	5.6 (9.7)	

Discussion

Six-membered aromatic nitrogen heterocyclic compounds are generally known to be more basic in the lowest excited singlet state than in the ground state,[1,10] usually by five or more orders of magnitude. The large red shifts of the fluorescences of the heterocycles studied in these experiments, upon protonation in the mid-pH range, indicate that this is the case here as well. However, the fluorimetric titration characteristics of the 6-methoxyquinolinium, 8-methoxyquinolinium, and 6-methylquinolinium ions are essentially identical with their absorptiometric titration characteristics. Moreover, although the fluorimetric titrations of the quinolinium, isoquinolinium, 2-methylquinolinium, and 4-methylquinolinium ions show buffer regions in slightly more basic solutions than do their absorptiometric titrations, the differences between the ground- and excited-state dissociation constants ($pK_a^* = pH_{1/2}$ in Table II) are nowhere near the differences suggested by the red shifts of the fluorescence spectra produced by protonation. It would appear that the diffusion-limited protonation or deprotonation of the ring nitrogens in these compounds is too slow for prototropic equilibrium to obtain in the lowest excited singlet state. In the latter group of cations the rates of proton exchange in the excited state and the rates of fluorescence are apparently of comparable magnitude. This subject has been discussed extensively by Weller.[10]

In 8-methylquinolinium ion, the buffer region centered at pH 4.6 in the fluorimetric titration coincides with the buffer region in the absorptiometric titration. Thus, the quenching of 8-methylquinolinium ion fluorescence in this region is static. However, the second buffer region in the fluorimetric titration of this ion is not accompanied by changes in absorption spectra and the quenching centered at pH 9.7 must therefore be dynamic. Moreover, the fluorimetric titration curve in the latter buffer region approximates a typical acid–base titration curve in the pH range covered by the buffer region. Consequently the value of 9.7 is approximately the pK_a^* of the 8-methylquinolinium ion in its lowest excited singlet state. The same arguments are also valid for the acridinium ion fluorescence ($pK_a^* = 9.7$).

The fluorimetric titrations of the quinolinium cation and its 2-, 4-, and 6-methyl derivatives in the Hammett acidity range appear to be the result of protonation in an electronically excited state because of the failure of the absorption spectra to change in this acidity region, the similarity of the titrations to typical acid–base titration curves, and the identity of titration data obtained in sulfuric and perchloric acid media. The pK_a^* values derived from these titrations are all considerably more acidic than the ground state pK_a values.

It was considered that the reaction of concern might consist of protonation at a carbon atom in the aromatic ring of the excited quinolinium ion. However, protonation of the aromatic ring would localize a pair of electrons on the protonated carbon atom and would partially destroy the aromaticity of the cation. This should result either in quenching or substantial hypsochromic shifting of the blue quinolinium fluorescence and is clearly not in accord with the observed enhancement of the blue fluorescence in concentrated acid. Consequently this explanation was dismissed.

An explanation which, however, is consistent with the experimental observations is as follows. If the ^1L_a and ^1L_b states of the quinolinium ion are very nearly degenerate, it would be possible to excite both simultaneously and to have thermal equilibrium between them. If the nitrogen atom in one of these states is less acidic than in the ground state, by virtue of the direction of the $^1L_a \rightarrow {}^1A$ or $^1L_b \rightarrow {}^1A$ transition moment, and in the other state is more acidic than in the ground state, then thermal equilibrium between the two states of the cation can only obtain when the solution is sufficiently acidic that the nitrogen atom is protonated in both excited states. In this case emission from both states may occur and the emission wavelengths should be very nearly equal by virtue of their degeneracy. Since protonation of the more acidic state would result in an increase in the number of potential emitters, the observed result would be an increase in fluorescence intensity as the solution becomes acidic enough to protonate the latter state. Support for this hypothesis comes from the observation of emission from the neutral species in the pH region 4–0, where although the cation is the only species excited only the more basic state of the cation fluoresces, and from the fact that the fluorimetric titration curve in the Hammett acidity region occurs only in those compounds which show degeneracy of the ^1L_a and ^1L_b states in the absorption spectra of the cations.

Attempts to identify the fluorescing states by polarization studies were unsuccessful as the emissions of the neutral species of quinoline and its 2-, 4-, and 6-methyl derivatives were too weak to allow polarized excitation spectra to be obtained with our apparatus. Moreover, although polarized excitation spectra of the cations showed some resolution of two transitions under the long wavelength absorption envelope, the distinction of the two transitions was insufficient to identify

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either. This is indeed an unfortunate circumstance. However, the protonation red shifts of the ^1L_a absorption bands (but not of the ^1L_b bands) of quinoline and its 2-, 4-, and 6-methyl derivatives are comparable in magnitude to the protonation red shift observed for the fluorescence spectra of these compounds. It is tempting to speculate that the ^1L_a state of the neutral species of the latter quinoline derivatives is the fluorescing state. This would mean that either fluorescence arises from the second excited singlet state in these compounds or that the thermally relaxed ^1L_a state lies below the thermally relaxed ^1L_b state. However, in the absence of corroborative data this must remain only a speculation.

Microwave Spectrum of 2-Pyrone and the Molecular Zeeman Effect in Tropone, 2-Pyrone, and 4-Pyrone. Suppression of Nonlocal Contributions to the Out-of-Plane Molecular Magnetic Susceptibilities by the Insertion of a Carbonyl Group into an Aromatic Ring

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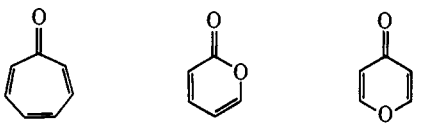
Abstract: The microwave spectrum of 2-pyrone is assigned and gives rotational constants of $A = 5677.64 \pm 0.02$ MHz, $B = 2882.24 \pm 0.01$ MHz, and $C = 1912.13 \pm 0.01$ MHz. The high-field (20,000 G) molecular Zeeman effect is observed and analyzed in 2-pyrone, 4-pyrone, and tropone. The molecular g values, magnetic susceptibility anisotropies, diagonal elements in the paramagnetic and diamagnetic susceptibility tensors, and the molecular quadrupole moments are listed for 2- and 4-pyrone, and the magnetic susceptibility anisotropy for tropone is given. Magnetic susceptibility anisotropies are analyzed in terms of local and nonlocal contributions, and it is shown that 2-pyrone, 4-pyrone, and tropone have negligibly small nonlocal contributions and should be considered nonaromatic by the magnetic criterion. The observation that formal insertion of a carbonyl group into an aromatic ring leads to almost complete suppression of nonlocal contributions to the out-of-plane molecular magnetic susceptibility is noted for the present cases.

Molecular Zeeman studies in our laboratory have resulted in the direct measurement of magnetic susceptibility anisotropies of a large number of isolated and unperturbed molecules. We have established a set of rules to determine the magnitude of local contributions to this anisotropy,[1] and these rules have been used to demonstrate a large nonlocal negative contribution to the anisotropies of molecules known to be aromatic, attributable to $4n + 2$ π-electron delocalization in the cyclic conjugated system leading to a "ring current."[1-5] From this work it appears that use of microwave determined magnetic susceptibility anisotropies offers at present the most reliable method for investigation of the relationship between magnetic properties and aromatic character. Although many observations have been reported which relate ring currents to aromatic character, these measurements often have involved indirect measurements or estimates of the out-of-plane molecular magnetic susceptibility anisotropies.

The perturbation of aromatic character introduced by insertion of a carbonyl group into the ring of an aromatic compound has been a matter of interest for some time. Tropone (**1**), which can be viewed formally as a benzene ring with a carbonyl group incorporated, 2-pyrone (**2**), and 4-pyrone (**3**), which can be considered



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carbonyl insertion derivatives of furan, have been considered both aromatic and nonaromatic at different times and by different criteria.[1,6,7] Tropone especially has been discussed by many investigators and most recently has been assessed as nonaromatic.[6] The 2-

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